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Synthesis of Pd(II) and Pt(II) complexes possessing bicyclo[3.2.0]heptanyl phosphinite ligands: Identification of a novel Pd(II) precatalyst for 1,6-diene cycloisomerisation ☆

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Abstract

The synthesis of monodentate and bidentate phosphinite ligands, possessing the unusual bicyclo[3.2.0]heptane framework, are reported. A convenient, tin-free synthesis of a key intermediate, namely 3-*endo*-6-*endo*-dihydroxybicyclo[3.2.0]heptane, is described. The air-sensitive phosphinite ligand **1** was either protected as the borane adduct, which is air-stable, or reacted directly with bis(acetonitrile)palladium(II)chloride to give the novel air and moisture stable palladium(II) complex **11**. A platinum(II) relative **12** has also been synthesised by reaction of phosphinite **1** with bis(benzonitrile)platinum(II)chloride. Each complex has been thoroughly characterised and their molecular structures confirmed by X-ray diffraction studies. In catalytic applications, such as cross-coupling reactions of organometallic reagents with organohalides, an unexpectedly poor activity has been established for **11**. For example, Suzuki–Miyaura cross-coupling of activated and deactivated aryl bromides with aryl boronic acids, in the presence of catalytic quantities of **11**, proceed in low yield, accompanied by substantial homocoupling. Palladium agglomeration, to produce catalytically inactive Pd black, is rapid in these reactions, under both aqueous and non-aqueous conditions. The poor reactivity is proposed to arise through an unfavourable near tetrahedral '(PP′)Pd(0)' geometry, which slows the oxidative addition step in the catalytic cycle with either activated or deactivated aryl halides. The steric bulk of the ligand and the associated large P–M–P′ bite angle, particularly at the palladium zero oxidation state, is proposed to account for the poor reactivity. However, we have established that cationic derivatives of **11** promote the cycloisomerisation of diallylmalonate in a regioselective fashion.

Keywords: Palladium; Cross-coupling; Suzuki; Dienes; Atom economic 3

1. Introduction

Transition metal catalysed reactions are extremely versatile methods for a variety of synthetic transformations, not least in the formation of carbon–carbon and carbon–heteroatom bonds, through cross-coupling processes [1]. A focus on the development of highly active catalysts (that exhibit high TONs and TOFs) for Heck,

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Sonogashira, Stille and Suzuki reactions, is very apparent. Significant advances have culminated to provide an important step-change in this field [2]. As well as creating highly active catalysts for these reactions, selectivity, particularly chemo-, regio-, stereo- and enantio-selectivity, is of the utmost importance. For cyclisation approaches (non-metathesis type), a defined effort is still required to improve these individual parts, more so if these reactions are to be routinely employed in target-directed synthesis. We have interests in selectivity [3] and the employment of more demanding substrates in Sonogashira, Stille and Suzuki reactions [4]. Roberts and co-workers [5] reported the synthesis of bidentate phosphinite ligands **1**, based on the bicyclo[3.2.0]heptane ring system, and their uses in Rh-catalysed asymmetric hydrogenation reactions (Fig. 1). This ligand has great potential in catalysis, as the donor phosphinite substituents are ideally positioned for bidentate coordination to transition metals, offering potentially large bite angles with interesting geometry (non-symmetric *P,P*-metal coordination). There is also interest outside our own group in utilisation of bicyclo[3.2.0]heptane chiral ligands for application in asymmetric reactions [6]. We believe that bidentate ligand **1**, and the related monodentate ligands **2** and **3**, could generally prove useful in other transition metal-catalysed reactions, particularly for palladium.

On a general note, phosphinite ligands [7], as well as their variants such as aminophophinites [8], amidophosphinites [9], and phosphinite-oxazolines [10], have been used in key reactions such as asymmetric allylic alkylation [11], hydroformylation [12], and in cross-coupling processes [13]. Thus, ligands based on the bicyclo[3.2.0]heptane framework could find further application in these areas of catalysis. The availability of both enantiomeric forms of the bicyclo[3.2.0]heptane framework, and the stereoselective functionalisation that is possible, could promote use of these ligands, generally, in asymmetric processes, as well as other types of transition metal mediated reactions, where the unusual bicyclo[3.2.0]heptane ring system could infer interesting catalytic activity and selectivity.

We herein describe details for the preparation of **1**–**3**; some limitations with the original synthetic route to **1** and improvements; the preparation of novel Pd(II) and Pt(II) complexes, **11** and **12**, respectively, containing phosphinite **1**. The Pd(II) complex of **3**, appears to be complicated by a competing β-hydrogen elimination pathway. Pd(II) complex **11** has been screened for catalytic activity (as a precatalyst) in Suzuki–Miyaura cross-coupling reactions. Surprisingly, poor catalytic activity is seen using **11**, which we attribute to an increase in the natural P–Pd–P′ bite angle, in the '(PP′)Pd(0)' species, which appears to exacerbated by conformational changes (*endo*- to *exo*-envelope ring flip) in the bicyclo[3.2.0]heptane backbone. Monocationic derivatives of **11**, generated in situ, are active and regioselective catalysts for the cycloisomerisation of diallylmalonate.

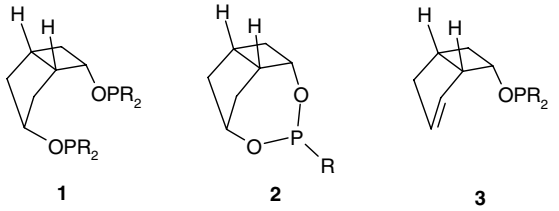
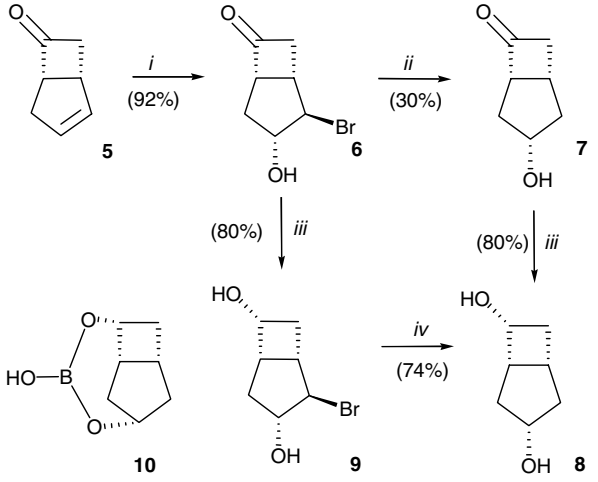


Fig. 1. Phosphinite ligands based on the bicyclo[3.2.0]heptane ring system **1**–**3**.

2. Synthesis of ligands from 3-*endo*-6-*endo*-dihydroxybicyclo[3.2.0]heptane (8)

Commercially available bicyclo[3.2.0]hept-2-en-6-one (**5**) was used as the starting point for the synthesis of **8** [14]. Regio- and stereo-selective bromohydration of **5** to give **6** can be achieved in greater than >92% yield using either *N*-bromosuccinimde (NBS), *N*-bromoacetamide (NBA) or *N,N*-dibromo-dimethylhydantoin in a acetone/water mixture (Scheme 1).

This reaction is higher yielding with unpurified brominating reagent, where it appears that trace quantities of bromine are beneficial for the reaction (*note: that significant amounts of succinimide sometimes accompanies the product when performed on large scale, >50 g*). The hydrodebromination of **6** using *n*-tributyltin hydride in the presence of catalytic AIBN in dry toluene at 80 °C gives **7** after 1 h. Alcohol **7** is volatile and care should be taken on removal of toluene in

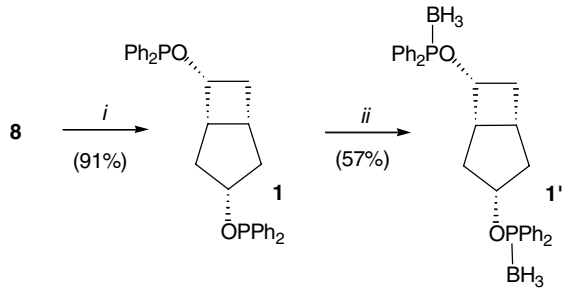


Scheme 1. Reagents and conditions: (i) NBS, acetone/H_2O (3/1, v/v); (ii) *n*-Bu_3SnH (1.1 equiv.), AIBN, toluene, reflux, 4 h; (iii) $NaBH_4$, MeOH, −78 °C, 2 h; (iv) EPHP (10 equiv.), AIBN, toluene, reflux, 24 h.

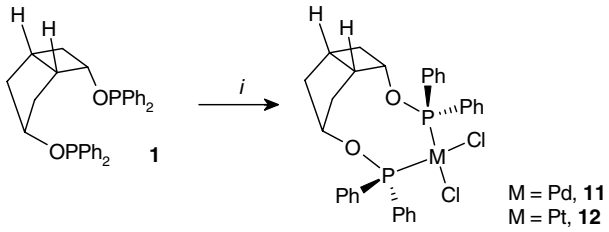
vacuo (temperatures on removal of the solvent should be <20 °C at 12 mmHg, making toluene removal cumbersome). The inherent volatility of **7** contributes to the low yield (30%). We also had problems removing trace quantities of tin residues (n-Bu_3SnBr). Indeed, these were clearly visible in the ^1H and ^{13}C NMR spectra of **7**. Alternative work-up procedures were investigated such as partitioning the crude product between acetonitrile and hexane; stirring the crude product with aqueous KF for 1 h, followed by extraction with ether; or a DBU/I_2/Et_2O procedure [15], without success. Compound **7** was stereoselectively reduced using sodium borohydride in methanol at −78 °C to give **8** in 80% yield. However, this material still contained trace quantities of tin containing by-products. In order to provide large quantities of **8** in pure form and in high yield, the synthetic route was optimised. We identified that a 'tin-free' hydrodebromination reaction could be beneficial, but importantly we wanted to avoid volatile alcohol **7**. Bromohydrin **6** was reduced stereoselectively using $NaBH_4$ in methanol at −78 °C to give diol **9** in 80% yield, in crystalline form. We identified a phosphoryl radical mediated hydrodebromination reaction as a suitable 'tin-free' procedure. Ethyl piperidine hypophosphate (EPHP) was employed in presence of the radical initiator, AIBN, in toluene at reflux to give **8** in 74% yield [16]. Purification was easier than the tin-mediated hydrodebromination procedure.

Having established a tin-free route to diol **8**, the phosphinite ligand **1** was prepared. Treatment of **8** with diphenylchlorophosphine, in the presence of triethylamine (Et_3N) or diazabicyclo[2.2.2]octane (DABCO) in THF at 0 °C and subsequent warming to room temperature with stirring (for 3 h), gave ligand **1** in 91% yield. The air sensitivity of the free phosphinite ligand **1** is a limitation. However, protection of **1** as the borane adduct, stabilises it toward oxidation, indeed **1′** is indefinitely stable in air (Scheme 2).

Use of DABCO as a base in the borane protection reaction is essential. Switching to Et_3N results in the production of substantial amounts of the borane adduct, $Et_3N \cdot BH_3$, that could not be separated, even by careful chromatography, from the desired product **1′** (the borane adduct of DABCO is observed which can be separated from **1′**).



Scheme 2. Reagents and conditions: (i) Ph_2PCl (2 equiv.), DABCO, THF, 0–25 °C; (ii) $BH_3 \cdot THF$ (3 equiv.), THF, 0–25 °C.



Scheme 3. Reagents and conditions: (i) $(CH_3CN)_2PdCl_2$ (1 equiv.) or $(PhCN)_2PtCl_2$ (1 equiv.), ligand **1** (1 equiv.), CH_2Cl_2, rt, 3 h.

In a stoichiometric reaction, ligand **1** was reacted with $(CH_3CN)_2PdCl_2$ and $(PhCN)_2PtCl_2$ to give complexes **11**and **12** in quantitative yield, respectively. This synthesis is relatively straightforward, when the ligands are taken in semi-purified form in dry, degassed CH_2Cl_2 at 25 °C (Scheme 3).

