$PdCl_2$-promoted reactions of diaryl-substituted methylenecyclopropanes†

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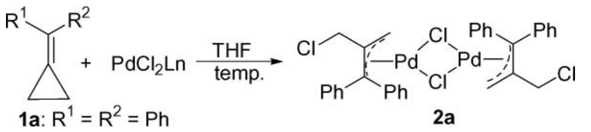
The $PdCl_2$-promoted reactions of methylenecyclopropanes (MCPs) **1** bearing diaryl substituents on the terminal double bond were carefully investigated. The solvents employed significantly affected the reaction outcomes. It was found that dimeric allylpalladium(II) complexes **2a–2f** can be obtained as the sole products in acceptable to good yields under mild reaction conditions with THF as the solvent, while dimeric allylpalladium(II) complexes **2a–2f** along with another type of dimeric allylpalladium(II) complexes **4a–4e** can be obtained in good to high total yields if *N*,*N*-dimethylacetamide (DMAc) was used as the solvent. Moreover, using *N*,*N*-dimethylformamide (DMF) as the solvent in the presence of water, it was found that water can also participate in the reaction to form another type of dimeric allylpalladium(II) complex **6** as the minor product. All of these dimeric allylpalladium(II) complexes reported in the paper have been characterized by X-ray crystal structure diffraction.

Introduction

Methylenecyclopropanes (MCPs) **1** are highly strained but readily accessible molecules that have served as useful building blocks in organic synthesis.[1] The transition metal-mediated chemistry of MCPs **1** has been widely explored during the past few decades and the developments in this field have been comprehensively reviewed by Binger,[2] Donaldson,[3] Lautens,[4] Yamamoto,[5] Rubin and Gevorgyan.[6] Besides transition metals, Lewis acids such as $Ln(OTf)_3$ (Ln = Yb, Sc, La, *etc.*) mediated reactions of MCPs **1** have are also been extensively investigated in the past decade and it was found that the corresponding products can be obtained *via* the selective cleavage of the proximal bond.[7] In the early 1980s, Hughes and co-workers extensively investigated the $PdCl_2(PhCN)_2$-mediated chloropalladation reaction of MCPs bearing substituent(s) on the cyclopropyl ring to give the corresponding dimeric allylpalladium(II) complex at room temperature,[8] in contrast, MCP bearing two methyl groups on the terminal double bond (isopropylidenecyclopropane) showed no tendency to undergo the chloropalladation reaction and was unchanged even after refluxing with $PdCl_2(PhCN)_2$ in benzene for 8 h.[8] In 2008, Huang and co-workers reported that in the presence of $PdCl_2(NHC)$ (NHC = *N*-heterocyclic carbene) catalyst, MCPs **1** can undergo the cycloisomerization reaction to give the corresponding dihydronaphthalene derivatives.[9] In our laboratory, it was found that in the presence of $PdCl_2$, the chloropalladation reactions of MCPs **1** bearing two aryl groups on the terminal double bond can afford dimeric allylpalladium(II) complexes **2a–2f**, **4a–4e**, **5** and **6** in good to high yields under different reaction conditions. Herein we wish to report these results in detail.[10]

Table 1 Optimization for the reaction of MCP **1a** with Pd source



Entry[a]	Ln	Temp.	Time/h	Yield/%[b]
1	none	rt	24	58
2	none	50 °C	24	74
3	none	reflux	24	74
4	$(CH_3CN)_2$	50 °C	24	57
5	$(PhCN)_2$	50 °C	24	52
6	$(PPh_3)_2$	50 °C	24	N.R.
7	dppe	50 °C	24	28

[a] All reactions were carried out using MCP **1a** (0.3 mmol), Pd source (0.33 mmol) and THF (1.0 mL) at the listed temperature.
[b] Isolated yields.

Results and discussion

Formation of dimeric allylpalladium(II) complexes

Initial examinations were carried out using MCP **1a** ($R^1 = R^2 = Ph$) (0.3 mmol) and $PdCl_2$ (0.33 mmol) as the substrates under various conditions. Of the solvents and reaction temperatures screened, it was found that when the reaction was carried out at 50 °C or under reflux in THF, the best result can be obtained with the formation of the dimeric allylpalladium(II) complex **2a** in 74% yield in both cases (Table 1, entries 2 and 3) and **2a** was obtained in 58% yield at room temperature (20 °C) (Table 1, entry 1) (please see ESI for more details†). For all other $PdCl_2$ complexes investigated instead of $PdCl_2$ for this reaction, inferior results were obtained under the standard conditions. For instance, when $PdCl_2(CH_3CN)_2$ and

