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Journal of Organometallic Chemistry 693 (2008) 103–108
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

New synthesis and thermal studies of palladacycloalkanes and their precursors

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Received 7 September 2007; received in revised form 15 October 2007; accepted 16 October 2007
Available online 22 October 2007

Abstract

A series of new palladacycloalkanes of formula *cis*-[$PdL_2(CH_2)_n$] (**9**. $n = 6$, L = PPh_3; **10**. $n = 6$, L_2 = dppe; **11**. $n = 8$, L = PPh_3; **12**. $n = 8$, L_2 = dppe) have been prepared by two routes. In the first route, the precursor bis(1-alkenyl) complexes *cis*-[$PdL_2((CH_2)_nCH{=}CH_2)_2$] (**1**. $n = 2$, L = PPh_3, **2**. $n = 2$, L_2 = dppe, **3**. $n = 3$, L = PPh_3, **4**. $n = 3$, L_2 = dppe) were allowed to react with Grubb's 2nd generation catalyst to give the palladacycloalkenes, *cis*-[$PdL_2(CH_2)_nCH{=}CH(CH_2)_n$] (**5**. $n = 2$, L = PPh_3, **6**. $n = 2$, L_2 = dppe, **7**. $n = 3$, L = PPh_3, **8**. $n = 3$, L_2 = dppe), which were then hydrogenated to the palladacycloalkanes, **9**–**12**. In the second route, the di-Grignard reagents $BrMg(CH_2)_nMgBr$ ($n = 6$, 8) were reacted with the palladium complex [$PdCl_2$(COD)] followed by immediate ligand displacement to form the respective palladacycloalkanes **10** and **12**. The complexes obtained were characterized by a range of spectroscopic and analytical techniques. Thermal decomposition studies were carried out on the palladacycloalkanes **9**–**12** and the main organic products shown to be 1-alkenes and 2-alkenes.
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Keywords: Palladacycloalkanes; Bis(1-alkenyl) precursors; Ring closing metathesis; Thermal decomposition

1. Introduction

Metallacycloalkanes are an important class of compounds [1] that can be key intermediates in various catalytic reactions [2]. In spite of this importance of medium to large metallacycloalkanes as intermediates, very little is known about such compounds. Noteworthy, up to now, no higher metallacycloalkanes containing more than 9-membered rings are known [3]. On decomposition, various metallacycloalkanes have shown an interesting organic product distribution, depending on several factors [4]. Recently we have shown a novel route to the synthesis of medium to large platinacycloalkanes from their bis(1-alkenyl) precursors by ring closing metathesis reaction using Grubbs' catalysts [5]. These platinacycloalkanes were found to be stable at room temperature and the thermal stability of these compounds depends on the nature of the phosphine donor ligands. Using this methodology, we now report the preparation, characterization and thermal decomposition of novel palladacycloalkanes and their precursors.

2. Results and discussion

2.1. Synthesis and characterization of palladacycles

The preparation of the new palladacycloalkane complexes (**9**–**12**) employed two reaction routes which are shown in Scheme 1.

Route 1 is a new approach for the synthesis of metallacycloalkane complexes using ring-closing metathesis (RCM) with the Grubbs catalyst, which we have successfully used in making medium and large platinacycloalkanes [5]. Herein, we applied this route to synthezis new medium palladacycloalkane complexes.

The bis(1-alkenyl) complexes were prepared by the reaction of [$PdCl_2$(COD)] with the corresponding Grignard