Complexes **11** and **12** are stable to air, moisture and light (over several months), as expected for 16-electron late transition metal M(II) complexes. The X-ray structure of **11** (Fig. 2) exhibits a distorted *cis*-square coordination of the Pd atom, with a bidentate, *P*,*P*-chelating role of the diphosphinite ligand. The chelation is slightly asymmetric, the Pd–P distances

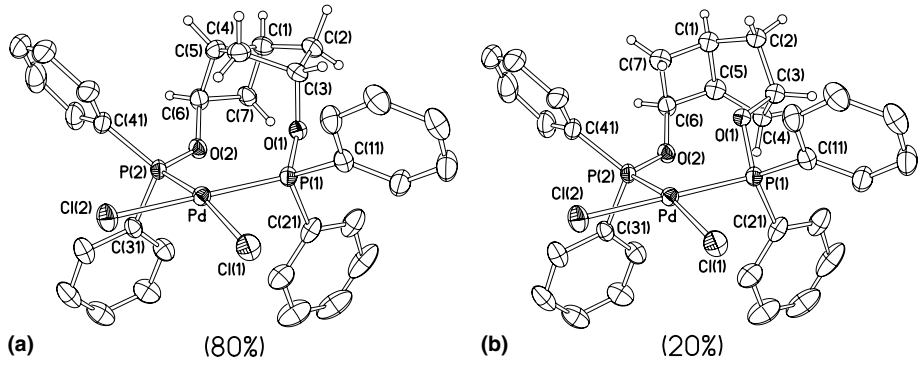


Fig. 2. Two possible structures of **11** in crystal, due to the disorder of the bicyclo[3.2.0]heptane-O(1) moiety. Thermal ellipsoids are drawn at 50% probability level, phenyl H atoms omitted.

Table 1
Selected bond distances (Å) and angles (°) in **11** (M = Pd) and **12** (M = Pt)

Complex	**11**	**12**
Bond		
M–P(1)	2.2568(6)	2.215(2)
M–P(2)	2.2345(7)	2.232(2)
M–Cl(1)	2.3501(7)	2.368(2)
M–Cl(2)	2.3503(6)	2.349(2)
O(1)–P(1)	1.623(2)	1.605(4)
O(2)–P(2)	1.600(2)	1.598(4)
P(1)···P(2)	3.337(1)	3.274(2)
Angle		
P(1)–M–P(2)	95.99(2)	94.84(6)
P(1)–M–Cl(1)	87.08(2)	91.45(6)
P(1)–M–Cl(2)	178.32(2)	176.70(7)
P(2)–M–Cl(1)	168.54(2)	170.09(6)
P(2)–M–Cl(2)	85.56(2)	85.45(6)
Cl(1)–M–Cl(2)	91.53(2)	87.83(6)
M–O(1)–P(1)	123.28(7)	120.8(2)
M–O(2)–P(2)	113.76(7)	115.8(2)

differing by ca. 0.02 Å (see Table 1). Both Pd–P and Pd–Cl distances are practically the same as in five previously reported *cis*-$(ROPh_2P)_2PdCl_2$ complexes, whether containing a chelating diphosphinite ligand or two monophosphinite ones [17]. The metal coordination deviates substantially from planarity: while the Pd, P(1), P(2) and Cl(2) atoms are coplanar, Cl(1) is tilted out of their mean plane by 0.47 Å, away from the bicyclo[3.2.0]heptane system. With respect to the latter, the $PdCl_2$ moiety adopts an *exo*-orientation. It is noteworthy that the entire bicyclo[3.2.0]heptane backbone, together with the O(1) atom, is disordered in a 4:1 ratio between two positions, which correspond to opposite enantiomeric configurations of the backbone. The crystal being centrosymmetric (racemic), the molecules shown and their inversion equivalents are present in equal amounts.

The coordination mode in $CDCl_3$ solution of **11** is the same as in the solid-state, exhibiting a pair of doublets (P_1 at δ 100.49; P_2 at δ 106.69, $\Delta\delta_{PP} = 6.20$). A large $^2J_{PP}$ spin–spin coupling (51.1 Hz) was observed, derived from *cis*-coordination of the ligand to Pd(II). In stark contrast, the Pt(II) analog **12** shows a much smaller $^2J_{PP}$ coupling (7.7 Hz), although showing the expected inequivalent phosphorus environments (P_1 at δ 74.05; P_2 at δ 79.07, $\Delta\delta_{PP} = 5.02$). The expected spin–spin coupling is seen between ^{135}Pt and ^{31}P ($^1J_{PtP2} = 2126$; $^1J_{PtP1} = 2140$ Hz). The molecular structure of **12** is very similar to that of the major component of **11**, but exhibits no disorder (Fig. 3). The P–M–P bite angle in **12** is ca. 1° smaller and the M–P(1) bond is ca. 0.04 Å shorter than in **11** (although the M–P(2) distance is practically the same), cumulating in a 0.06 Å shortening of the intramolecular P···P distance (Table 1). The Cl(1) and Cl(2) atoms deviate from the PtP_2 plane by 0.31 and 0.14 Å, respectively, away from the bicycloheptane moiety; thus **12** (line **11**) shows simultaneously a tetrahedral and a pyramidal distortion of the square coordination of the metal. Besides one molecule of **12**, the asymmetric unit contains two DCM molecules, all H atoms of which form close contacts with the Cl(1) and Cl(2) atoms (2.67–2.85 Å, cf. the sum of van der Waals radii [18] of 2.86 Å).

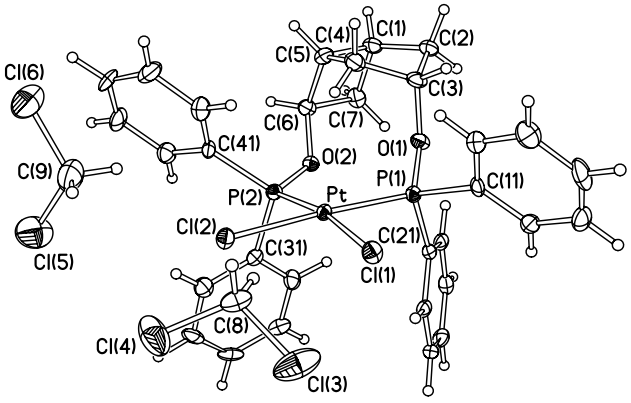
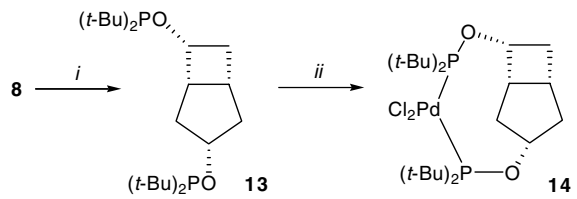


Fig. 3. An asymmetric unit in the crystal structure of **12** · $2CH_2Cl_2$.

We were also interested in the incorporation of *tert*-butyl phosphinite substituents into the bicyclo[3.2.0]heptane framework. We expected that the stronger σ-donor properties of this ligand could be useful for cross-coupling reactions, particularly with respect to use of unactivated aryl chlorides. It was anticipated that this ligand could be air-sensitive, and as with ligand **1**, it was synthesised and then added directly to a CH_2Cl_2 solution of $(MeCN)_2PdCl_2$ at 25 °C (Scheme 4).

Compound **8** did react with $(t\text{-Bu})_2PCl$ under the standard conditions (as ajudged by disappearance of **8** by rigorous TLC analysis of the reaction mixture and by the formation of a stoichiometric quantity of $Et_3N \cdot HCl$) to give **13**. The complexation reaction to $(MeCN)_2PdCl_2$ also appeared to have worked (the colour of the solution went from yellow to colourless). The volatiles were removed in vacuo to provide a white solid. The ^{31}P NMR spectrum of this material in $CDCl_3$ exhibited two broad singlets, which we believe is attributable to the non-equivalent phosphorus environments in **14** (P_1 at δ 143.71; P_2 at δ 151.12, $\Delta\delta_{P1P2} = 7.41$). However, the ^{1}H NMR spectrum of **14** was very broad and it was not possible to assign proton environments. The



Scheme 4. Reagents and conditions: (i) $(t\text{-Bu})_2PCl$ (2 equiv.), Et_3N, THF, 0–25 °C; (ii) $(MeCN)_2PdCl_2$ (1 equiv.), CH_2Cl_2, 25 °C.

material was slowly recrystallised from CH_2Cl_2/ether (1/5, v/v, c = 0.1 M) over two months at −20 °C, which produced colourless crystals. The ^{1}H NMR spectrum of these crystals showed only high field resonances (attributable to *t*-Bu and OH) and the curious absence of the bicyclo[3.2.0]heptane unit. A single crystal X-ray diffraction study has shown the new material to be **15**, possessing a *trans*-square planar geometry around the Pd atom, which occupies a crystallographic inversion centre (Fig. 4). Both the Pd–P and Pd–Cl distances (2.3450(3) and 2.3132(3) Å, respectively) are longer than in the only one previously studied *trans*-bis-phosphinite-dichloropalladium(II) complex, $PdCl_2(PPh_2OR)_2$, where R is a bulky calixarene moiety (Pd–P 2.325(1), Pd–Cl 2.301(1) Å) [19]. The differences in Pd–P distances can be attributed to weaker electron withdrawal by *t*-Bu compared to Ph groups and hence higher basicity of the P atom in **15**, while the elongation of Pd–Cl is probably caused by intramolecular hydrogen bonds O-H···Cl (Fig. 4). The ^{31}P NMR spectrum exhibited two sharp singlets at δ 123.35 and 124.63 in a ratio of ~15:1, attributable to the *cis*- and *trans*-forms of **15**, the former being the major isomer in solution (identical to an authentic sample containing both isomers).

Molecular models of the *cis*- and *trans*-forms of **14** show severe steric constraints imposed on the bicyclo[3.2.0]heptane skeleton, which we believe promotes β-hydrogen elimination to yield **15** and 1,4-diene **16** (Scheme 5), although we have been unable to fully characterise **16** which is highly volatile and probably undergoes

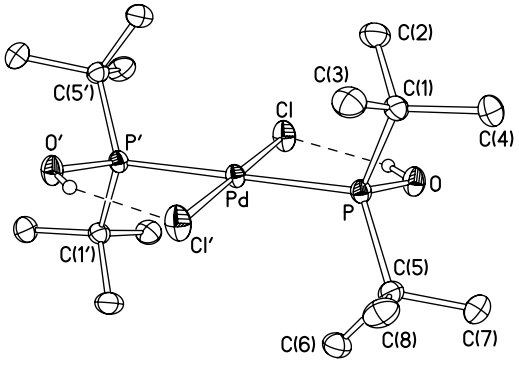
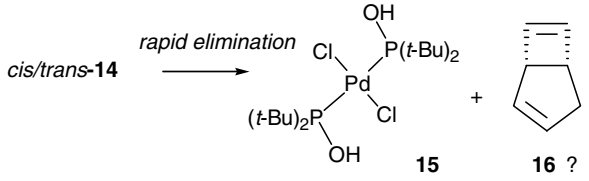


Fig. 4. X-ray structure of **15**, showing intramolecular hydrogen bonds. Atoms generated by the inversion centre are primed, methyl H atoms are omitted; P–O distance 1.613(1) Å, Cl–Pd–P angle 88.98(1)°.



Scheme 5. Rapid elimination of the bicyclo[3.2.0]heptane backbone to give **15** and bicyclic diene **16**.

rapid ring-opening/rearrangement. The filtrate from the crystallisation of **15** contains alkene-containing side-products, as shown by ^{1}H NMR spectroscopy, thus a β-hydrogen elimination pathway appears most plausible.

Interestingly, complex **15** (and the related dimeric complexes) has recently been reported as a highly active Pd-catalyst for cross-coupling of deactivated aryl halides [20].

The elimination pathway represents a useful synthetic approach to the exclusive formation of *trans*-**15**, which is usually isolated as a mixture of *cis*- and *trans*-isomers (in $CDCl_3$ solution at 25 °C their distribution does not alter to any great extent, as shown by ^{31}P NMR spectroscopy). The near exclusive formation of *trans*-**15** is intriguing, as it is to be expected that the bidendate ligand, being *cis*-chelating, should eliminate to release *cis*-**15** (isomerisation to *trans*-**15**) should be slow, vide supra but at least a roughly equal mixture of *cis*- and *trans*-isomers should be seen. We have considered that this bulky bidendate ligand is *trans*-chelating, promoted by conformational changes in the constrained bicyclo[3.2.0]heptane framework (Fig. 5).

Given the large steric congestion around the Pd(II) centre in **14**, a conformational change from the *cis*-*endo*-envelope form I to a *cis*-*exo*-envelope II is expected to be fast. The large natural bite angle (>100 °) in the *cis*-*exo*-envelope II conformation should enable slow isomerisation to the *trans*-*exo*-envelope III. Elimination of $H_{7\text{-}exo}$ in III is expected to occur first to give *trans*-*exo*-envelope IV, given that elimination at $H_{4\text{-}exo}$ and $H_{2\text{-}exo}$ are positioned unfavourably. Once elimination has occurred, however, a rapid ring-flip to give *trans*-*endo*-envelope V facilitates elimination from either $H_{4\text{-}exo}$ (as shown) or $H_{2\text{-}exo}$ to give **15**.