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† Electronic supplementary information (ESI) available: Experimental procedures, spectroscopic data and crystallographic information files for complexes **2a**, **3a**, **4a**, **3b**, **6** and **7**. CCDC reference numbers 620092, 621667, 646598, 744566, 744567, 758823. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00059k

$PdCl_2(PhCN)_2$ were used in this reaction, complex **2a** was formed in 57 and 52% yields, respectively (Table 1, entries 4 and 5). When $PdCl_2(dppe)$ [dppe = 1,2-bis(diphenylphosphino)ethane] was employed in this reaction, only 28% yield of complex **2a** was formed (Table 1, entry 7), while $PdCl_2(PPh_3)_2$ showed no activity for this transformation (Table 1, entry 6). The structure of complex **2a** was unambiguously determined by X-ray diffraction. The ORTEP drawing is shown in Fig. 1 and its CIF data are presented in the ESI.†[11] It should also be noted here that **2a** may exist in two isomers (*trans*-**2a** and *cis*-**2a**).[12] On the basis of its ^1H NMR, ^{13}C NMR and X-ray diffraction, it may be concluded here that only the *trans*-isomer was obtained as the thermodynamically favored isomer as previously reported by Hughes.[8]

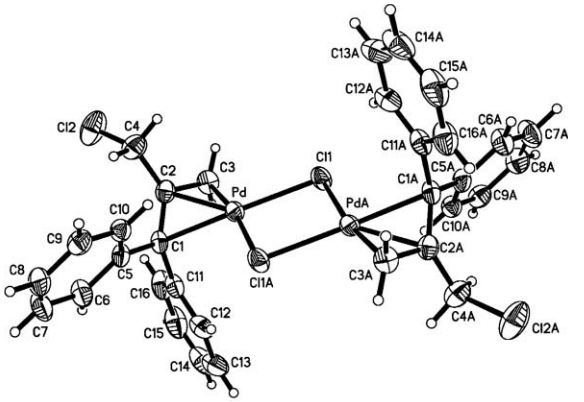
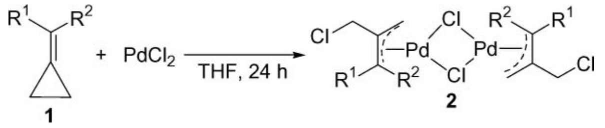


Fig. 1 ORTEP drawing of dimeric allylpalladium(II) complex **2a** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): C_1–C_2 = 1.420(5), C_2–C_3 = 1.416(6), Pd–C_1 = 2.158(3), Pd–C_2 = 2.107(4), Pd–C_3 = 2.088(4), Pd–Cl_1 = 2.3832(10), Pd–Cl_{1A} = 2.4178(11), C_3–Pd–C_2 = 39.44(15), C_2–Pd–C_1 = 38.88(14), C_3–Pd–C_1 = 69.44(16), Cl_1–Pd–Cl_{1A} = 87.95(3), C_3–Pd–Cl_1 = 99.95(12), C_1–Pd–Cl_{1A} = 102.09(11).

Under the optimized reaction conditions, a variety of MCPs **1** were investigated to examine the reaction generality and the results are summarized in Table 2. As shown in Table 2, in the cases of the symmetrical diaryl-substituted MCPs **1** such as **1b**, **1c** and **1e**, the corresponding dimeric allylpalladium(II) complexes **2b**, **2c** and **2e** could be obtained in moderate yields within 24 h under identical conditions (Table 2, entries 1, 2 and 4). As for MCP **1d**, which has two methoxy groups on the phenyl rings, the reaction became disordered at 50 °C and no detectable product was obtained. We found that if the corresponding reaction was carried out at room temperature (25 °C), the corresponding product **2d** could also be obtained though only in 19% isolated yield (Table 2, entry 3). As for the unsymmetrical diaryl-substituted MCP **1f**, the reaction only gave the corresponding product **2f** in 26% yield as a *Z*,*Z*- and *Z*,*E*-isomeric mixture, in which the ratio could not be determined by ^1H NMR spectroscopic data (see ESI† for details) (Table 2, entry 5). It should also be noted here that for other MCPs as R^1 = aryl, R^2 = alkyl or hydrogen and R^1, R^2 = alkyl, the reactions became disordered and although some major products can be isolated from these reactions in low to acceptable yields, their structures remain undetermined at this stage.