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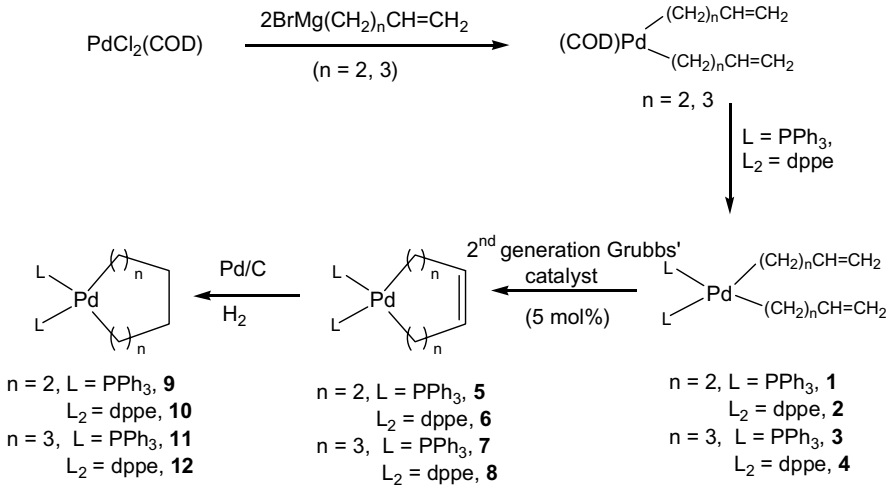
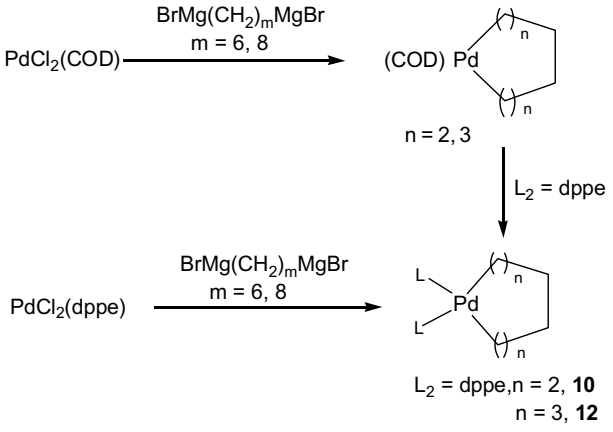
doi:10.1016/j.jorganchem.2007.10.025



(**a**) Route 1



(**b**) Route 2

Scheme 1. Preparation of palladacycloalkanes.

reagents followed by ligand displacement as shown in Scheme 1. Formation of the products was signaled by dissolution of the palladium species. The resulting complexes were found to be unstable in the reaction mixture above 0 °C, giving reductive elimination products, 1,7-octadiene in the case of **1** and **2** and 1,9-decadiene in the case of **3** and **4**, as well as some elemental palladium (palladium black) and these observations are in agreement with the literature [6]. The reaction mixture was worked up immediately after the hydrolysis of the excess Grignard reagent at 0 °C. The left-over product, after decomposition, was found to be relatively stable below room temperature. The palladacycloalkenes were prepared from the bis(1-alkenyl) complexes by the ring closing metathesis (RCM) reaction using Grubbs' 2nd generation catalyst in moderate yields. Grubbs' 2nd generation catalyst was used in all the reactions as the longer reaction times were necessary with the Grubbs' 1st generation catalyst. Hydrogenation of these palladacycloalkenes with Pd/C yielded the desired saturated palladacycloalkanes in good yields.

In the conventional route 2, the pallacycloalkane complexes with dppe ligand **10** and **12** were also prepared by the reaction of di-Grignard reagents using the method reported by Whitesides et al. for the synthesis of a series of platinacyclopentanes and a platinacycloheptane [7]. By treating a solution of [$PdCl_2$(COD)] in diethyl ether with the di-Grignard reagents {$BrMg(CH_2)_6MgBr$ for **10** and $BrMg(CH_2)_8MgBr$ for **12**} at −78 °C, followed by ligand displacement gave complexes **10** and **12** in very low yield (<15%), respectively. This reaction had to be quenched in a very short time (ca. 20 min when the reaction warmed to −30 °C) as the mixture easily decomposed even at low temperature. The intermediates involved, palladacycloalkane with COD ligand, are soluble in any solvent and thermally unstable at room temperature, this might be the major reason to give the product in very low yields. Assuming the absence of COD ligand would increase the product yields, we then treated [$PdCl_2$(dppe)], a much more stable complex than [$PdCl_2$(COD)], with the di-Grignard reagents. The reaction mixture was stable at room temper-

ature for more than 5 h and resulted in a moderate yield ca. 50% of the desired products.

