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ARTICLE

Dinuclear NHC–Palladium Complexes Containing Phosphine Spacers: Synthesis, X-Ray Structures and Their Catalytic Activities towards Hiyama Coupling Reaction

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Six dinuclear *N*-heterocyclic carbene (NHC) palladium complexes, [PdCl₂(IMes)]₂(μ-dppe) (**1**), [PdCl₂(IPr)]₂(μ-dppe) (**2**), [PdCl₂(IMes)]₂(μ-dppb) (**3**), [PdCl₂(IPr)]₂(μ-dppb) (**4**), [PdCl₂(IMes)]₂(μ-dpph) (**5**), and [PdCl₂(IPr)]₂(μ-dpph) (**6**) [IMes = *N,N'*-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene; IPr = *N,N'*-bis-(2,6-di(*iso*-propyl)phenyl)imidazol-2-ylidene; dppe = 1,2-bis(diphenylphosphino)ethane, dppb = 1,4-bis(diphenylphosphino)butane; and dpph = 1,6-bis(diphenylphosphino)hexane] have been synthesized through the bridge-cleavage reactions of chloro-bridged dimeric compounds, [Pd(μ-Cl)(Cl)(NHC)]₂ with the corresponding diphosphine ligands. The obtained compounds were fully characterized by ¹H NMR, ¹³C NMR and ³¹P NMR spectroscopy, FT-IR, elemental analysis and single-crystal X-ray crystallography. Moreover, further explorations of the catalytic potential of the dinuclear carbene palladium complexes as catalysts for the Pd-catalyzed transformations have been examined under microwave irradiation conditions, and the complexes exhibit moderate to good catalytic activity in the Hiyama coupling reaction of trimethoxyphenylsilane with aryl chlorides.

Introduction

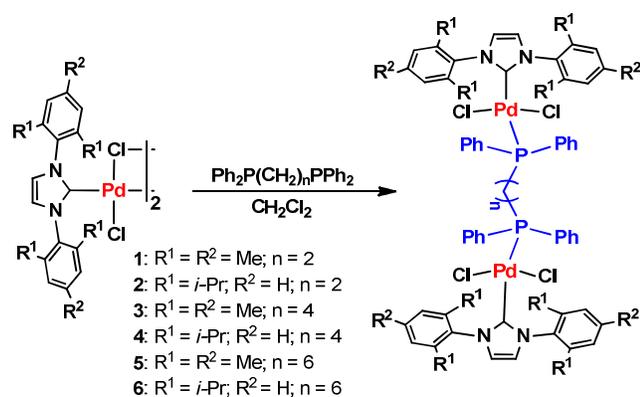
Since the successful isolation of the first stable carbene by Arguengo in 1991, *N*-heterocyclic carbenes (NHCs) have attracted increasing attention and have been intensively explored as spectator ligands on transition metals.¹ The strong metal-carbene σ-bond provides numerous opportunities for the development of transition metal catalysts. In particular, carbene palladium complexes derived from imidazolium precursors have been successfully developed as highly active pre-catalysts in a wide range of organic transformations including Buchwald-Hartwig amination, Heck olefin arylation, and Suzuki, Kumada, Hiyama, Stille, Negishi and Sonogashira coupling reactions of chloroarenes.² However, NHCs ligands in palladium complexes, which have been compared to the classic trialkylphosphine

ligands, appear to be stronger coordinating ligands which undergo little dissociation from the metal in solution and probably render the intermediate cationic allylpalladium compounds poorly electrophilic, thereby disfavoring the nucleophilic addition step.³ Therefore, different strategies have been adopted in order to modify the carbene complexes. One strategy consists in tuning of electronic properties of the carbene ligands by introduced suitable functional groups on the carbene ligands. Recently years, a number of modified carbene ligands with various functional groups and the corresponding palladium complexes have been efficiently prepared and applied in cross-coupling reactions.⁴ Another strategy is to introduce an ancillary ligand to the metal core, thereby enhancing the potential for hemilability and heterometallation of the carbene ligands. The introduction of an ancillary ligand at the metal core could present a synthetically convenient strategy for tuning the electronic and steric properties of the coordination sphere. Recent studies have illustrated that the provision of functional ancillary ligand to complement the strongly binding NHCs could promote a reversible coordination and dissociation mechanism which is highly suitable for catalytic applications.⁵ Towards this, various heteroatom donors have been used to join in the coordination with the NHC–Pd

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† Electronic supplementary information (ESI) available: Selected bond lengths and angles for compounds **1–6** and ¹H, ¹³C and ³¹P NMR spectra of compounds **1–6**. CCDC reference numbers 950139–950142, 971319–971320. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.