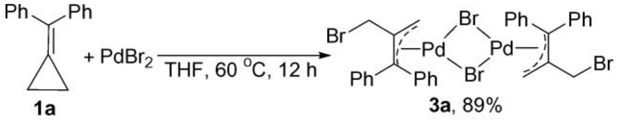
Table 2 Reactions of MCPs **1** with $PdCl_2$ in THF



Entry[a]	**1** (R^1/R^2)	Yield/%[b]
1	**1b** (4-MeC_6H_4/4-MeC_6H_4)	**2b**, 62
2	**1c** (4-FC_6H_4/4-FC_6H_4)	**2c**, 68
3[c]	**1d** (4-$MeOC_6H_4$/4-$MeOC_6H_4$)	**2d**, 19
4	**1e** (4-ClC_6H_4/4-ClC_6H_4)	**2e**, 59
5	**1f** (4-ClC_6H_4/C_6H_5)	**2f**, 26[d]

[a] Otherwise specified, all reactions were carried out using **1** (0.3 mmol), $PdCl_2$ (0.33 mmol) and THF (1.0 mL) at 50 °C for 24 h. [b] Isolated yields. [c] The reaction was carried out at room temperature for 24 h. [d] Mixture of *Z*,*Z*- and *Z*,*E*-isomers.

When $PdBr_2$ was used as the reagent to the reaction with MCP **1a**, the corresponding dimeric allylpalladium(II) complex **3a** was obtained in 89% yield at 60 °C under standard conditions (Scheme 1). The structure of **3a** was also determined by X-ray diffraction (Fig. 2) and its CIF data are presented in the ESI.†[13]



Reagents and conditions: MCP **1a** (0.3 mmol), $PdBr_2$ (0.33 mmol), THF (1.0 mL), 60 °C, 12 h.

Scheme 1 Reaction of MCP **1a** with $PdBr_2$ in THF.

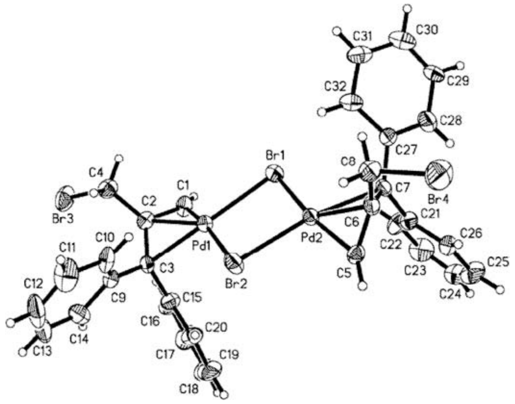
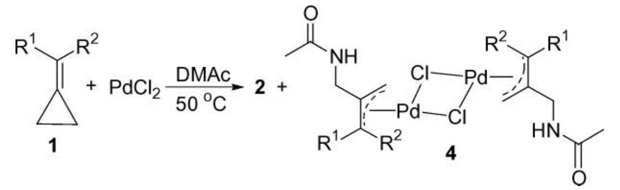


Fig. 2 ORTEP drawing of dimeric allylpalladium(II) complex **3a** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): C_1–C_2 = 1.429(19), C_2–C_3 = 1.44(2), Pd_1–C_1 = 2.089(15), Pd_1–C_2 = 2.117(14), Pd_1–C_3 = 2.168(13), Pd_1–Br_1 = 2.5095(17), Pd_1–Br_2 = 2.535(2), C_2–Pd_1–C_3 = 39.3(5), C_1–Pd_1–C_2 = 39.7(5), C_1–Pd_1–C_3 = 70.1(6), Br_1–Pd_1–Br_2 = 87.70(6), C_1–Pd_1–Br_1 = 97.9(4), C_3–Pd_1–Br_2 = 103.3(4).

When the above transformations were carried out at 50 °C using *N*,*N*-dimethylacetamide (DMAc) as the solvent instead of THF, complexes **2a–2f** were obtained in comparable to higher yields along with another type of complexes **4a–4f** in low yields in most cases (Table 3), which clearly showed that solvent could participate in this chloropalladation reaction as previously mentioned by Hughes.[8] It seems that the reaction temperature slightly affects the ratio between products **2a–2f** and **4a–4e**. For example, when the reaction of **1a** with $PdCl_2$ was carried out at room temperature,

Table 3 Reaction of MCPs **1** with $PdCl_2$ in DMAc



Entry[a]	**1** (R^1/R^2)	Time/h	Yield/%[b] **2**	**4**
1[c]	**1a** (C_6H_5/C_6H_5)	30	**2a**, 65	**4a**, 21
2	**1a**	30	**2a**, 88	**4a**, 9
3	**1b** (4-MeC_6H_4/4-MeC_6H_4)	24	**2b**, 57	**4b**, 5
4	**1c** (4-FC_6H_4/4-FC_6H_4)	24	**2c**, 77	**4c**, 14
5	**1d** (4-$MeOC_6H_4$/4-$MeOC_6H_4$)	24	**2d**, 38	—
6	**1e** (4-ClC_6H_4/4-ClC_6H_4)	24	**2e**, 45	**4d**, 28
7	**1f** (4-ClC_6H_4/C_6H_5)	24	**2f**, 80[d]	**4e**, 13[d]