All new complexes were characterized by ^{1}H and ^{31}P NMR spectroscopy as well as mass spectrometry. The complexes were found to be unstable in air. Exposure of the complexes to air at room temperature for a few hours resulted in complex decomposition to give an intense red product initially and then gradually turns to black residue after longer periods (ca. 20 h). In contrast, the analogous platinacycles and their precursors are quite stable to moderate temperatures except in few cases when PPh_3 ligand is used [5b].

The ^{1}H NMR spectra of the bis(1-alkenyl) complexes, (**1**–**4**), show characteristic signals for the protons in the terminal alkenes (see Section 4 for details). The products obtained from the RCM reaction showed broad alkene proton shifts in the region 5.3–5.6 ppm in ^{1}H NMR, similar to their platinum analogs, which are due to the *E* and *Z* isomers of the palladacycloalkenes and these isomers could not be isolated. Formation of the ring-closed complexes, **5**–**8**, was indicated by the appearance of the broad multiplet between 5 and 6 ppm, which is due to the alkene protons in the palladacycloalkenes. Appearance of this new peak was accompanied by the disappearance of the terminal alkene protons in the bis(1-alkenyl) precursors. The methylene protons attached to the metal as well as other methylene protons in the metallacyclic moiety appeared as broad multiplets together in the region 1.1–2.5 ppm. The palladacycloalkanes were obtained by the hydrogenation reaction of the palladacycloalkenes, **5**–**8**. Reaction progress was monitored by ^{1}H NMR. Product formation was indicated by the reduction and eventual disappearance of the alkene protons during the hydrogenation reaction. ^{1}H NMR spectra of complexes **1**–**12** show the same trends reported for analogous platinum complexes [5].

The ^{31}P NMR spectra of the bis(1-alkeny), palldacycloalkene and palladacycloalkane complexes all show a similar pattern. The signals in the ^{31}P NMR appeared in the region 25.5–29.7 ppm for the PPh_3 complexes and 30.1–33.5 ppm for the dppe complexes. For the palladacycloalkanes, the ^{31}P NMR spectra showed a small signal close to the main singlet, indicating the possible presence of different conformational isomer.

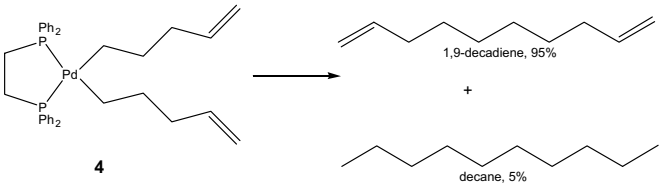
The mass spectra of the complexes show molecular ion peaks corresponding to the molecular masses of the expected products. The fragmentation patterns of the complexes also show peaks corresponding to the loss of the ligands as well as the hydrocarbon fragments. It is interesting to note that higher molecular masses, i.e., beyond the molecular ion peaks were observed in all the palladacycles. This could be due to either the formation of various products under the experimental conditions with FAB or the presence of dimeric species. C, H analysis of the bis(1-alkenyl) complexes showed that solvent (hexane) molecules were trapped in the products. The number of trapped solvent molecules ranged between 2 and 5. Attempts to completely remove the solvent from the products resulted in the complexes decomposing.

2.2. Thermal decomposition studies

Thermal decomposition of the palladacycloalkanes and their corresponding bis(1-alkenyl) precursors were studied directly, without any solvent in order to minimize any solvent effects [4]. Thermolysis was carried out by dissolving the freshly prepared complexes in dichloromethane, removing the solvent and drying at least for 3 h under vacuum, then heating the complexes in a thermostatted bath. The reaction mixture was quenched by cooling the tube at −78 °C. The volatile organic products were extracted by pentane and analyzed by GC–MS. These results were compared with the literature reports [4,5], especially with the results for the platinum analogs.