3. Attempted synthesis of monodentate ligand 2

The synthesis of the novel monodentate phosphinite ligand based on **2** was next attempted. Compound **8** was reacted with $PhPCl_2$ in THF, in the presence of DABCO or Et_3N, to give **2a**, under similar conditions employed for the synthesis of **1** (see Scheme 6).

Complete disappearance of **8** was confirmed by TLC analysis. Compound **2a** was isolated as an oil and found to be very air sensitive, oxidising rapidly in the presence of trace quantities of air to give oxide **17a** (<5 min). The combined yield of the material produced from this reaction was 24%; oligomerisation/oxidation account for this inadequate yield [21]. The ^{31}P NMR spectrum of the material produced from the reaction carried out in the presence of Et_3N shows two singlets (δ 176.88 and 178.12), expected for diastereoisomeric phosphinates (**2a**′ and **2a**″). A broad peak is observed between δ 23 and 34, which is attributable to diastereoisomeric phosphonates (**17a**′ and **17a**″), as well as polymerised,

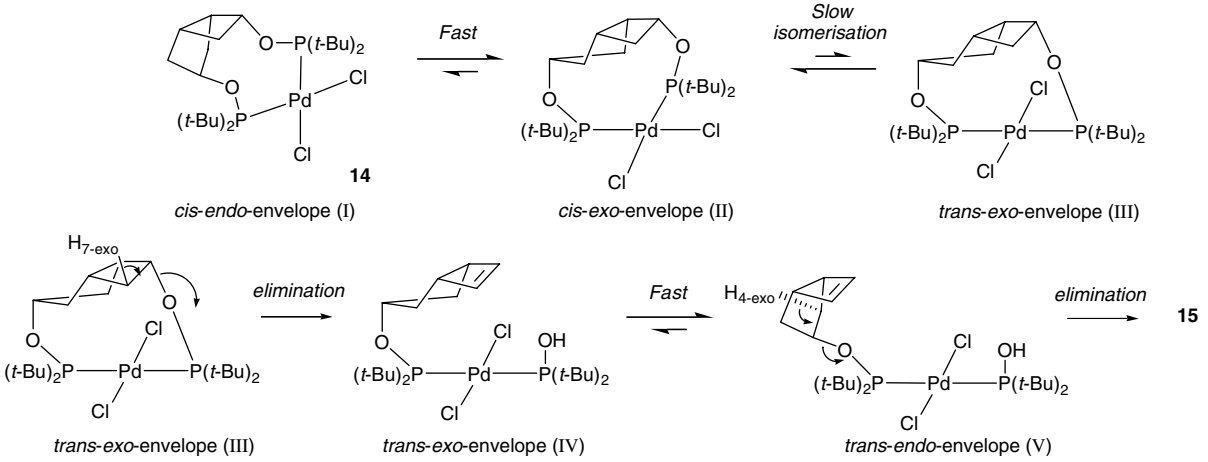
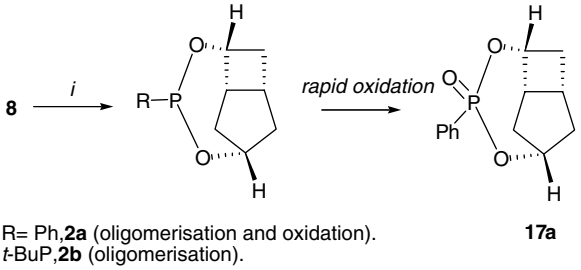


Fig. 5. Proposed conformational changes in the strained bicyclo[3.2.0]heptane backbone.



Scheme 6. Reagents and conditions: (i) $ArPCl_2$ (1 equiv., Ar = Ph, **2a**; *t*-Bu, **2b**), DABCO or Et_3N (1.2 equiv.), THF, 0–25 °C; (ii) $(CH_3CN)_2PdCl_2$ (1 equiv.), ligand **2a**/**2b** (2 equiv.), CH_2Cl_2, rt, 3 h.

ring-opened phosphonates. Further evidence for oligomerisation is seen in an attempt to synthesise the *tert*-butyl phosphinite derivative **2b**. FAB-MS shows that dimeric and trimeric species *m*/*z* (461 [2M + 1]), ESI (483 [2M + Na]; 713 [3M + Na]) are produced in this reaction. (see Fig. 6)

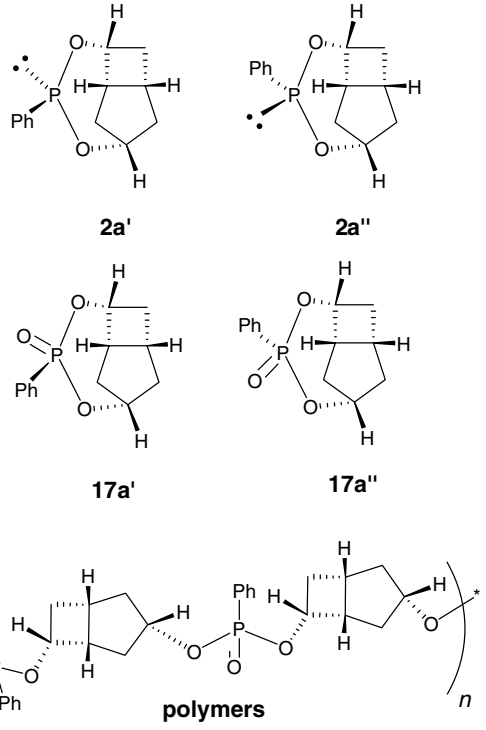


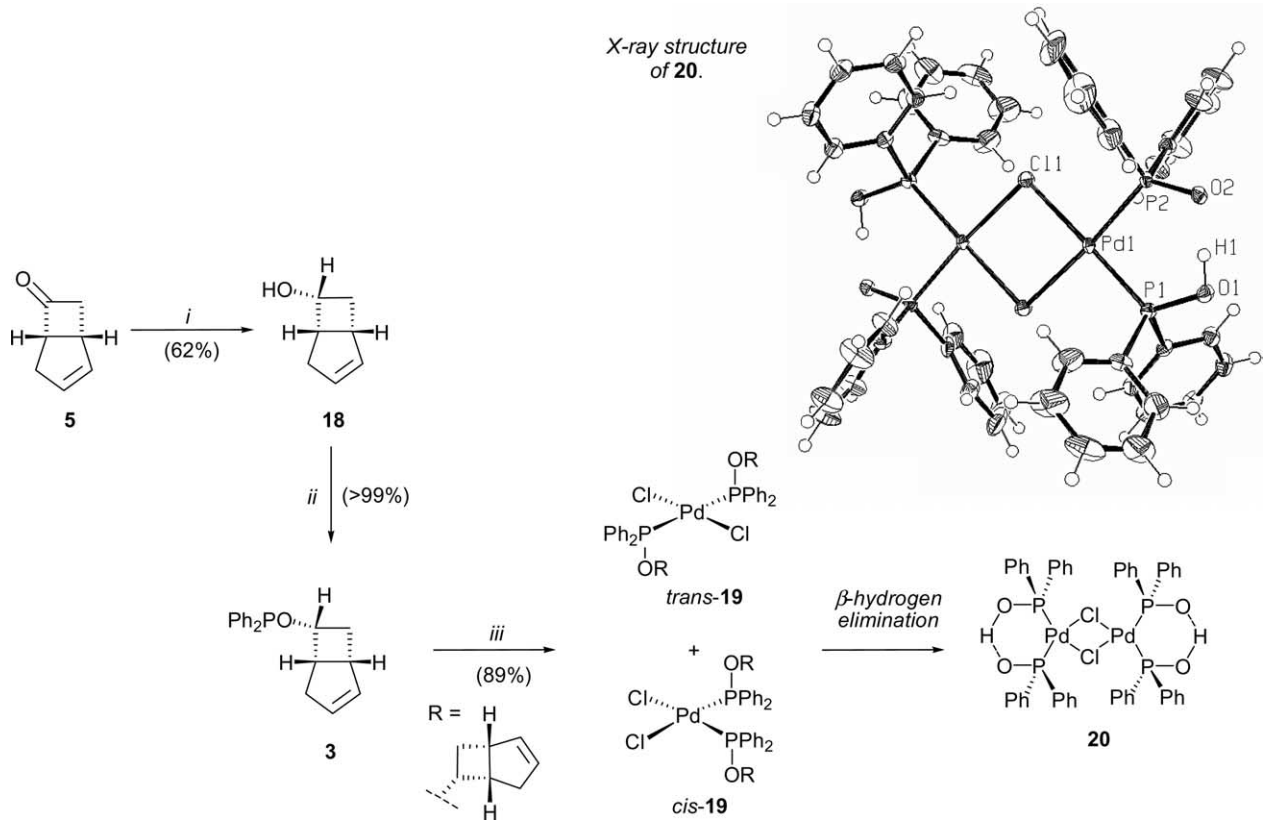
Fig. 6. Compounds **2a′**/**2a″** and other side-products.

4. Synthesis of monodentate ligand 3 and its Pd(II) complex 19

A diphenylphosphinite monodentate ligand **3** was synthesised from ketone **5**. Stereoselective carbonyl reduction using $NaBH_4$ in MeOH at −78 °C gave *endo*-alcohol **18** in 62% yield (Scheme 7).

The phosphinite ligand **3** was produced by reaction of **18** with Ph_2PCl in the presence of Et_3N in THF at −78 °C to give **3** in quantitative yield. The air sensitivity of **3** is again a problem (we have included selected NMR spectroscopic data in Section 8), however, direct complexation with $(MeCN)_2PdCl_2$ does afford *trans*-**19** in 89% yield. In $CDCl_3$ solution, the ^1H and ^{31}P NMR spectra of *trans*-**19** indicated the presence of the bicyclic ring and that it is bound to phosphorus (H_6 is characteristic at δ 4.64), which is coordinated to Pd. However, three phosphorus species are observed (Fig. 7). The signal at δ 109.84 is spin–spin coupled with the signal at δ 98.4 ($^2J_{PP'} = 25.97$ Hz) and this is attributed to *cis*-**19**. The similar chemical shift of δ 107.30, but absence of spin–spin coupling, is attributed to *trans*-**19**. The preferred conformations of the bicyclo[3.2.0]heptane ring may account for the inequivalent phosphorus environments seen in the more sterically hindered *cis*-**19**.

The signal at δ 78.12 is attributed to the product derived from decomposition of *cis*/*trans*–**19** to **20** in $CDCl_3$ solution (previously stored over activated molecular sieves). X-ray crystallography provided the means to



Scheme 7. Reagents and conditions: (i) $NaBH_4$, MeOH, −78 °C, 2 h; (ii) Ph_2PCl, Et_3N, THF, −78 °C to rt; (iii) $(MeCN)_2PdCl_2$, CH_2Cl_2, 25 °C. In X-ray structure drawing for **20**, a disordered CH_2Cl_2 is omitted.

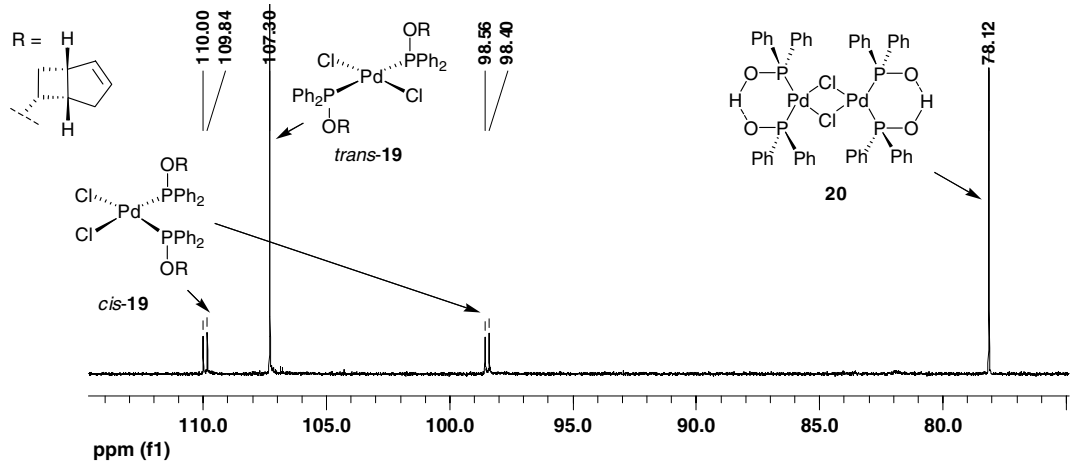
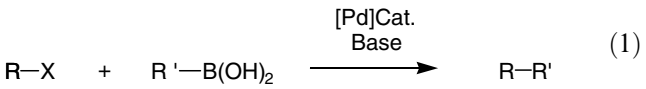


Fig. 7. ^{31}P NMR (162 MHz) spectrum of a $CDCl_3$ solution of material produced in the reaction of **3** with $(MeCN)_2PdCl_2$.

prove the identify of this as $[\mu_2$-ClPd(PPh_2-OH)(PPh_2O)$]_2$ (**20**). The solid material produced from the reaction was recrystallised by layering a relatively concentrated CH_2Cl_2 solution (~0.2 M) with hexane/ether (1/1, v/v) at 25 °C over two days. Only **20** crystallised from solution. A literature survey reveals that **20** has been produced from other phosphinite ligands, and that HCl or trace quantities or water are responsible for elimination [22].