[a] Unless otherwise specified, all reactions were carried out using **1** (0.3 mmol), $PdCl_2$ (0.33 mmol), DMAc (1.0 mL) at 50 °C for the listed time. [b] Isolated yields. [c] The reaction was carried out at room temperature. [d] Mixture of *Z*,*Z*- and *Z*,*E*-isomers.

product **2a** was obtained in 65% yield along with 21% yield of product **4a** (Table 3, entry 1). For example, when the reaction was carried out at 50 °C, the yield of **2a** was increased to 88% while the yield of **4a** was decreased to 9% (Table 3, entry 2). In the case of MCP **1d**, the corresponding dimeric allylpalladium(II) complex **2d** was obtained as the sole product in relatively higher yield (Table 2, entry 3 *vs.* Table 3, entry 5). For the reaction of unsymmetrical MCP **1f** with $PdCl_2$, the yield of product **2f** was increased dramatically to 80% along with the formation of product **4e** in 13% yield in DMAc (Table 2, entry 5 *vs.* Table 3, entry 7). The structure of complex **4a** was unambiguously determined by X-ray diffraction (Fig. 3) and its CIF data are presented in the ESI.†[14]

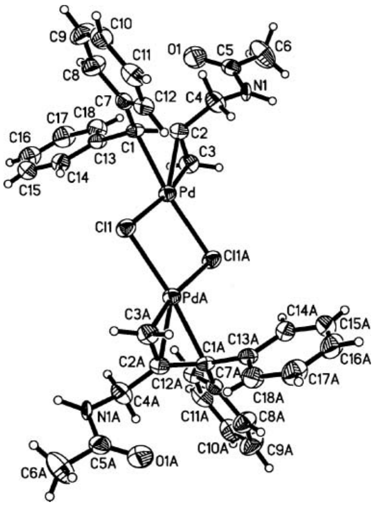
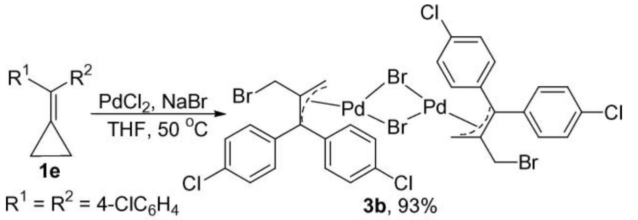


Fig. 3 ORTEP drawing of dimeric allylpalladium(II) complex **4a** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): $C_1–C_2$ = 1.429(5), $C_2–C_3$ = 1.393(5), $Pd–C_1$ = 2.165(3), $Pd–C_2$ = 2.112(4), $Pd–C_3$ = 2.089(4), $Pd–Cl_1$ = 2.4184(11), $Pd–Cl_{1A}$ = 2.4117(10), $C_3–Pd–C_2$ = 38.72(14), $C_2–Pd–C_1$ = 39.00(14), $C_3–Pd–C_1$ = 69.07(15), $Cl_{1A}–Pd–Cl_1$ = 88.16(4), $C_3–Pd–Cl_{1A}$ = 98.53(12), $C_1–Pd–Cl_1$ = 104.11(11).

When 3.0 equiv of NaBr was introduced into the reaction of MCP **1e** with $PdCl_2$ in THF at 50 °C, interestingly, it was found that complex **3b** was formed in 93% yield as the sole product (Scheme 2). The structure of complex **3b** was unambiguously determined by X-ray diffraction (Fig. 4) and its CIF data are presented in the ESI.†[15]



Reagents and conditions: **1e** (0.3 mmol), $PdCl_2$ (0.33 mmol), NaBr (0.9 mmol), THF (1.0 mL), 50 °C.

Scheme 2 Reaction of MCP **1e** with $PdCl_2$ in the presence of NaBr in THF at 50 °C.

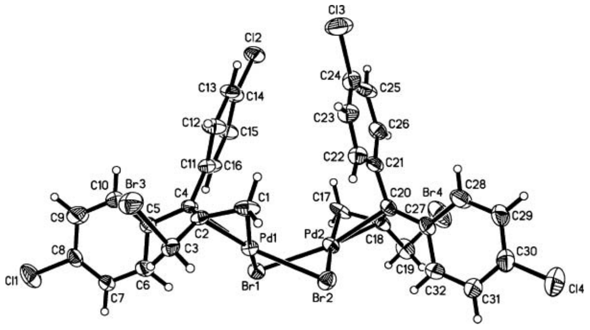
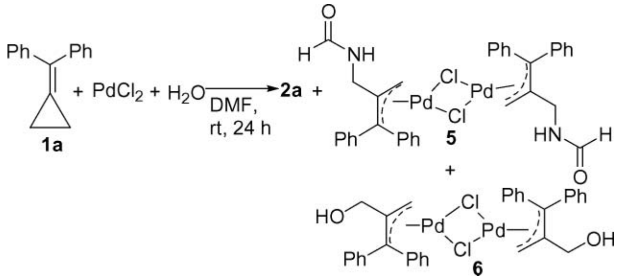