2.2.1. Thermolysis of bis(1-alkenyl)palladium(II) complexes, *1*–*4*

Bis(1-pentenyl)palladium(II) complex, **4**, was initially decomposed at room temperature during the synthesis and the decomposition was also carried out at 170 °C in solid phase to give 1,9-decadiene as the major product (95%) in both the cases via the reductive elimination reaction. These organic products were confirmed by NMR spectra and GC–MS. *n*-Decane was also found as the minor product.



(1)

Even though no decomposition studies have been reported on bis(1-alkenyl)palladium(II) complexes, the possible decomposition pathways of this class of complexes have been summarized, in which the long chain diene products are formed by reductive elimination [5c]. The formation of 1,9-decadiene in the thermolysis of **4** is consistent with the reductive elimination pathway and also agrees with the findings by Ozawa and Yamamoto [8]. They observed that thermal decomposition of *cis*-$PdEt_2L_2$ complexes afforded reductive elimination products exclusively. The small amount of *n*-decane could be the result of reductive elimination followed by hydrogenation. The source of hydrogen could be either the activation of solvent or the phenyl groups in phosphine ligands by the zerovalent metal species under those experimental conditions.

In contrast to the reductive elimination reaction that occurred for **4**, the thermolysis of complexes **1**–**3** in solid state indicated the formation of mixture of products through the β-hydride elimination as well as reductive elimination reactions. For example, bis(1-pentenyl)palladium(II) complex with PPh_3 ligand, **3**, decomposed to

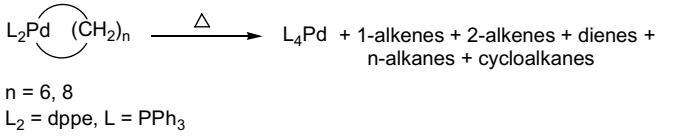
Table 1
Products for the thermal decomposition of the palladacycloalkanes **9**–**12**

Complex	Products observed (%)				
	1-Alkene	2-Alkenes	Diene	*n*-Alkane	Cycloalkane
9	43	17	6	18	16
10	52	24	11	6	7
11	33	32	17	15	3
12	17	71	2	10	<1

give *n*-pentane (17%), 1,4-pentadiene (54%) and 1-decene (30%). A similar trend was observed in the decomposition of bis(1-butenyl) complexes (**1**, **2**).

2.2.2. Thermolysis of palladacycloalkane complexes, 9–12

Thermal decomposition of palladacycloalkanes in the solid phase at 170 °C gave the alkene products presented as a mixture of isomers as well as *n*-alkanes (Table 1). The decomposition is accompanied by the formation of a black residue, which could be palladium metal and some [L_4Pd] complex shown as [9].



(2)

1-Alkene and 2-alkenes are the major products in all cases whereas 1-alkene predominates except for complex **12**. The formation of 1-alkene might go through the β-hydride elimination and the occurrence of isomerization either during or after decomposition could give the 2-alkenes.

For complex **12**, the isomerization to 2-alkenes is much easier than for other complexes, and there might be two factors influenced the decomposition pathway here. One is the effect of ring size. It appears that the conformationally flexible larger size rings have lower thermal stability [10], which could make the decomposition via β-hydride elimination/isomerization more easy for the 9-membered ring. Another one is the effect of the ancillary ligand. Compared to their analogues, the complexes with the chelating ligand dppe formed higher yields of 2-alkenes (24% for **10** and 71% for **12**).

The observation of cycloalkanes as minor decomposition products is consistent with the palladacyclopentane system [9]. It was suggested that the production of cycloalkane is favoured only when the ancillary ligand dissociates easily. For instance, complexes **9** (16%) and **11** (3%) gave higher yield than their analogues with dppe ligand. In addition, *n*-alkane was also found as the minor product, which could be formed by intermolecular reactions involving a hydridopalladium(II) species [11], or intramolecular hydrogen abstraction from the ancillary ligand [12].