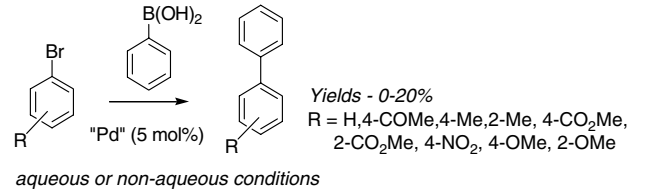
5. Suzuki–Miyaura cross-coupling reactions

To evaluate whether **11** could be a useful precatalyst for cross-coupling reactions, the Suzuki–Miyaura reaction[1] of organohalides with organoboronic acids, in the presence of base, was investigated. This reaction arguably represents one of the most applied reactions in academia and industry and therefore we expected it would be a useful test (Eq. (1)).



(1)

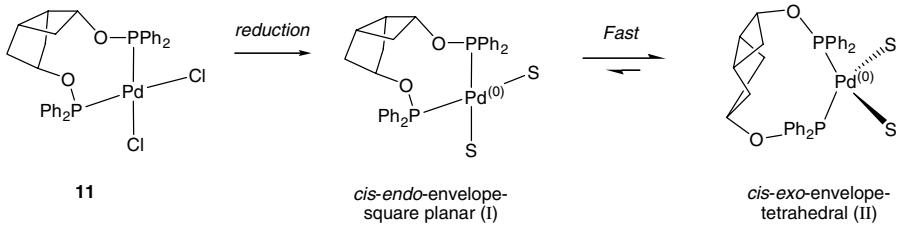
There are many highly active Pd-catalysts for this reaction, particularly for aryl halides; [23] the differences between these, most commonly, arise through changes in the coordinating ligand, e.g., use of electron rich alkyl phosphines, such as $(t\text{-Bu})_3P$ or biphenyl$(t\text{-Bu})_2P$ (developed by Littke and Fu [2] and Buchwald and co-workers [24], respectively), *N*-heterocyclic carbenes (Beller and co-worker [25] and Nolan and co-workers [26]) or phosphinites (particularly those developed by Bedford et al. [27]). An extensive screen of reactions mediated by **11**, under aqueous and non-aqueous conditions were performed. However, the cross-coupled product was at best produced in ~20% yield, although substantial quantities of homocoupled products, derived from oxidative dimerisation of the organoboronic acid, were detected by GC/NMR (>25%) (Scheme 8). Under aqueous conditions, Pd black was produced after ~ 10 min at 80 °C. Under non-aqueous conditions, the formation of Pd black was not seen after 24 h at the same temperature (both reactions were conducted employing identical reactant and catalyst concentration; 0.12 M, 5 mol% [Pd]). To assess whether Pd agglomeration [28] was a problem, lower Pd loadings (0.1–0.01 mol% [Pd]) were employed, but this was equally as ineffective. Our conditions were validated by use of $Pd(OAc)_2$ (5 mol%) in the presence of Ph_3P (10 mol%), under either aqueous or non-aqueous conditions, which showed that cross-coupling proceeds effectively for the substrates shown in Scheme 9 (within ~3 h and isolated yields of 70–95%). Similar results are seen using $(Ph_3P)_2PdCl_2$ (5 mol%) in our hands. Precatalyst **11** is, albeit surprisingly, ineffective at promoting the Suzuki–Miyaura cross-coupling reaction. In start contrast, Suzuki–Miyaura cross-coupling reaction of 4-bromoacetophenone with phenyl boronic acid to give 4-acetobiphenyl in the presence of **19** (1 mol%) did proceed well (86% conversion, 2 h). However, on testing the eliminated Pd dimer complex **20** (0.5 mol%), similar catalytic activity was observed (evolution profile, as shown by GC analysis, including reaction rate and % conversion after 2 h, is near identical for **19** and **20**). We believe that **19** represents a steady source of **20**, the latter complex is known to exhibit catalytic activity for this reaction.



Scheme 8. Aqueous conditions: [Pd] cat. (5 mol%), 2 M aq. Na_2CO_3, benzene/EtOH, 80 °C; 1 M aq. Na_2CO_3, THF, 60–80 °C. Non-aqueous conditions: KF (3 equiv.), dioxane or THF, 25–80 °C; CsF (3 equiv.), dioxane or THF, 25–80 °C.

We questioned why **11** was an ineffective for this reaction. The electron deficient ligand might account for the low level of catalytic reactivity, but the fact that other phosphinites have been employed with great success in these reactions, would count against this statement. Conformational changes are expected within the bicyclo[3.2.0]heptane backbone of the ligand, as proposed in Fig. 5; an *endo–exo* ring flip would increase the 'P–Pd–P' natural bite angle (β_n) dramatically, which is 96° in the *endo*-envelope **11**, to >106° in the *exo*-envelope (calculated by molecular mechanics using the models developed by Casey and Whiteker [29] and Dierkes and van Leeuwen [30]). This change would be manifested on reduction of Pd(II) to Pd(0). Van Leeuwen and co-workers studied the effect of β_n in chelating diphosphines on the activity and selectivity in palladium-catalysed cross-coupling reactions [31]. In the coupling of *sec*-butylmagnesium chloride with bromobenzene the optimal bite angle was found to 102.7°. Increasing β_n to >105° resulted in lower yields of the cross-coupled product and substantial amounts of homocoupling. Homocoupling was a problematic side reaction observed in reactions mediated by **11**. Increasing the natural bite angle of the ligand towards 109° could lead to distortion toward a tetrahedral coordination mode, explaining the decrease rate of reaction with aryl halides (Scheme 9).

The production of homocoupled product, from the organoboronic acid, in these reactions may be explained by reoxidation of Pd(0) back to Pd(II), possibly by



Scheme 9. Proposed conformational changes in the bicyclo[3.2.0]heptane backbone on reduction of Pd(II) to Pd(0).

adventitious oxygen. A classic Pd(II) reduction to give the homocoupled product is plausible. It is important to note, however, that aryl bromide homocoupling is not observed, excluding the involvement of a possible trigonal-bipyramidal Pd(IV) complex [32] (known to be stabilised by ligands with bite angles near 110°) which explains homocoupling, from aryl halides, in the system described by van Leeuwen and co-workers [31].

After determining the poor catalytic properties of the phosphinite Pd(II) complexes in Suzuki–Miyaura cross-coupling reactions, we considered their utilisation in other reactions. Electrophilic, neutral and cationic, Pd catalysts/precatalysts have been used to mediate the cycloisomerisation of 1,6-dienes to give cyclopentenes with varying functionality [33]. Investigations were thus initially pursued employing **11** as the precatalyst.

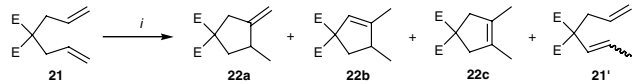
6. Cycloisomerisation of dimethyl diallylmalonate 22 mediated by Pd(II) complex 11

The *benchmark substrate* for 1,6-diene cycloisomerisation is dimethyl diallylmalonate **21** [33]. There are several palladium catalysts/precatalysts reported that promote cycloisomerisation of this substrate [34]. Three cycloisomerisation products (**22a–c**) are usually observed with varying distribution (Scheme 10). In addition, the isomerised 1,5-diene **21′** is often observed, sometimes exclusively.

In our first reaction, 5 mol% of **11** was added to a 1,2-dichloroethane solution of **21** under a nitrogen atmosphere and the reaction heated to 60 °C for 24 h. No products were formed under these conditions. Heating to 80 °C for several days showed no further changes. However, the addition of one equivalent of silver(I) salt with respect to Pd, in this case AgOTf (OTf = triflate), promoted cycloisomerisation at 60 °C, but this was accompanied by isomerisation (double bond migration) of **21** → **21′** (Table 2). Trace quantities of triflic acid (TfOH) presumably promote the isomerisation side reaction. A variety of silver(I) salts and reaction temperatures were studied to assess their affect on the production and distribution of the cycloisomerised products (**22a–c**), and isomerisation of **21** → **21′**. Some important observations come out of the results shown in Table 2. At 40 °C the formation of the kinetic exocyclic product **22a** is observed, an exception being $NaBAr'_4$ (Ar′ = bis(3,5-trifluoromethyl)benzene). In the presence of the OTf anion, this product disappears after 24 h, isomerised to either **22b** or **22c**, whereas for SbF_6 and BF_4 anions, **22a** still remains at this temperature. At both 60 and 80 °C, **22a** is not detected for any of the additives investigated. The highest selectivity is seen for the BAr'_4 anion at 60 °C, which after 24 h gave predominately **22b** (90% selective at 100% conversion). Although SbF_6 is selective for **22b** (~96%), percentage conversion to products (28%) is low. Increasing the temperature to 80 °C improves the conversion to products (99%), but at the expense of selectivity for **22b** (86%). It appears that the non-coordinating anion is essential for higher catalytic activity but not selectivity. At 60 °C, the more coordinating BF_4 anion produces **22b** exclusively (100%), at the expense of higher conversion (37%). Only after 72 h is the more thermodynamically stable symmetrical product **22c** observed ($AgBF_4$, 60 °C, 72 h; **21/22b/22c**, 26/73/1). Increasing the temperature to 80 °C gives higher conversions (64%), and reaction is still selective for **22b** (~98%).

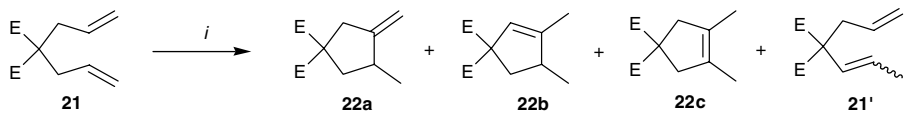
The evolution of cycloisomerised products **22b** and **22c**, mediated by **11** (5 mol%) in the presence of $NaBAr'_4$ (5 mol%) in DCE at 60 °C, is shown in Fig. 8. Significantly, the kinetic profile exhibits an absence of a period of induction under the reaction conditions.

Table 2
1,6-Diene cycloisomerisation selectivity using precatalyst **11** under monocationic conditions



Additive	Temperature (°C)	Time (h)[a]	
		4	24
AgOTf	40	70/5/21/4	39/0/49/12
	60	5/0/14/46[b]	8/0/5/57[c]
	80	28/0/21/51	11/0/25/64
$NaBAr'_4$	40	89/0/10/1	52/0/45/3
	60	46/0/54/0	0/0/95/5
	80	18/0/81/1	4/0/91/5
$AgSbF_6$	40	79/7/14/0	60/5/32/3
	60	90/0/10/0	72/0/27/1
	80	15/0/81/4	1/0/93/6
$AgBF_4$	40	80/3/17/0	60/8/32/0
	60	90/0/10/0	63/0/37/0
	80	65/0/35/0	36/0/63/1

[a] Ratio of **21/22a/22b/22c** as determined by ^{1}H NMR spectroscopy.
[b] Isomerised starting material **21′** (35%) was observed.
[c] Isomerised starting material **21′** (30%) was observed.



Scheme 10. Reagents and conditions: (i) [Pd] (5 mol%), 1,2-dichloroethane (DCE), 25 °C.