Fig. 4 ORTEP drawing of dimeric allylpalladium(II) complex **3b** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): $C_1–C_2$ = 1.462(14), $C_2–C_4$ = 1.466(12), $Pd_1–C_1$ = 2.090(9), $Pd_1–C_2$ = 2.175(10), $Pd_1–C_4$ = 2.186(10), $Pd_1–Br_1$ = 2.5468(12), $Pd_1–Br_2$ = 2.5010(14), $C_2–Pd_1–C_4$ = 39.3(3), $C_1–Pd_1–C_2$ = 40.0(4), $C_1–Pd_1–C_4$ = 70.6(4), $Br_2–Pd_1–Br_1$ = 89.67(4), $C_2–Pd_1–Br_1$ = 140.4(3), $C_1–Pd_1–Br_2$ = 94.6(3).

Furthermore, we also found that water can significantly affect the reaction outcome (Table 4). For example, as for the reaction of MCP **1a** with $PdCl_2$ in *N*,*N*-dimethylformamide (DMF) at room temperature, when 0, 1.1 or 2.0 equiv of H_2O was added, complexes **2a** and **5** were formed in moderate total yields (Table 4, entries 1–3). While when the employed amount of H_2O was increased to 5 or 10 equiv, except that complex **2** was obtained as the major product, complex **6** was obtained in 17 and 8% yields as the minor product without the formation of complex **5** in both cases (Table 4, entries 4 and 5). The structure of complex **6** was also unambiguously determined by X-ray diffraction (Fig. 5) and its CIF data are presented in the ESI.†[16]

It was reported by Nolan and co-workers in 2006 that transforming simple [Pd(R–allyl)Cl]$_2$ into (NHC)Pd(R–allyl)Cl complexes [NHC: *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene or *N*,*N*′-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene; R = H, Me, *gem*-Me_2, Ph] can significantly improve the catalytic activity of the corresponding Pd complexes in Suzuki–Miyaura and Buchwald–Hartwig reactions.[17] In this laboratory, we also carried out a similar transformation with **2a** and IPr·HCl

Table 4 Reaction of MCP **1a** with $PdCl_2$ in DMF in the presence of H_2O



Entry[a]	H_2O (equiv)	Yield/%[b] **2a**	**5**	**6**
1	0	41	20	
2	1.1	30	31	
3	2	41	20	
4	5	30		17
5	10	32		8

[a] All reactions were carried out using MCP **1a** (0.3 mmol), $PdCl_2$ (0.33 mmol), DMF (1.0 mL) and the listed amount of H_2O at room temperature for 24 h. [b] Isolated yields.

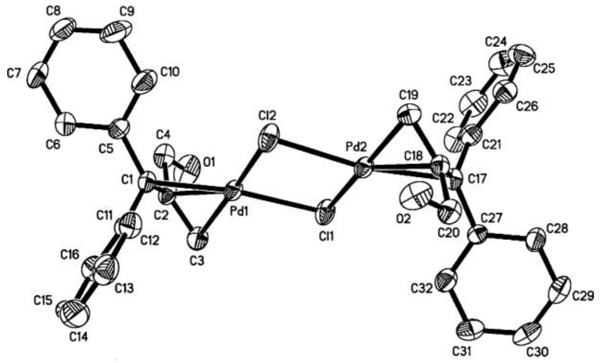
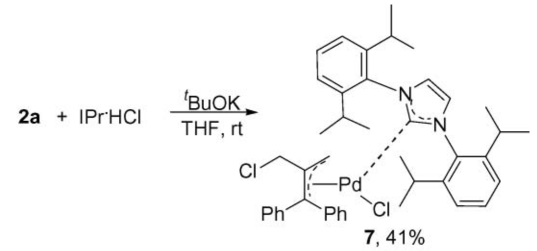


Fig. 5 ORTEP drawing of dimeric allylpalladium(II) complex **6** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): C_1–C_2 = 1.421(8), C_2–C_3 = 1.401(8), Pd_1–C_1 = 2.139(6), Pd_1–C_2 = 2.110(6), Pd_1–C_3 = 2.113(6), Pd_1–Cl_1 = 2.4080(16), Pd_1–Cl_2 = 2.4121(17), C_2–Pd_1–C_3 = 38.8(2), C_2–Pd_1–C_1 = 39.1(2), C_3–Pd_1–C_1 = 69.1(2), Cl_1–Pd_1–Cl_2 = 86.08(5), C_3–Pd_1–Cl_1 = 98.68(18), C_1–Pd_1–Cl_2 = 106.13(16).