3. Conclusions

New palladacycloalkane complexes have been prepared by two routes. In the ring-closing metathesis (RCM) with the Grubbs catalyst route, the new precursor complexes, bis(1-alkenyl)palladium(II) and palladacycloalkenes, have also been prepared. These complexes exhibit low stability at room temperature and are sensitive to moisture and air. It appeared that the RCM methodology is better than the di-Grignard route in terms of yields of the palladacycloalkanes.

Although the palladacycloalkane complexes **9**–**11** present different distribution of the decomposition products, their decomposition demonstrates that the β-hydride elimination to form 1-alkene is the major decomposition pathway. Due to the effect of ring size and ancillary ligands, the thermal decomposition of complex **12** gives 2-alkenes as major products easily. In addition, the possible pathways for the formation of the minor products are also proposed. Reductive elimination of cycloalkane appears to be a favorable reaction in the complex with easily dissociated ligand, and the formation of *n*-butane could involve intermolecular or intramolecular hydrogen abstraction reactions. In addition, we are currently performing insertion reactions of small molecules such as carbon monoxide and carbon dioxide into the metal carbon bonds of the palladacycloalkane compounds.

4. Experimental

4.1. General

All reactions were carried out under nitrogen or argon atmosphere using a dual vacuum/nitrogen line and standard Schlenk line techniques. $PdCl_2$ was obtained from Johnson Matthey. All other reagents were obtained commercially from Aldrich and, unless otherwise stated, were used as received without further purification. The reagents $PdCl_2$(COD) [13], $PdCl_2$(dppe) [14], $BrMg(CH_2)_nCH{=}CH_2$ ($n = 2$, 3) and $BrMg(CH_2)_nMgBr$ ($n = 6$, 8) [15] were prepared as previously reported. Solvents were dried and distilled, and all procedures were carried out under nitrogen. Microanalysis was carried out using a Fisons EA 1108 CHNS Elemental Analysis apparatus. Melting points were recorded using a Kofler hot stage microscope (Riechert Thermovar). NMR spectra were recorded on Varian XR300 MHz and XR400 MHz spectrometers using deuterated benzene as a solvent. Gas chromatographic analyses were performed on a Varian 3900 instrument and GC–MS analyses were carried out with an Agilent 5973 instrument.

4.2. Synthesis of palladacycloalkanes and their precursors

*4.2.1. cis-[Pd{$(CH_2)_2CH{=}CH_2$}$_2$(PPh_3)$_2$] (**1**)*

$BrMg(CH_2)_2CH{=}CH_2$ (2.3 ml of 2.39 M diethyl ether solution, 5.36 mmol) was slowly added to a suspension of $PdCl_2$(COD) (0.51 g, 1.79 mmol) in diethyl ether (15 ml) at −78°C. The suspension was stirred for 40 min, then warmed to room temperature and stirred for another 20 min. The reaction was quenched by adding a saturated

solution of NH_4Cl (5 ml). The product was extracted with hexane and the organic layer was collected and dried over anhydrous $MgSO_4$. Excess solvent was removed under reduced pressure and the product was obtained as a bright yellow oil, which was then dried under vacuum. The yellow oil obtained was dissolved in Et_2O and PPh_3 (0.47 g, 1.78 mmol) was added. The solution was stirred for 1 h at room temperature, after which the solvent was removed and the product was obtained as bright yellow oil (0.67 g, 50%). Anal. Calc. for $C_{59}H_{80}P_2Pd$ (with 2.5 mol. of C_6H_{14}): C, 74.00; H, 8.42. Found: C, 73.51; H, 7.67%. ^{1}H NMR: 7.47–7.70 (m, 30H, Ph), 5.84 (m, 2H, =CH), 4.94–5.07 (m, 4H, $=CH_2$), 1.43–2.34 (m, 8H, CH_2). ^{31}P NMR: 29.2 (PPh_3). Mass spec. (FAB): *m/z* 740.1 $[M]^+$, 687.1 $[M-CH_2CH_2CH=CH_2]^+$, 629.8 $[M-2CH_2CH_2CH=CH_2]^+$, 477.8 $[M-PPh_3]^+$, 215 $[M-2PPh_3]^+$.