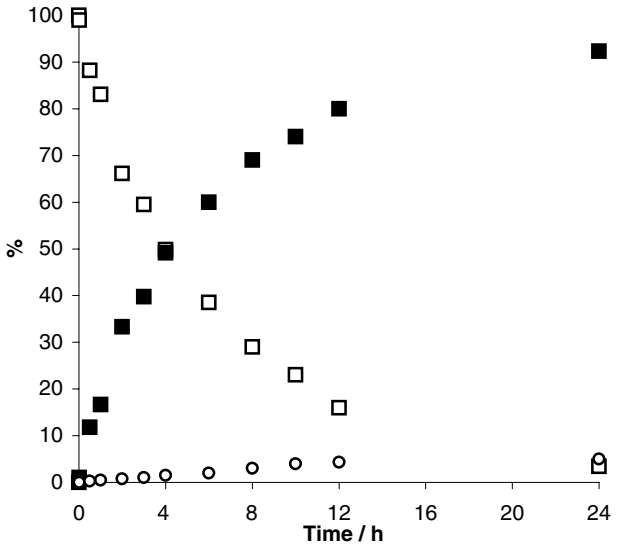


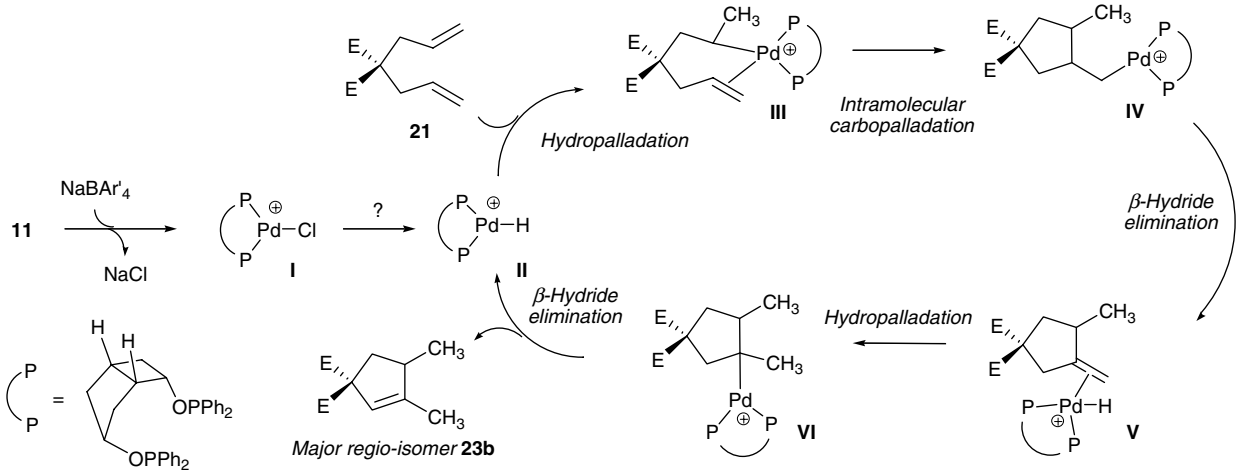
Fig. 8. Kinetic profile for the cycloisomerisation of dimethyl diallylmalonate **21** by **11** (5 mol%), $NaBAr'_4$ (5 mol%), DCE, 60 °C (monitored by ^1H NMR spectroscopy; [**21**] at $t_0 = 0.245$ M). Key: □, 1,6-diene **22**; ■, endocyclic product **23b**; ○, tetrasubstituted cyclopentene **23c**.

Prolonged reaction to 72 h shows negligible isomerisation of **22b** to **22c** (remains at ~95:5). The linear formation of the endocyclic product **22b** is seen up to ~50% conversion (4 h). The rate of reaction then slows and it is at this point that the formation of **22c** is observed.

We have also evaluated the ability of Pt(II) complex **12** to mediate dimethyl diallylmalonate cycloisomerisation, under both neutral and cationic (using $NaBAr'_4$; **12** : $NaBAr'_4$, 1 : 1) conditions in DCE at 60 °C. Negligible conversion to products (~10% after 48 h) is seen in each case, but **22a** was the only cycloisomerisation product.

It is assumed, but not proven, that a "Pd–H" species is involved in the catalytic cycle. The mechanism is expected to be similar to that proposed by Widenhoefer and co-workers [35] for cationic palladium phenanthroline complexes (Scheme 11). The catalytic cycle is dependent on the generation of cationic palladium hydride complex [36], $(P,P')PdH^+$ (**II**) from cationic palladium complex, $(P,P')PdCl^+$ (**I**). The P,P′ ligand is expected to undergo a series of associative/dissociative processes (bidentate → monodentate) throughout the catalytic cycle. Hydropalladation of an alkene in **21** would form palladium alkyl alkene intermediate **III**. Intramolecular carbopalladation of **III** reveals palladium cyclopentylmethyl complex **IV** which then undergoes β-hydride elimination to form palladium methylenecyclopentane complex **V**. A second hydropalladation event provides the tertiary palladium cyclopentylmethyl complex **VI**, from which a regioselective β-hydride elimination process from the secondary hydrogen atom in **VI** forms the tri-substituted cyclopentene **23b**, with regeneration of the active cationic palladium hydride species **II**.

It remains a remote possibility that the generated cation $(P,P')PdCl^+$ might react with the counterions BAr'_4, SbF_6 and BF_4 at elevated temperatures in DCE, via anion abstraction (Ar'^- or F^-), to release trace quantities of the Lewis acids BAr'_3, SbF_5 and BF_3, and (P,P′)PdClY (where Y = F or Ar′). However, to the best of our knowledge there is no literature precedent for Lewis acid assisted 1,6-diene cycloisomerisation (note: enyne cycloisomerisation mediated by Lewis acids has been reported) [37]. To assess this possibility, the separate reactions of **21** mediated by SbF_5 and $BF_3 \cdot Et_2O$ (5 mol%) in DCE at 60 °C were conducted. ^1H NMR spectroscopic analysis of samples withdrawn from each reaction at 2, 4 and 24 h intervals showed no detectable cycloisomerisation products, derived from **21**, under the



Scheme 11. Proposed mechanism for 1,6-diene cycloisomerisation by cationic palladium bisphosphinite complex **11**.

Lewis acid promoted conditions. However, for each Lewis acid, extensive double bond isomerisation was observed (**21** → **21′**, >75% in both cases).

7. Conclusion

In summary, we have described the synthesis of novel Pd(II) and Pt(II) complexes possessing bicyclo[3.2.0]heptane ligands based on **1**. Alteration of phosphinite substituents from phenyl to *tert*-butyl resulted in rapid elimination of the bicyclic backbone to give pure *trans*-**15**. The attempted synthesis of ligands **2** and **3** was complicated by rapid oxidation and ring-opening/polymerisation reactions. Although **3** was isolated and reacted directly with $(MeCN)_2PdCl_2$ to give **20**, a β-hydrogen elimination pathway affords Pd(II) dimer **21**. The catalytic activity of **11** in Suzuki–Miyaura cross-coupling was surprisingly poor. However, the unusual bicyclic framework was utilised in promoting dimethyl diallylmalonate cycloisomerisation. Here, in situ generated cationic Pd(II) species are essential and the judicious choice of the anion led to the development of a highly regioselective cationic catalytic system for the endocyclic cycloisomerisation product **22b**. Studies are in progress to determine the most likely mechanism for the cycloisomerisation reactions mediated by cationic derivatives of **11**, as well as other bidentate phosphinite and phosphine complexes.

8. Experimental

THF, toluene and benzene were dried over sodium-benzophenone ketyl (distilled prior to use). Dry CH_2Cl_2, Et_3N and CH_3CN were distilled over calcium hydride. All reactions were conducted under an inert atmosphere of Ar or N_2 on a Schlenk line. $(MeCN)_2PdCl_2$ was either purchased from Aldrich or prepared by refluxing $PdCl_2$ with dry acetonitrile for 4 h. Melting points were recorded on an electrothermal IA9000 Digital Melting Point Apparatus and are uncorrected. TLC analysis was performed on Merck 5554 aluminium backed silica gel plates and compounds visualised by ultraviolet light (254 nm), 1% ninhydrin in EtOH or dilute $KMnO_4$ aqueous solution (containing a drop of H_2SO_4). The relative proportion of solvents in mixed chromatography solvents refers to the volume/volume ratio. Infrared spectra were recorded on a ATI Mattson Genesis FT-IR. Mass spectrometry was carried out using a Fisons Analytical (VG) Autospec instrument. High-resolution masses are within 5 ppm of theoretical values. ^1H NMR spectra were recorded at 270 MHz using a JEOL EX270 spectrometer, at 400 MHz using a JEOL ECX400 spectrometer or 500 MHz on a Bruker 500 spectrometer; ^{13}C NMR spectra at 68 or 100 MHz; ^{31}P NMR spectra at 109, 162 or 202 MHz. 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), br (broad). The characterisation data for compounds **5**–**7** have previously been reported [5]. Compounds **21**, **21′** and **22a**–**c** have previously been characterised [34h].

8.1. 2-exo-Bromo-3-endo-6-endo-dihydroxybicyclo[3.2.0]heptane (9)

To a magnetically stirred solution of **6** (5.00 g, 24.5 mmol) in methanol (50 mL) was at −78 °C was added $NaBH_4$ (1.38 g, 1.5 equiv.) in small portions. On complete addition (∼0.2 h) the reaction mixture was stirred at −78 °C for 3 h. The reaction was quenched with a 2 M hydrochloric acid solution (50 mL) and then concentrated in vacuo to half volume (until complete removal of MeOH was accomplished) and then the aqueous phase was extracted with Et_2O (3 × 100 mL) (use of EtOAc as the extraction solvent gives a product containing succinimide). The combined organic extracts were washed with water (100 mL), brine (100 mL), dried ($MgSO_4$) and concentrated in vacuo to give a clear oil (4.01 g, 79.5%). $R_f = 0.17$ (EtOAc/PE, 1/1, v/v); ν_{max} (CH_2Cl_2, cm^{-1}) 3306, 2941, 1430, 1276, 1167, 1147, 1106, 1021, 973, 944; δ_H ($CDCl_3$, 400 MHz) 1.84 (1H, m, $H_{7\text{-}exo}$), 2.02 (1H, d, $^2J = 14.9$, $H_{4\text{-}endo}$), 2.29 (1H, m, $H_{4\text{-}exo}$), 2.57 (1H, m, $H_{7\text{-}endo}$), 2.83 (1H, m, H_1), 3.27 (1H, m, H_5), 4.07 (1H, s, $H_{2\text{-}endo}$), 4.21 (1H, m, $H_{3\text{-}exo}$), 4.49 (1H, d, $J = 4.9$, $H_{6\text{-}exo}$), 4.57 (1H, OH/D), 5.33 (1H, OH/D); δ_C ($CDCl_3$, 100 MHz) 31.35 (CH_2 C_4), 37.27 (CH_2 C_7), 42.81 (CH, C_5), 45.44 (CH, C_1), 60.30 (CH, C_2), 63.76 (CH, C_6), 81.79 (CH, C_3); MS (CI) *m/z* 224 ($M^+ + NH_4$, 99), 206 (M^+, 6), 190 (54), 144 (100), 127 (51); HRMS (CI) calcd. for $C_7H_{15}O_2BrN$: 224.02862. Found: 224.02824.

8.2. 4,6-Dioxa-5-bora-tricyclo[5.2.1.0^{3,9}]decan-5-ol (10)

To a Schlenk flask containing **7** (3.57 g, 28 mmol) in methanol (120 mL) at −78 °C was added sodium borohydride (1.38 g, 36.4 mmol, 1.3 equiv.) in portions and the reaction stirred at this temperature for 2 h. The reaction mixture was quenched at −78 °C with saturated aqueous ammonium chloride (15 mL) and was allowed to stir for 1 h. The mixture was allowed to warm to room temperature and extracted with EtOAc (100 mL × 3). The combined organic extracts were washed with water (100 mL) and brine (100 mL). The solution was dried ($MgSO_4$) and concentrated in vacuo to give a yellow oil (1.31 g, 30.8%). M.p. 108–109 °C; ν_{max} (CH_2Cl_2, cm^{-1}) 3211, 1779, 1429, 1345, 1181, 1165; δ_H

($CDCl_3$, 270 MHz) 1.69 (1H, br), 1.74 (2H, m), 2.11 (1H, br), 2.49 (1H, m), 2.64 (2H, m), 3.10 (1H, m), 4.26 (1H, m), 4.52 (1H, m); δ_C ($CDCl_3$, 100 MHz) 32.71 (*C*H), 35.49 (*C*H_2), 38.35 (*C*H_2), 43.21 (*C*H_2), 45.62 (*C*H), 65.29 (*C*H), 76.37 (*C*H); δ_B ($CDCl_3$, 160 MHz) 18.19; MS (CI) *m/z* 172 ($M^+ + NH_4$, 52), 154 (M^+, 100), 129 (58), 111 (35), 84 (40); HRMS (CI) calcd. for $C_7H_{15}O_3BN$: 172.11449. Found: 172.11395.