[IPr·HCl = 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride] as the substrates and ^{t}BuOK as the base. It was found that the corresponding (NHC)Pd(allyl)Cl complex **7** could be obtained in 41% yield (Scheme 3). The structure of complex **7** was also unambiguously determined by X-ray diffraction (Fig. 6) and its CIF data are presented in the ESI.†[18]

Preliminary investigations on the reaction mechanism

Based on the previously reported results, the plausible mechanism for this type of halopalladation reaction of MCPs **1** is shown in Scheme 4.[8] Firstly, coordination of PdX_2 to MCPs **1** gives intermediate **8**. Secondly, migration of the halogen atom directly from the Pd center gives the halopalladation products **2** (X = Cl) or **3** (X = Br) with the distal bond cleavage in high selectivity (Scheme 4).



Reagents and conditions: **2a** (0.05 mmol), IPr·HCl (0.11 mmol), ^{t}BuOK (0.25 mmol), THF (1.0 mL), rt, 12 h.

Scheme 3 Synthesis of (NHC)–Pd complex **7** from **2a**.

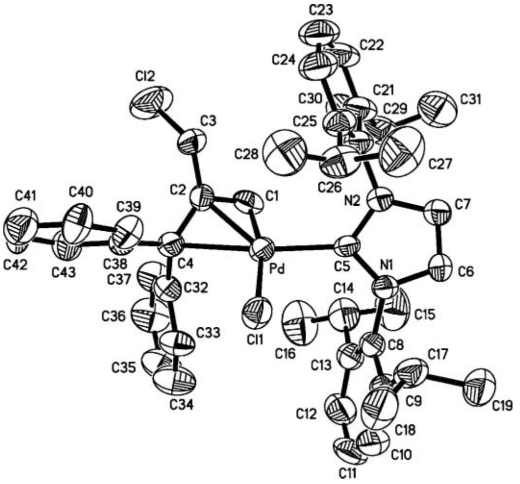
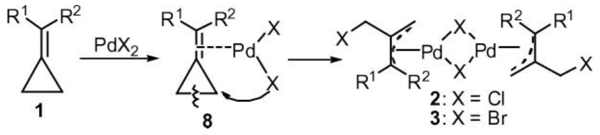


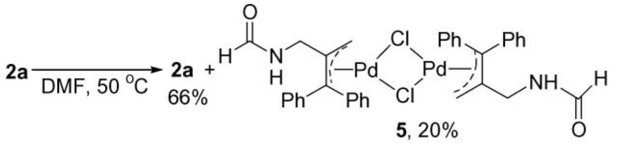
Fig. 6 ORTEP drawing of dimeric allylpalladium(II) complex **7** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): C_1–C_2 = 1.410(7), C_2–C_4 = 1.407(7), Pd–C_1 = 2.074(5), Pd–C_2 = 2.107(5), Pd–C_4 = 2.257(6), Pd–C_5 = 2.028(5), Pd–Cl_1 = 2.3560(15), C_2–Pd–C_4 = 37.43(19), C_1–Pd–C_2 = 39.4(2), C_1–Pd–C_4 = 68.5(2), C_2–Pd–Cl_1 = 130.83(17), C_4–Pd–Cl_1 = 99.71(15), C_1–Pd–Cl_1 = 168.08(17).



Scheme 4 Plausible mechanism for the halopalladation of MCPs **1**.

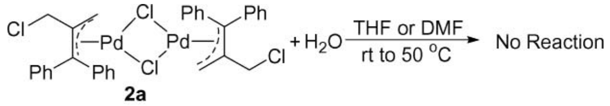
To further illustrate the formation of complexes **3b**, **4** or **5** and **6** in detail, some control experiments were carried out. One is that **2a** (0.1 mmol) was stirred in DMF (1.0 mL) at 50 °C for 24 h. The result showed that besides the starting materials **2a** was recovered in 66% yield, complex **5** was obtained in 20% yield (Scheme 5). This result suggested that **5** may be derived from the reaction of product **2a** with DMF, but the real mechanism for the formation of product **5** is unclear at this stage.

The second is that a mixture of **2a** (0.15 mmol) and H_2O (0.90 mmol) was stirred in THF (1.0 mL) or DMF (1.0 mL) at room temperature (rt) to 50 °C for 12 h, respectively (Scheme 6). The results showed that no reaction occurred in both cases. These results suggested that complex **6** may not be derived from product **2a** *via* hydrolysis. But the real mechanism for the formation of complex **6** also remains unclear at this stage.