Complexes **2**–**4** were prepared in a similar manner. All of the complexes were found to be yellow oils with moderate yields (ca. 50%). Microanalyses of these oils showed the presence of solvent molecules.

*4.2.2. cis-Pd(CH$_2$CH$_2$CH=CH$_2$)$_2$(dppe)] (**2**)*

Anal. Calc. for $C_{46}H_{66}P_2Pd$ (with 2 mol. of C_6H_{14}): C, 70.17; H, 8.45. Found: C, 70.12; H, 9.76%. ^{1}H NMR: 7.44–7.68 (m, 20H, Ph), 5.82 (m, 2H, =CH), 4.96–5.10 (m, 4H, $=CH_2$), 1.72–2.36 (m, 8H, CH_2), 3.44 (t, 4H, P–CH_2). ^{31}P NMR: 31.0 (–PPh_2). Mass spec. (FAB): *m/z* 614.0 $[M]^+$, 560.0 $[M-CH_2CH_2CH=CH_2]^+$, 502.9 $[M-2CH_2CH_2CH=CH_2]^+$, 215.4 $[M-dppe]^+$.

*4.2.3. cis-[Pd(CH$_2$CH$_2$CH$_2$CH=CH$_2$)$_2$(PPh$_3$)$_2$] (**3**)*

Anal. Calc. for $C_{76}H_{118}P_2Pd$ (with 5 mol. of C_6H_{14}): C, 76.06; H, 9.91. Found: C, 76.84; H, 10.66%. ^{1}H NMR: 7.01–7.88 (m, 30H, Ph), 5.80 (m, 2H, =CH), 4.86–4.96 (m, 4H, $=CH_2$), 1.63–2.10 (m, 12H, CH_2). ^{31}P NMR: 29.7 (PPh_3). Mass spec. (FAB): *m/z* 767.9 $[M]^+$, 698.1 $[M-CH_2CH_2CH_2CH=CH_2]^+$, 629.8 $[M-2CH_2CH_2CH_2CH=CH_2]^+$, 505.9 $[M-PPh_3]^+$, 243.5 $[M-2PPh_3]^+$, 135.1 $[2CH_2CH_2CH_2CH=CH_2]^+$, 68.2 $[CH_2CH_2CH_2CH=CH_2]^+$.

*4.2.4. cis-[Pd(CH$_2$CH$_2$CH$_2$CH=CH$_2$)$_2$(dppe) (**4**)*

Anal. Calc. for $C_{60}H_{98}P_2Pd$ (with 4 mol. of C_6H_{14}): C, 72.96; H, 10.06. Found: C, 73.11; H, 9.67%. ^{1}H NMR: 7.45–7.89 (m, 20H, Ph), 5.81 (m, 2H, =CH), 4.94–5.01 (m, 4H, $=CH_2$), 2.52 (t, 4H, P–CH_2), 1.31–2.37 (m, 12H, CH_2). ^{31}P NMR: 30.1 (–PPh_2). Mass spec. (FAB): *m/z* 642.1 $[M]^+$, 572.9 $[M-CH_2CH_2CH_2CH=CH_2]^+$, 503.8 $[M-2CH_2CH_2CH_2CH=CH_2]^+$, 243.6 $[M-dppe]^+$.

*4.2.5. Palladacycloheptene (L = PPh$_3$) (**5**)*

Grubbs' 2nd generation catalyst was added a solution of **1** (0.32 g, 0.45 mmol) in benzene (30 ml). The mixture was refluxed with stirring at 50 °C for 18 h, then cooled to room temperature. The solvent was removed under reduced pressure gave a maroon residue which was extracted with hexane (4 × 5 ml). The product was obtained as brown oil (0.25 g, 80%). ^{1}H NMR: 7.44–7.71 (m, 30 H, Ph), 5.44 (br m, 2H, =CH), 2.31 (m, 4H, CH_2), 1.62 (m, 4H, Pd–CH_2). ^{31}P NMR: 29.3 (PPh_3). Mass spec. (FAB): *m/z* 712.1 $[M]^+$, 629.1 $[M-C_6H_{10}]^+$, 449.8 $[M-PPh_3]^+$, 188.9 $[M-2PPh_3]^+$. Complexes **6**–**8** were prepared in a similar manner. All of the complexes are yellow brown oils at 70–80% yields.