8.3. 3-endo-6-endo-Dihydroxybicyclo[3.2.0]heptane (**8**)

8.3.1. Synthesis of ethylpiperidine hypophosphite

A magnetically stirred solution of aqueous hypophosphorous acid (50%, w/w) was dried in vacuo at 50 °C (~7 mmHg). After complete removal of water, the acid was placed under an inert atmosphere (N_2) and cooled to 0 °C. 1-Ethylpiperidine (1 equiv.) was added to the acid at 0 °C, whilst stirring slowly to precipitate out a white salt (hygroscopic). The reaction proceeds in quantitative yield. This salt was used without any further purification as a reagent. EPHP is commercially available but it is relatively expensive given that it may be prepared on large scale very easily (100 g). The acid must be thoroughly dried, otherwise the product formed is a viscous oil, which is extremely difficult to dry – this was noticed on larger scale reactions, where trace quantities of water could still be present. In our hands, the salt does not form immediately. This seems to be dependant on the scale of the preparation (~0.3 h). EPHP must be stored at −20 °C in a sealed flask, but can be weighed out in air.

8.3.2. Hydrodebromination procedure

To a solution of **9** (0.206 g, 1 mmol, 1 equiv.) in dry toluene (20 mL), was added EPHP (10 equiv.) and AIBN (0.05 equiv.) in one portion under an inert atmosphere (N_2). The reaction mixture was heated to reflux and monitored by TLC, until all starting material had been consumed (16 h). The reaction was allowed to cool, then quenched with water and extracted with ether (20 mL × 4). All the organic extracts were combined, dried ($MgSO_4$) and concentrated in vacuo. The product was purified by column chromatography using EtOAc/PE (1/1, v/v increased by gradient elution to 2/1, v/v) to give the product as a white crystalline solid (0.095 g, 74%). R_f = 0.10 (EtOAc/PE, 1/1, v/v); δ_H ($CDCl_3$, 270 MHz) 1.67 (4H, m, $H_{4\text{-}exo}$, $H_{2\text{-}endo}$ and $H_{2\text{-}exo}$, $H_{7\text{-}exo}$), 2.09 (1H, d, ^2J = 15.1, $H_{4\text{-}endo}$), 2.48 (1H, m, H_1), 2.62 (1H, m, $H_{7\text{-}endo}$), 3.10 (1H, m, H_5), 3.53 (1H, m, H_3) 4.28 (2H, OH/D), 4.51 (1H, d, ^3J = 4.3, H_6); δ_C ($CDCl_3$, 68 MHz) 32.79 (*C*H, C_1), 35.61 (*C*H_2, C_2), 38.16 (*C*H_2, C_4), 42.98 (*C*H_2, C_7), 45.52 (*C*H, C_5), 65.29 (*C*H, C_3), 75.82 (*C* H, C_6); LRMS (CI) *m/z* 146 ($M^+ + NH_4$, 77), 129 ($M^+ + H$, 100), 111 (37), 93 (24), 67 (9); HRMS (CI) calcd. for $C_7H_{16}O_2N$: 146.11810. Found: 146.11798.

8.4. Synthesis of **1** and its borane adduct **1′**

Under an atmosphere of argon a THF solution (2 mL) of **8** (73.0 mg, 0.6 mmol, 1 equiv.) was cooled to 0 °C and then DABCO (78.5 mg, 0.7 mmol, 1.2 equiv., vacuum dried) in THF (2 mL) was added via cannula and allowed to stir at this temperature for 0.5 h. Chlorodiphenylphosphine (286.8 mg, 0.24 mL, 1.3 mmol, 2.2 equiv.) was added dropwise slowly at 0 °C. DABCO · HCl formed immediately (precipitate). The mixture was allowed to warm to 25 °C and stirring was continued for 16 h. After this time, the mixture was passed through Celite® under nitrogen atmosphere (washed through with THF (50 mL). The solvent was removed in vacuo to give **1** as a viscous colourless oil (which was reacted directly with the M(II) precursors or $BH_3 \cdot THF$).

8.4.1. Borane adduct **1′**

As above, the reaction mixture was not filtered. The reaction mixture was cooled to 0 °C and then $BH_3 \cdot THF$ (1.8 mmol) was added dropwise. The mixture was allowed to stir for 1 h at 0 °C and then warmed to 25 °C and stirring continued for 3 h. The reaction was quenched by the addition of water (5 mL), and the mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography gave the product as viscous yellow oil (0.18 g, 57%). ν_{max} (CH_2Cl_2, cm^{-1}) 3400 (br), 1966, 1897, 1820, 1732, 1589, 1483, 1437, 1374, 1268, 1113, 1065, 1033, 1001, 980, 941, 919. δ_H ($CDCl_3$, 500 MHz) 1.75 (3H, m, H_{4endo} & H_{4exo} & $H_{7\text{-}exo}$), 2.20 (4H, m, $H_{2\text{-}endo}$ & $H_{2\text{-}exo}$ & H_5 & $H_{7\text{-}endo}$), 2.87 (1H, m, H_1), 3.30–3.52 (6H, m, 2× BH_3), 4.64 (1H, m, $H_{3\text{-}exo}$), 4.83 (1H, m, H_{6exo}), 7.17 (20H, m, Aryl). δ_C ($CDCl_3$, 100 MHz) 31.17 (CH), 34.34 (CH), 36.71 (CH_2), 41.08 (CH_2), 65.94 (CH), 68.62 (CH), 83.21 (CH), 128.59, 128.64, 128.70, 131.38, 131.80. δ_P ($CDCl_3$, 202 MHz) 103.499 (P1, attached to C6), 104.258 (P2, attached to C3). δ_{11B} ($CDCl_3$, 160 MHz) −39.48 (B1, attached to C6), −39.87 (B2, attached to C3). LRMS (CI) *m/z* 542 ($M^+ + NH_4$, 26), 509 (77), 420 (31), 242 (69), 203 (61), 186 (100), 108 (62). HRMS (CI) calcd. for $C_{31}H_{40}B_2NO_2P_2$: 542.27204. Found: 542.27312.

8.5. [3-endo-6-endo-Bis(diphenylphosphinooxy)bicyclo-[3.2.0]heptanyl]palladium(II)chloride (**11**)

To a solution of **1** (1.06 g, 2.13 mmol, 1 equiv.) in dry CH_2Cl_2 (3.0 mL) was added via cannula transfer a solution of bis(acetonitrile)palladium(II)chloride (0.44 g, 2.13 mmol, 1 equiv.) in CH_2Cl_2 (5.0 mL). The solution was allowed to stir overnight at 25 °C. The solvent was removed in vacuo to yield a yellow

solid (1.30 g, 91%). M.p. 147–149 °C (decomp.); ν_{max} (CH_2Cl_2, cm^{-1}) 3063, 3046, 2949, 1435, 1275, 1103, 1082, 1046, 1032, 1007, 962, 778, 763, 738, 723, 707, 696. δ_H ($CDCl_3$, 500 MHz) 1.74 (3H, m, $H_{2\text{-}endo}$, $H_{2\text{-}exo}$ and $H_{4\text{-}exo}$), 1.93 (1H, d, $^2J = 16.0$ $H_{4\text{-}endo}$), 2.19 (1H, m, $H_{7\text{-}exo}$), 2.42 (2H, m, H_1 and H_5), 3.74 (1H, d, $^2J = 15.5$, $H_{7\text{-}endo}$), 4.23 (1H, m, $H_{3\text{-}exo}$), 4.43 (1H, dd, $^3J = 4.0$, 8.0, $H_{6\text{-}exo}$), 7.16 (20H, m, Ar-H). δ_P ($CDCl_3$, 109 Hz) 100.48 (d, ^2J=51.1), 106.69 (d,$^2J = 51.1$). MS (FAB) *m/z* 637 ($M^+ - Cl$, 62), 529 (72), 460 (53), 307 (28), 154 (100); HRMS (FAB) calcd. for $C_{31}H_{30}O_2P_2ClPd$: 637.044. Found 637.045. Anal. Calc. for $C_{31}H_{30}O_2P_2Cl_2Pd$: C, 55.09; H, 4.77. Found: C, 55.33; H, 4.76%.

8.6. [3-endo-6-endo-Bis(diphenylphosphinooxy)bicyclo-[3.2.0]heptanyl]platinum(II)chloride (**12**)

To a solution of **1** (0.240 g, 0.48 mmol, 1 equiv.) in dry DCM (5.0 mL) was added via cannula transfer a solution of bis(benzonitrile)platinum(II)chloride (0.229 g, 0.48 mmol, 1 equiv.) in CH_2Cl_2 (25 mL). The solution was allowed to stir for 2 h at 25 °C. A colour change from pale green to a pale yellow was observed on ligand complexation. The solvent was removed in vacuo to yield a yellow solid (0.298 g, 81%). M.p. 65–66 °C (decomp.). δ_H ($CDCl_3$, 400 MHz) 1.74 (3H, m, $H_{2\text{-}endo}$, $H_{2\text{-}exo}$ and $H_{4\text{-}exo}$), 1.92 (1H, d, $^2J = 14.9$, $H_{4\text{-}endo}$), 2.26 (1H, m, $H_{7\text{-}exo}$), 2.46 (2H, m, H_1 and H_5), 4.02 (1H, d, $^2J = 15.2$, $H_{7\text{-}endo}$), 4.29 (1H, m, $H_{3\text{-}exo}$), 4.53 (1H, m, $H_{6\text{-}exo}$), 7.15 (20H, m, Ar-H). δ_C ($CDCl_3$, 100 MHz, selected peaks) 81.88 (C6, $^3J_{PtC6} = 7.7$ Hz), 74.56 (C6, $^3J_{PtC3} = 13.8$ Hz), 45.45 (C1), 42.62 (C7, d, $^4J_{PtC7} = 7.7$ Hz), 35.96 (C2/4, d, $^4J_{PtC2/4} = 3.8$ Hz), 34.57 (C2/4, d, $^4J_{PtC2/4} = 9.2$ Hz), 32.87 (C5). δ_P ($CDCl_3$, 162 MHz) 74.05 (P2, attached to C3, dd, $^2J_{PP} = 7.7$ Hz; $^1J_{PtP2} = 2140$ Hz) and 79.07 (*P1* attached to C6, dd, $^2J_{PP} = 7.7$ Hz; $^1J_{PtP2} = 2126$ Hz). MS (FAB) *m/z* 727 ($M^+ - Cl$, 60), 598 (7), 529 (16), 307 (22), 219 (86), 154 (100); HRMS (FAB) calcd. for $C_{31}H_{30}O_2P_2ClPd$: 727.051. Found: 727.106. We have been unable to obtain accurate elemental analysis for this complex. The ^{31}P NMR solution spectrum shows a phosphorus purity of >95% to the limits of detection.

8.7. trans-Bis(di-tert-butylphosphinic acid)palladium(II)-chloride (**15**)

δ_H ($CDCl_3$, 400 MHz) 1.30 (1H, s, OH), 1.33 (1H, s, OH), 1.37 (38H, t, $^3J_{HP} = 7.64$). δ_C ($CDCl_3$, 68 MHz) 27.64 (CH_3), 39.30 (C). δ_P ($CDCl_3$, 162 MHz) 123.35 (s). MS(FAB) *m/z* 503 (M^+, 80%), 468 (40), 411 (67), 389 (6), 375 (8), 285 (25), 215 (100), 181 (16). Anal. Calc. for $C_{16}H_{38}Cl_2O_2P_2Pd$: C, 38.30; H, 7.63. Found: C, 38.48; H, 7.81%.

8.8. 5-Phenyl-cis-4,6-dioxa-5-phosphatricyclo[5.2.1.0^{3,9}]-decane (**2a**)

8.8.1. Attempted preparation

To a THF solution (15 mL) of **8** (0.537 g, 4.2 mmol, 1 equiv.) at 0 °C was added Et_3N (0.935 g, 9.2 mmol, 2.2 equiv.). Dichlorophenylphosphine (0.751 g, 4.2 mmol, 1 equiv.) was added dropwise at 0 °C. Once the addition was complete, the reaction was allowed to warm to 25 °C and allowed to stirred overnight. The mixture was filtered through a pad of dried alumina layered over dried Celite®, and was concentrated on the schlenk line to yield a pale viscous yellow oil (24.5%). See main text for selected δ_P NMR spectroscopic data. LRMS (CI) *m/z* 271 (M + HCl, 64%), 235 (M + H, 24%), 160 (100%); HRMS (CI) calcd. for $C_{13}H_{16}O_2P$: 235.08879. Found: 235.08914.