Reagents and conditions: **2a** (0.1 mmol), DMF (1.0 mL), 50 °C, 24 h.

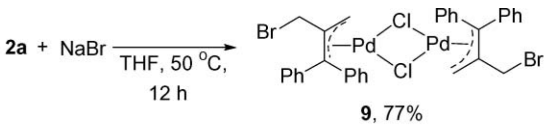
Scheme 5 Transformation of **2a** in DMF at 50 °C.



Reagents and conditions: **2a** (0.15 mmol), H_2O (0.9 mmol), THF or DMF (1.0 mL), rt to 50 °C, 12 h.

Scheme 6 Reaction of **2a** with H_2O in THF or DMF.

The third is that **2a** (0.15 mmol) was treated with NaBr (0.90 mmol) in THF (1.0 mL) at 50 °C for 12 h. Only another complex **9**, instead of complex **3b** as expected, was obtained as the sole product in 77% yield, which may be derived from transhalogenation of **2a** with NaBr (Scheme 7). The structure of complex **9** was determined by ^{1}H NMR, ^{13}C NMR, MS and HRMS (see the ESI for details†). This result suggested that compound **3b** might be obtained *via* the reaction of MCP **1e** with $PdBr_2$ derived from $PdCl_2$ and NaBr (Scheme 2 *vs.* Scheme 7).



Reagents and conditions: **2a** (0.15 mmol), NaBr (0.9 mmol), THF (1.0 mL), 50 °C, 12 h.

Scheme 7 Reaction of **2a** with NaBr in THF at 50 °C.

Conclusions

In conclusion, we have described the $PdCl_2$ mediated reactions of MCPs in THF for the formation of dimeric allylpalladium(II) complexes in this paper. The dimeric allylpalladium(II) complexes were isolated and were fully characterized by X-ray diffraction. The examination of solvent effects revealed that in DMAc, DMF and H_2O, other novel dimeric allylpalladium(II) complexes could be isolated though in low yields. Efforts are underway to further illustrate the mechanistic details of the transition metal mediated reactions of MCPs in this laboratory.

Experimental

General procedure for the reaction of MCPs 1 with $PdCl_2$ in THF

Under an argon atmosphere, a mixture of MCPs **1** (0.30 mmol) and $PdCl_2$ (0.33 mmol) was stirred in anhydrous THF (1.0 mL) at 50 °C for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to give complex **2**.

Procedure for the reaction of MCP 1a with $PdBr_2$ in THF

Under an argon atmosphere, a mixture of MCP **1a** (0.30 mmol) and $PdBr_2$ (0.33 mmol) was stirred in anhydrous THF (1.0 mL) at 60 °C for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to give complex **3a**.

General procedure for the reaction of MCPs 1 with $PdCl_2$ in DMAc

Under an argon atmosphere, a mixture of MCPs **1** (0.30 mmol) and $PdCl_2$ (0.33 mmol) was stirred in anhydrous DMAc (1.0 mL) at 50 °C for 24 h. The reaction solution was diluted with EtOAc, washed with saturated brine, dried over anhydrous Na_2SO_4, and then purified by flash column chromatography on silica gel to give complexes **2** and **4**.

Procedure for the reaction of MCP 1e with $PdCl_2$ in THF in the presence of NaBr

A mixture of MCP **1e** (0.30 mmol), $PdCl_2$ (0.33 mmol) and NaBr (0.9 mmol) was stirred in anhydrous THF (1.0 mL) at 50 °C for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to give complex **3b**.

Procedure for the reaction of MCP 1a with $PdCl_2$ in DMF in the presence of H_2O

Under an argon atmosphere, a mixture of MCP **1a** (0.30 mmol), $PdCl_2$ (0.33 mmol) and H_2O (0.6 mmol to 3 mmol) was stirred in anhydrous DMF (1.0 mL) at room temperature for 24 h. The reaction solution was diluted with EtOAc, washed with saturated brine, dried over anhydrous Na_2SO_4, and then purified by flash column chromatography on silica gel to give complexes **2** and/or **5** and/or **6**.

Procedure for the formation of complex 7

Under an argon atmosphere, a mixture of complex **2a** (0.05 mmol), IPr·HCl (0.11 mmol) and ^{t}BuOK (0.25 mmol) was stirred in anhydrous THF (1.0 mL) at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give complex **7**.