*4.2.6. Palladacycloheptene (L$_2$ = dppe) (**6**)*

^{1}H NMR: 7.46–8.01 (m, 20H, Ph), 5.40 (br m, 2H, =CH), 2.54 (t, 4H, P–CH_2), 2.05 (m, 4H, CH_2), 1.79 (m, 4H, Pd–CH_2). ^{31}P NMR: 32.9 (–PPh_2). Mass spec. (FAB): 585.9 $[M]^+$, 503.8 $[M-C_6H_{10}]^+$, 189.4 $[M-dppe]^+$.

*4.2.7. Palladacyclononene (L = PPh$_3$) (**7**)*

^{1}H NMR: 7.47–7.90 (m, 30H, Ph), 5.45 (br m, 2H, =CH), 1.70–2.27 (br m, 8H, CH_2), 1.51 (m, 4H, Pd–CH_2). ^{31}P NMR: 28.6 (PPh_3). Mass spec. (FAB): *m/z* 740.2 $[M]^+$, 628.9 $[M-C_8H_{14}]^+$, 477.8 $[M-PPh_3]^+$, 217.1 $[M-2PPh_3]^+$.

*4.2.8. Palladacyclononene (L$_2$ = dppe) (**8**)*

^{1}H NMR: 7.45–7.76 (m, 20H, Ph), 5.41 (br m, 2H, =CH), 2.58 (t, 4H, P–CH_2), 2.01–2.38 (br m, 8H, CH_2), 1.87 (m, 4H, Pd–CH_2). ^{31}P NMR: 32.9 (–PPh_2). Mass spec. (FAB): *m/z* 614.1 $[M]^+$, 503.9 $[M-C_8H_{14}]^+$, 216.9 $[M-dppe]^+$.

*4.2.9. Palladacycloheptane (L = PPh$_3$) (**9**)*

Ten percent of Pd/C (20 mg) was added to the solution of **5** (0.21 g, 0.29 mmol) in Et_2O (20 ml). The solution was stirred under 1 atm hydrogen gas for 46 h. The mixture was then filtered and excess solvent was removed under reduced pressure and the product was obtained as a brownish yellow solid (0.19 g, 90%), m.p. 48–59 °C (dec.); ^{1}H NMR: 7.35–7.82 (m, 30H, Ph), 2.30 (m, 8H, CH_2), 2.05 (m, 4H, Pd–CH_2). ^{31}P NMR: 27.3 (PPh_3). Mass spec. (FAB): *m/z* 714. 2 (M^+), 451.8 $(M-PPh_3)^+$, 189.7 $(-2PPh_3)^+$, 629.1 $(M-C_6H_{12})^+$. Complexes **10**–**12** were prepared in a similar fashion. All of the complexes were obtained in good yields as pale yellow brown solids (80–90%).

*4.2.10. Palladacycloheptane (L$_2$ = dppe) (**10**)*

M.p. 65–73 °C (dec.); ^{1}H NMR: 7.44–7.71 (m, 20H, Ph), 3.36 (t, 4H, P–CH_2), 2.50 (m, 8H, CH_2), 2.01 (m, 4H, Pd–CH_2). ^{31}P NMR: 32.7 (–PPh_2). Mass spec. (FAB): *m/z* 587.9 $[M]^+$, 503.8 $[M-C_6H_{12}]^+$, 189.9 $[M-dppe]^+$.