8.9. 6-endo-Hydroxybicyclo[3.2.0]hept-2-ene (**18**)

To a MeOH (30 mL) solution containing $NaBH_4$ (0.62 g, 16.4 mmol, 1.2 equiv.) at −78 °C was added a MeOH (10 mL) solution of **5** (1.48 g, 13.7 mmol, 1 equiv.) dropwise over ~0.5 h. The mixture was allowed to stir at this temperature for 3 h, after which time TLC analysis indicated the complete disappearance of the starting material and the appearance of a new product. The reaction was quenched with water (20 mL), followed by dilute hydrochloric acid (1 M, 20 mL). The aqueous mixture was extracted with ether (3 × 30 mL), which were combined, washed with saturated aqueous NaCl (1 × 30 mL), dried ($MgSO_4$) and concentrated in vacuo to yield a pale yellow oil. This was purified by column chromatography using EtOAc/PE (7/3, v/v) to give the *title compound* as a pale yellow oil (0.94 g, 62%). ν_{max} (neat, cm^{-1}) 3339 (br OH), 3048, 2930, 2850, 1607 (C=C), 1432, 1350, 1324, 1210, 1167, 1108. δ_H ($CDCl_3$, 400 MHz) 1.57 (1H, m, $H_{4\text{-}endo}$), 2.35 (1H, m, $H_{4\text{-}exo}$), 2.50 (1H, br s, OH), 2.66 (2H, m, $H_{7\text{-}endo}$ and H_5), 2.99 (1H, m, $H_{7\text{-}exo}$), 3.12 (1H, m, H_1), 4.41 (1H, m, $H_{6\text{-}exo}$), 5.84 (2H, m, H_2 and H_3). δ_C ($CDCl_3$, 100 MHz) 31.51 (CH_2 C_4), 39.72 (CH_2 C_7), 40.47 (CH, C_1), 42.32 (CH, C_5), 66.89 (CH, C_6), 132.53 (CH, C_3), 135.45 (CH, C_2). LRMS (CI) *m/z* 128 ($M^+ + NH_4$, 75), 110 (M^+, 40), 93 (M^+–OH, 100), 81 (28), 66 (84). HRMS (CI) calcd. for $C_7H_{14}NO$: 128.1075. Found: 128.1073.

8.10. 6-endo-(Diphenylphosphinite)bicyclo[3.2.0]-hept-2-ene (**3**)

ν_{max} (neat, cm^{-1}) 3339 (br OH), 3048, 2930, 2850, 1607 (C=C), 1432, 1350, 1324, 1210, 1167, 1108. δ_H ($CDCl_3$, 270 MHz) 1.79 (1H, m), 2.30 (1H, m), 2.59 (1H, m), 2.86 (1H, m), 3.14 (1H, m), 4.56 (1H, m), 4.56 (1H, m), 5.77 (2H, m), 7.32 (10H, m). δ_P ($CDCl_3$,

109 MHz) 107.15. LRMS (CI) *m/z* 294 (M^+, 24), 262 (11), 245 (53), 201 (100), 108 (8), 92 (20), 66 (16).

8.11. trans-Bis(6-endo-diphenylphosphinooxy)bicyclo-[3.2.0]hept-2-enyl)palladium(II)chloride (trans-**20**)

To a CH_2Cl_2 solution (5 mL) of **18** (0.59 g, 2.0 mmol, 1 equiv.) under an atmosphere of nitrogen was added a solution of bis(acetonitrile)palladium(II)chloride (0.26 g, 0.1 mmol, 0.5 equiv.) in CH_2Cl_2 (25 mL) via cannula. A colour change from deep orange to bright yellow occurred within minutes. The mixture was stirred for 3 h at 25 °C, and then the solvent was removed in vacuo to give a pale yellow solid. The solid was purified by dissolution in fresh CH_2Cl_2, filtered through a cotton wool plug to give a bright yellow filtrate which was concentrated in vacuo to give a pale yellow solid (0.68 g, 89%). M.p. 92 °C (decomp.). δ_H ($CDCl_3$, 400 MHz) 1.90 (4H, m, 2× H_{4endo} H_{4exo}), 2.09 (2H, m, 2× H_1), 2,37 (2H, m, 2× H_5), 2.59 (2H, m, 2× $H_{7\text{-}endo}$), 2.94 (2H, m, 2× $H_{7\text{-}exo}$), 4.64 (2H, m, 2× H_{6exo}), 5.65 (4H, m, 2× H_2 and H_3), 7.22 (20H, m, Ar-H). δ_C ($CDCl_3$, 100 MHz) 32.77 (CH_2), 39.05 (CH_2), 39.55 (CH), 43.32 (CH), 74.63 (CH), 128.20 (CH), 128.54 (CH), 132.33 (CH), 132.46 (CH), 132.58 (CH), 134.22 (CH). δ_P ($CDCl_3$, 109 MHz) 107.30 (s). LRMS (FAB, +ve mode) 764 (M^+, 1), 729 (M^+ − Cl, 40), 601 (M^+-2×C_7H_9, 67), 509 (42), 279 (100), 219 (81), 154 (84). HRMS (FAB, +ve mode) calcd. for $C_{38}H_{38}0_2P_2Cl_2Pd$: 764.076. Found: 764.077 (exhibits the correct isotopic distribution for this formula). Anal. Calc. for $C_{39}H_{39}Cl_3O_2P_2Pd$ ($M + \frac{1}{2}CH_2Cl_2$): C, 57.51; H, 4.83. Found: C, 57.84; H, 5.35%.

8.12. X-ray crystallography

X-ray quality single crystals of **11** were grown by slow evaporation of a CH_2Cl_2/hexane solution (5/1, v/v), those of **12** from a solution of CH_2Cl_2 (~0.3 M) layered with ether/hexane (1/1, v/v), which gave the **12** · $2CH_2Cl_2$ solvate. The X-ray diffraction experiment (Durham) for **11** was carried out on a Bruker 3-circle diffractometer with a SMART 6000 CCD area detector, using graphite-monochromated Mo Kα radiation ($\bar{\lambda} = 0.71073$ Å). The X-ray diffraction experiments (York) for **12**, **15** and **20** were carried out on a Bruker Smart Apex diffractometer with Mo Kα radiation ($\bar{\lambda} = 0.71073$ Å) using a SMART CCD camera. Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow gas cryostat. The reflection intensities were corrected for absorption by a semi-empirical method based on the intensities of Laue equivalents and multiple measurements of identical reflections [38]. The structures were solved by the Patterson and Fourier technique and refined by full-matrix least-squares against F^2 of all reflections, using SHELXTL software [39]. All non-H atoms were refined in anisotropic approximation, all H atoms in **11** and **12** were treated in 'riding' model. In **15**, methyl and hydroxyl groups were refined as rigid bodies, rotating around the C–C and O–P axes. In **11**, the atoms O(1), C(1), C(2), C(3), C(4), C(7), H(1), H(21), H(22), H(3), H(41), H(42), H(5), H(71) and H(72) are disordered between positions A (80%) and B (20%). Crystal data and other experimental details are listed in Table 3.

Table 3
Crystal data and X-ray experimental parameters

	11	**12**	**15**
Empirical formula	$C_{31}H_{30}Cl_2O_2P_2Pd$	$C_{31}H_{30}Cl_2O_2P_2Pt \cdot 2CH_2Cl_2$	$C_{16}H_{38}Cl_2O_2P_2Pd$
Formula weight	673.79	932.33	501.70
T (K)	120(2)	115(2)	115(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (# 14)	$P\bar{1}$ (#2)	$P2_1/n$ (# 14)
a (Å)	10.859(1)	10.8684(14)	8.3569(5)
b (Å)	16.635(5)	12.8477(17)	14.5098(8)
c (Å)	16.145(2)	13.3514(17)	9.2099(5)
α (°)	90	100.216(2)	90
β (°)	103.69(1)	92.062(3)	96.070(1)
γ (°)	90	108.848(3)	90
V (Å^3)	2833.6(10)	1727.6(4)	1110.0(1)
Z	4	2	2
D_{calc} (Mg m^{-3})	1.579	1.792	1.500
Absorption coefficient (mm^{-1})	0.99	4.65	1.23
Crystal size (mm^3)	0.46 × 0.46 × 0.29	0.19 × 0.09 × 0.03	0.17 × 0.13 × 0.12
Number of reflections collected	50630	10244	7526
Number of independent reflections	8269	6691	2556
R_{int}	0.044	0.040	0.016
Refelections with $I > 2\sigma(I)$	6705	5275	2412
R [$I > 2\sigma(I)$]	0.032	0.041	0.016
wR (F^2), all data	0.085	0.093	0.040

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for **11**, **12** and **15** have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 228634 (**11**), 250070 (**12**) and 250069 (**15**). Copies of this information can be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.01.037.

References

[1] (a) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457;
(b) S.P. Stanforth, Tetrahedron 54 (1998) 263;
(c) A. Suzuki, J. Organomet. Chem. 576 (1999) 147.

[2] A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176, and references cited therein.

[3] (a) C.M. Crawforth, I.J.S. Fairlamb, R.J.K. Taylor, Tetrahedron Lett. 45 (2004) 461;
(b) C.M. Crawforth, S. Burling, I.J.S. Fairlamb, R.J.K. Taylor, A.C. Whitwood, Chem. Commun. (2003) 2194.

[4] (a) L.R. Marrison, J.M. Dickinson, R. Ahmed, I.J.S. Fairlamb, Tetrahedron Lett. 43 (2002) 8853;
(b) I.J.S. Fairlamb, S.M. Syvanne, A.C. Whitwood, Synlett (2003) 1691;
(c) L.R. Marrison, J.M. Dickinson, I.J.S. Fairlamb, Bioorg. Med. Chem. Lett. 12 (2002) 3509;
(d) I.J.S. Fairlamb, F.J. Lu, J.P. Schmidt, L.R. Marrison, J.M. Dickinson, Bioorg. Med. Chem. 12 (2004) 4285;
(e) E.H. Niemela, A.F. Lee, I.J.S. Fairlamb, Tetrahedron Lett. 45 (2004) 3593.

[5] (a) N. Derrien, C.B. Dousson, S.M. Roberts, U. Berens, M. Burk, M. Ohff, Tetrahedron: Asymmetry 10 (1999) 3341;
(b) B. Adger, U. Berens, M.J. Griffiths, M.J. Kelly, R. McCague, J.A. Miller, C.F. Palmer, S.M. Roberts, R. Selke, U. Vitinus, G. Ward, Chem. Commun. (1997) 1713.

[6] A paper detailing the synthesis of bicyclo[3.2.0]heptane-2-*endo*-7-*endo*-diols has recently been reported: F. Peri, E. Binassi, A. Manetto, E. Marotta, A. Mazzanti, P. Righi, N. Scardovi, G. Rosini, J. Org. Chem. 69 (2004) 1353.

[7] T. Sell, S. Laschat, I. Dix, P.G. Jones, Eur. J. Org. Chem. (2000) 4119.

[8] (a) F. Agbossou-Niedercorn, I. Suisse, Coordin. Chem. Rev. 242 (2003) 145;
(b) C. Blanc, J. Hannedouche, F. Agbossou-Niedercorn, Tetrahedron Lett. 44 (2003) 6469;
(c) P.W. Galka, H.B. Kraatz, J. Organomet. Chem. 674 (2003) 24;
(d) T.V. RajanBabu, A.L. Casalnuovo, T.A. Ayers, N. Nomura, J. Jin, H. Park, M. Nandi, Curr. Org. Chem. 7 (2003) 301;
(e) C. Pasquier, S. Naili, A. Mortreux, F. Agbossou, L. Pelinski, J. Brocard, J. Eilers, I. Reiners, V. Peper, J. Martens, Organometallics 19 (2000) 5723;
(f) T.V. RajanBabu, B. Radetich, K.K. You, T.A. Ayers, A.L. Casalnuovo, J.C. Calabrese, J. Org. Chem. 64 (1999) 3429.

[9] (a) N. Feiken, P. Pregosin, G. Trabesinger, Organometallics 17 (1998) 4510;
(b) P. Le Gendre, M. Offenbecher, C. Bruneau, P.H. Dixneuf, Tetrahedron: Asymmetry 9 (1998) 2279.