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11 The crystal data of **2a** have been deposited in CCDC with number 620092. Empirical Formula: $C_{32}H_{28}Cl_4Pd_2$; Formula Weight: 767.14; Crystal color, Habit: yellow, prismatic; Crystal dimensions: 0.193 × 0.122 × 0.099 mm; Crystal system: Monoclinic; Lattice parameters: a = 9.1826(8) Å, b = 15.1250(13) Å, c = 11.1711(10) Å, α = 90°, β = 97.164(2)°, γ = 90°, V = 1539.4(2) Å^3; T = 293(2) K; Space group: $P2_1/n$; Z = 2; D_c = 1.655 g cm^{-3}; F_{000} = 760; Diffractometer: Bruker SMART; Reflections collected/unique: 8947/3355 (R_{int} = 0.0605); Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0404, wR_2 = 0.0781.

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13 The crystal data of **3a** have been deposited in CCDC with number 744567. Empirical Formula: $C_{32}H_{26}Br_4Pd_2$; Formula Weight: 942.97; Crystal color, Habit: green, prismatic; Crystal dimensions: 0.256 × 0.103 × 0.094 mm; Crystal system: Triclinic; Lattice parameters: a = 9.3228(16) Å, b = 12.311(2) Å, c = 14.328(2) Å, α = 88.057(4)°, β = 77.018(3)°, γ = 82.383(3)°, V = 1588.3(5) Å^3; T = 293(2) K; Space group: $P\bar{1}$*vphantom*1; Z = 2; D_c = 1.972 g cm^{-3}; F_{000} = 900; Diffractometer: Bruker SMART; Reflections collected/unique: 8721/6108 (R_{int} = 0.0322); Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0786, wR_2 = 0.2723.

14 The crystal data of **4a** have been deposited in CCDC with number 744566. Empirical Formula: $C_{36}H_{36}Cl_2N_2O_2Pd_2$; Formula Weight: 812.37; Crystal color, Habit: yellow, prismatic; Crystal dimensions: 0.176 × 0.105 × 0.051 mm; Crystal system: Monoclinic; Lattice parameters: a = 13.8340(11) Å, b = 10.3767(8) Å, c = 12.6185(10) Å, α = 90°, β = 112.7140(10)°, γ = 90°, V = 1670.9(2) Å^3; T = 293(2) K; Space group: $P2_1/c$; Z = 2; D_c = 1.615 g cm^{-3}; F_{000} = 816; Diffractometer: Bruker SMART; Reflections collected/unique: 9528/3615 (R_{int} = 0.0706); Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0390, wR_2 = 0.0711.

15 The crystal data of **3b** have been deposited in CCDC with number 758823. Empirical Formula: $C_{32}H_{24}Br_4Cl_4Pd_2$; Formula Weight: 1082.75; Crystal color, Habit: green, prismatic; Crystal dimensions: 0.265 × 0.113 × 0.101 mm; Crystal system: Monoclinic; Lattice Parameters: a = 10.7816(6) Å, b = 27.7470(16) Å, c = 25.1259(15) Å, α = 90°, β = 98.5670(10)°, γ = 90°, V = 7432.7(7) Å^3; T = 293(2) K; Space group: $P2_1/n$; Z = 8; D_c = 2.011 g cm^{-3}; F_{000} = 4296; Diffractometer: Bruker SMART; Reflections collected/unique: 40804/14600 (R_{int} = 0.0648); Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0524, wR_2 = 0.1493.

16 The crystal data of **6** have been deposited in CCDC with number 621667. Empirical Formula: $C_{32.67}H_{30.67}Cl_4O_2Pd_2$; Formula Weight: 809.84; Crystal color, Habit: yellow, prismatic; Crystal dimensions: 0.507 × 0.281 × 0.224 mm; Crystal system: Monoclinic; Lattice parameters: a = 14.9609(9) Å, b = 20.8396(13) Å, c = 15.0025(9) Å, α = 90°, β = 92.0760(10)°, γ = 90°, V = 4674.4(5) Å^3; T = 293(2) K; Space group: $P2_1/c$; Z = 6; D_c = 1.677 g cm^{-3}; F_{000} = 2352; Diffractometer: Bruker SMART; Reflections collected/unique: 25386/9165 (R_{int} = 0.0519); Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0504, wR_2 = 0.1373.

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18 The crystal data of **7** have been deposited in CCDC with number 646598. Empirical Formula: $C_{43}H_{50}Cl_2N_2Pd$; Formula Weight: 772.15; Crystal color, Habit: yellow, prismatic; Crystal dimensions: 0.501 × 0.234 × 0.196 mm; Crystal system: Tetragonal; Lattice parameters: a = 26.1371(13) Å, b = 26.1371(13) Å, c = 23.7475(16) Å, α = 90°, β = 90°, γ = 90°, V = 16223.1(16) Å^3; T = 293(2) K; Space group: $I4(1)/a$; Z = 16; D_c = 1.265 g cm^{-3}; F_{000} = 6432; Diffractometer: Bruker SMART; Reflections collected/unique: 45818/8412 (R_{int} = 0.1242); Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0607, wR_2 = 0.1348.