*4.2.11. Palladacyclononane (L = PPh$_3$) (**11**)*

M.p. 39–49°C (dec.); ^{1}H NMR: 7.64–7.98 (m, 30H, Ph), 1.22–1.62 (m, 12H, CH_2), 0.87 (m, 4H, Pd–CH_2). ^{31}P NMR: 25.5 (PPh_3). Mass spec. (FAB): *m/z* 742.9 $[M]^+$, 630.0 $[M-C_8H_{16}]^+$, 489.9 $[M-PPh_3]^+$, 216.9 $[M-2PPh_3]^+$.

*4.2.12. Palladacyclononene (L$_2$ = dppe) (**12**)*

M.p. 55–67°C (dec.); ^{1}H NMR: 7.10–7.85 (m, 20H, Ph), 2.24 (t, 4H, P–CH_2), 1.33 (br m, 8H, CH_2), 0.90 (br m, 8H, Pd–CH_2–CH_2). ^{31}P NMR: 33.5 (–PPh_2). Mass spec.

(FAB): *m/z* 616.0 $[M]^+$, 503.4 $[M-C_8H_{16}]^+$, 217.5 $[M-dppe]^+$.

4.3. Synthesis of palladacycloalkanes by di-Grignard route

A twofold excess solution of $BrMg(CH_2)_nMgBr$ ($n = 6$, 8) in anhydrous THF was slowly added to a suspension of $PdCl_2(COD)$ (0.50 g, 1.75 mmol) in Et_2O (30 ml) at −78°C. The mixture was stirred for 30 min, then warmed to room temperature and stirred for another 30 min. Pentane (5 ml) was then added to the tube and excess di-Grignard reagent precipitated out of solution. The supernatant was filtered and the solvent was removed under reduced pressure to form the yellow oil of the COD complexes, *cis*-$[Pd(CH_2)_n(COD)]$ (when $n = 6$, yield: 0.31 mmol, 18%; when $n = 8$, 0.28 mmol, 16%), which were then dissolved in Et_2O (20 ml) and an excess of dppe was added. The product immediately precipitated out of solution. The mixture was stirred for a further 30 min and the supernatant was removed. The pale yellow solid obtained was washed with diethyl ether (4×5 ml). The solid was dried under vacuum for half an hour. The same procedure was followed for the preparation of other complexes. Complex **10**: (0.15 g, 15%), complex **12**: (0.12 g, 11%). These two complexes were also prepared (yield ca. 48%) from the reaction of di-Grignard reagents with $PdCl_2(dppe)$.

4.4. General procedure for the thermal decomposition experiments

Thermolysis reactions were carried out in clean, dry, sealed evacuated Schlenk tubes of 1-cm o.d. and 10-cm length. The palladium complex was dissolved in DCM and transferred into the tube; the solvent was removed under vacuum and dried at least for 3 h before themolysis. The samples were then immersed in a thermostated oil bath constant to 170 ± 5 °C. The tubes were removed at intervals (2 h) and quenched by immersion in liquid nitrogen. Decomposition products were extracted by 0.5 μl pentane containing 20 ml of chlorobenzene as internal standard and analyzed by GC/GCMS. Products were identified by comparison of retention times to those of authentic samples. Product yields were determined by response relative to the internal standard (chlorobenzene). Response factors were obtained from authentic samples.

GC analyses were performed using a Varian 3900 gas chromatograph equipped with an FID and a 30 m × 0.32 mm CP-Wax 52 CB column (0.25 μm film thickness). The carrier gas was helium at 5.0 psi. The oven was programmed to hold at 32 °C for 4 min and then to ramp to 200 °C at 10°/min and hold 5 min.

GC–MS analyses for peak identification were performed using an Agilent 5973 gas chromatograph equipped with MSD and a 60 m × 0.25 mm Rtx-1 column (0.5 μm film thicknesses). The carrier gas was helium at 0.9 ml/min. The oven was programmed to hold at 50 °C for 2 min and then ramp to 250 °C at 10°/min and hold 8 min.

Acknowledgements

We are thankful to AngloPlatinum Corporation, DST Centre of Excellence in Catalysis, C* Change, UCT, The UCT Chemistry EDP programme and Johnson Matthey for their support.

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