[10] (a) C. Bolm, T. Focken, G. Raabe, Tetrahedron: Asymmetry 14 (2003) 1733;
(b) G.S. Chen, X. Li, H.L. Zhang, L.Z. Gong, A.Q. Mi, X. Cui, Y.Z. Jiang, M.C.K. Choi, A.S.C. Chan, Tetrahedron: Asymmetry 13 (2002) 809;
(c) F. Menges, A. Pfaltz, Adv. Synth. Catal. 344 (2002) 40;
(d) G. Jones, C.J. Richards, Tetrahedron Lett. 42 (2001) 5553;
(e) K. Yonehara, K. Mori, T. Hashizume, K.G. Chung, K. Ohe, S. Uemura, J. Organomet. Chem. 603 (2000) 40;
(f) K. Yonehara, T. Hashizume, K. Mori, K. Ohe, S. Uemura, J. Org. Chem. 64 (1999) 9374.

[11] (a) A.A. Nazarov, C.G. Hartinger, V.B. Arion, G. Giester, B.K. Keppler, Tetrahedron 58 (2002) 8489;
(b) K. Yonehara, T. Hashizume, K. Mori, K. Ohe, S. Uemura, Chem. Commun. (1999) 415.

[12] (a) I.D. Kostas, Inorg. Chim. Acta 355 (2003) 424;
(b) J.I. van der Vlugt, R. Sablong, P. Magusin, A.M. Mills, A.L. Spek, D. Vogt, Organometallics 23 (2004) 3177;
(c) S.C. van der Slot, J. Duran, J. Luten, P.C.J. Kamer, P. van Leeuwen, Organometallics 21 (2002) 3873;
(d) R. Ewalds, E.B. Eggeling, A.C. Hewat, P.C.J. Kamer, P. van Leeuwen, D. Vogt, Chem. Eur. J. 6 (2000) 1496;
(e) Y.Z. Jiang, S. Xue, K.B. Yu, Z. Li, J.G. Deng, A.Q. Mi, A.S.C. Chan, J. Organomet. Chem. 586 (1999) 159;
(f) R.M. Deshpande, A. Fukuoka, M. Ichikawa, Chem. Lett. (1999) 13.

[13] (a) R.B. Bedford, S.L. Hazelwood, P.N. Horton, M.B. Hursthouse, Dalton Trans. (2003) 4164;
(b) R.B. Bedford, M.E. Blake, Adv. Synth. Catal. 345 (2003) 1107;
(c) R.B. Bedford, M.E. Blake, S.J. Coles, M.B. Hursthouse, P.N. Scully, Dalton Trans. (2003) 2805;
(d) I.D. Kostas, B.R. Steele, A. Terzis, S.V. Amosova, Tetrahedron 59 (2003) 3467;
(e) R.B. Bedford, S.L. Hazelwood, M.E. Limmert, J.M. Brown, S. Ramdeehul, A.R. Cowley, S.J. Coles, M.B. Hursthouse, Organometallics 22 (2003) 1364;
(f) R.B. Bedford, S.L. Hazelwood, D.A. Albisson, Organometallics 21 (2002) 2599;
(g) R.B. Bedford, S.L. Welch, Chem. Commun. (2001) 129;
(h) R.B. Bedford, S.M. Draper, P.N. Scully, S.L. Welch, New J. Chem. 24 (2000) 745.

[14] Bicyclo[3.2.0]hept-2-en-6-one is commercially available from Merck, although it is easily prepared by hydrodechlorination of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one, which is available on kilogram scale by reaction of 2,2-dichloroacetyl chloride with freshly distilled 1,3-cyclopentadiene in the presence of

triethylamine in hexane under vigourous mechanical stirring (caution: the initial precipitate in this reaction is not $Et_3N \cdot HCl$, but an acyl ammonium salt which is an intermediate to the dichloroketene).
[15] D.P. Curran, C.-T. Chang, J. Org. Chem. 54 (1989) 3140.
[16] D.H.R. Barton, D.O. Jang, J. Org. Chem. 58 (1993) 6838.
[17] (a) D.R. Powell, R.A. Jacobson, Cryst. Struct. Commun. 9 (1980) 1023;
(b) D. Seebach, E. Devaquet, A. Ernst, M. Hayakawa, F.N.M. Kuhnle, W.B. Schweizer, B. Weber, Helv. Chim. Acta 78 (1995) 1636;
(c) A.M. Trzesiak, H. Bartosz-Bechowski, Z. Ciunik, K. Niesyty, J.J. Ziolkowski, Can. J. Chem. 79 (2001) 752;
(d) D.R. Evans, M. Huang, J.C. Fettinger, T.L. Williams, Inorg. Chem. 41 (2002) 5986;
(e) P. Bergamini, V. Bertolasi, M. Cattabriga, V. Ferretti, U. Loprieno, N. Mantovani, L. Marvelli, Eur. J. Inorg. Chem. (2003) 918.
[18] R.S. Rowland, R. Taylor, J. Phys. Chem. 100 (1996) 7384.
[19] P. Faidherbe, C. Wieser, D. Matt, A. Harriman, A. De Cian, J. Fischer, Eur. J. Inorg. Chem. (1998) 451.
[20] (a) G.Y. Li, Angew. Chem. Int. Ed. 40 (2001) 1513;
(b) G.Y. Li, J. Org. Chem. 67 (2002) 3643;
(c) G.Y. Li, W. Marshall, J. Organometallics 21 (2002) 590;
(d) C. Wolf, R. Lerebours, J. Org. Chem. 68 (2003) 7551;
(e) C. Wolf, R. Lerebours, Org. Lett. 6 (2004) 1147;
(f) C. Wolf, R. Lerebours, J. Org. Chem. 68 (2003) 7077.
[21] Oligomerisation of monodentate phosphinites via ring-opening of the monomeric structure to give dimeric, trimeric, tetrameric (up to octameric) structures, has been reported, see: J.P. Dutatsa, A.C. Giumaraes, J.B. Robert, Tetrahedron Lett. 9 (1977) 804, The process is promoted by strongly electron donating phosphorus substituents (to a lesser extent by phenyl substituents).
[22] (a) D.R. Evans, M. Huang, J.C. Fettinger, T.L. Williams, Inorg. Chem. 41 (2002) 5986;
(b) T. Ghaffar, A. Kieszkiewicz, S.C. Nyburg, A.W. Parkins, Acta Crystallogr., Sect. C 50 (1994) 697.
[23] R.B. Bedford, Chem. Commun. (2003) 1787.
[24] J.P Wolfe, R.A. Singer, B.H. Yang, S.L. Buchwald, J. Am. Chem. Soc. 121 (1999) 9550.
[25] (a) A. Zapf, R. Jackstell, F. Rataboul, T. Riermeier, A. Monsees, C. Fuhrmann, N. Shaikh, U. Dingerdissen, M. Beller, Chem. Commun. (2004) 38;
(b) R. Jackstell, M. Gómez Andreu, A. Frisch, K. Selvakumar, A. Zapf, H. Klein, A. Spannenberg, D. Röttger, O. Briel, R. Karch, M. Beller, Angew. Chem. Int. Ed. 41 (2002) 986;
(c) A. Zapf, A. Ehrentraut, M. Beller, Angew. Chem. Int. Ed. 39 (2000) 4153;
(d) A. Zapf, M. Beller, Chem. Eur. J. 6 (2000) 1830.
[26] (a) O. Navarro, H. Kaur, P. Mahjoor, S.P. Nolan, J. Org. Chem. 69 (2004) 3173;
(b) N. Marion, O. Navarro, R.A. Kelly, S.P. Nolan, Synthesis (2003) 2590;
(c) G.A. Grasa, M.S. Viciu, J.K. Huang, C.M. Zhang, M.L. Trudell, S.P. Nolan, Organometallics 21 (2002) 2866;
(d) A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C.L. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69.
[27] (a) R.B. Bedford, S.M. Draper, P.N. Scully, S.L. Welch, New J. Chem. 24 (2000) 745;
(b) R.B. Bedford, S.L. Hazelwood, P.N. Horton, M.B. Hursthouse, Dalton Trans. (2003) 4164;
(c) R.B. Bedford, S.L. Hazelwood, M.E. Limmert, J.M. Brown, S. Ramdeehul, A.R. Cowley, S.J. Coles, M.B. Hursthouse, Organometallics 22 (2003) 1364;
(d) R.B. Bedford, S.L. Hazelwood, D.A. Albisson, Organometallics 21 (2002) 2599;
(e) R.B. Bedford, S.L. Welch, Chem. Commun. (2001) 1418;
(f) R.B. Bedford, S.L. Welch, Chem. Commun. (2001) 129.
[28] M.T. Reetz, J.G. de Vries, Chem. Commun. (2004) 1559.
[29] For calculation of the natural bite angle, see: C.P. Casey, G.T. Whiteker, Isr. J. Chem. 30 (1990) 299.
[30] For ligand preferred P–M–P–P angle, see: P. Dierkes, P.W.N.M. van Leeuwen, J. Chem. Soc., Dalton Trans. 1519 (1999).
[31] M. Kranenburg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, Eur. J. Inorg. Chem. (1998) 155.
[32] A. Gillie, J.K. Stille, J. Am. Chem. Soc. 102 (1980) 4933.
[33] For a comprehensive review on 1,6-diene cycloisomerisation, see: G.C. Lloyd-Jones, Org. Biomol. Chem. 1 (2003) 215, and references cited therein.
[34] (a) 1,6-Diene cycloisomerisation key references: R. Grigg, T.R.B. Mitchell, A. Ramasubbu, J. Chem. Soc., Chem. Commun. (1979) 669;
(b) R. Grigg, T.R.B. Mitchell, A. Ramasubbu, J. Chem. Soc., Chem. Commun. (1980) 27;
(c) R. Grigg, J.F. Malone, T.R.B. Mitchell, A. Ramasubbu, R.M. Scott, J. Chem. Soc., Perkin Trans. 1 (1984) 1745;
(d) B. Radetich, T.V. RajanBabu, J. Am. Chem. Soc. 120 (1998) 8007;
(e) A. Heumann, M. Moukhliss, Synlett (1999) 268;
(f) A. Heumann, M. Moukhliss, Synlett (1998) 1211;
(g) K.L. Bray, I.J.S. Fairlamb, G.C. Lloyd-Jones, Chem. Commun. (2001) 187;
(h) K.L. Bray, I.J.S. Fairlamb, J.-P.H. Kaiser, G.C. Lloyd-Jones, P.A. Slatford, Top. Catal. 19 (2002) 49;
(i) K.L Bray, J.P.H. Charmant, I.J.S. Fairlamb, G.C. Lloyd-Jones, Chem. Eur. J. 7 (2001) 4205;
(j) A.L. Goj, R.A. Widenhoefer, J. Am. Chem. Soc. 123 (2001) 11133;
(k) N.S. Perch, R.A. Widenhoefer, Organometallics 20 (2001) 5251;
(l) Cycloisomerisation/hydrosilyation of 1,6-dienes: G.A. Molander, P.J. Nichols, J. Am. Chem. Soc. 117 (1995) 4415;
(m) S. Onozawa, T. Sakakura, M. Tanaka, Tetrahedron Lett. 35 (1994) 8177;
(n) G.A. Molander, P.J. Nichols, B.C. Noll, J. Org. Chem. 63 (1998) 2292;
(o) G.A. Molander, E.D. Dowdy, H. Schumann, J. Org. Chem. 63 (1998) 3386;
(p) C.N. Stengone, R.A. Widenhoefer, Tetrahedron Lett. 40 (1999) 1451.
[35] P. Kisanga, L.A. Goj, R.A. Widenhoefer, J. Org. Chem. 66 (2001) 635.
[36] We have not, so far, detected chlorinated by-products that could result from reaction of $(P,P')PdCl^+$ with 1,6-diene **21**, whether that be through a cycloisomerisation process or alternative reaction pathway.
[37] (a) A. Fürstner, F. Stelzer, H. Szillat, J. Am. Chem. Soc. 123 (2001) 11863;
(b) For related work, see: S. Yamazaki, K. Yamada, K. Yamamoto, Org. Biomol. Chem. 2 (2004) 257;
(c) B.B. Snider, D.M. Roush, J. Org. Chem. 44 (1979) 4229;
(d) S. Yamazaki, K. Yamada, T. Otsubo, M. Haruna, E. Kutsuwa, H. Tamura, Chem. Commun. (2001) 69;
(e) S. Yamazaki, S. Inakoa, K. Yamada, Tetrahedron Lett. 44 (2003) 1429;
(f) S. Yamazaki, K. Yamada, S. Yamabe, K. Yamamoto, J. Org. Chem. 67 (2002) 2889.
[38] G.M. Sheldrick, SADABS V. 2.03, Bruker AXS, Madison, WI, 2001.
[39] G.M. Sheldrick, SHELXTL V. 6.12, Bruker AXS, Madison, WI, 2001.