Scheme 1 Overview the synthesis of the dinuclear *N*-heterocyclic carbene (NHC)-palladium complexes **1–6**.

complexes.⁶ Organ reported the first pyridine type ligands modified carbene palladium complexes as active catalysts for a series of cross-coupling (Suzuki, Negishi, Kumada, Stille and Buchwald-Hartwig amination) reactions.⁷ Nolan and Cazin reported a series of tertiary phosphine modified carbene palladium complexes as active catalysts for Suzuki cross-coupling and other reactions.⁸ Hahn reported a series of novel macrocyclic and multinuclear carbene complexes which were modified by the phosphine ligands.⁹ The use of heteroatom donors to support and activate the metal for catalysis is an emerging idea in coordination catalysis. Furthermore, following the initial reports of the mononuclear *N*-heterocyclic carbene palladium complexes, the di-, and multi-nuclear *N*-heterocyclic carbene complexes containing various bridging ligands continue to attract a great deal of attention.¹⁰ The use of different spacers with different liabilities in a multinuclear framework could provide a model to test the catalytic benefits of dissociative ligand and non-interacting multi-metallic catalytic sites.

We have recently reported a simple pathway to the synthesis of dinuclear NHC-palladium complexes with bridging *N*-heterocyclic ligands.^{10k} Following our interest on the construction of functionalized complexes that can enter into an array of di- and multi-nuclear systems, herein, we extended the methodology to introduction of the bridging diphosphine ligands to the NHC-palladium complexes and reported the synthesis and structural characterization of six diphosphine ligands bridged dinuclear *N*-heterocyclic carbene palladium complexes. Furthermore, the catalytic applications of the dinuclear NHC-palladium complexes in Hiyama coupling reaction of trimethoxyphenylsilane with a range of aryl chlorides under microwave irradiation conditions were studied.

Results and discussion

Synthesis of NHC-palladium complexes

Following the method for the synthesis of mononuclear *N*-heterocyclic carbene (NHC)/PR₃ palladium(II) complexes,^{8a,11} reactions of the chloro-bridged dimeric compounds [Pd(μ -Cl)(Cl)(NHC)]₂ with the bridging diphosphine ligands in

CH₂Cl₂ at the ambient temperature were done, and the corresponding dinuclear NHC-palladium complexes [PdCl₂(IMes)]₂(μ -dppe) (**1**), [PdCl₂(IPr)]₂(μ -dppe) (**2**), [PdCl₂(IMes)]₂(μ -dppb) (**3**), [PdCl₂(IPr)]₂(μ -dppb) (**4**), [PdCl₂(IMes)]₂(μ -dpph) (**5**), and [PdCl₂(IPr)]₂(μ -dpph) (**6**) were obtained in good yields. The synthetic route is straightforward, and all complexes have been isolated as yellow and air-stable solid. Moreover, we have attempted to carry out the *N*-heterocyclic carbene palladium complexes formation through one-pot reactions from their respective imidazolium chloride salts by reaction with PdCl₂ and the bridging diphosphine ligands in presence of K₂CO₃ as a base in various solvents (e.g., THF, CH₃CN, toluene and dioxane), but the reaction resulted in rapid decomposition of the reactants. Thus, it appeared that the one-pot reaction is unsuitable for the synthesis of the diphosphine-bridged dinuclear *N*-heterocyclic carbene palladium complexes.

NMR studies

The diphosphine-bridged *N*-heterocyclic carbene palladium complexes **1–6** were first characterized by the NMR analysis and the selected ¹³C NMR and ³¹P NMR data were summarized in Table 1. The formation of the dinuclear complexes was evident from the distinctive stoichiometric proton signal resonances of the *N*-heterocyclic carbene ligands and diphosphine ligands in the ¹H NMR spectra. In addition, the ¹³C NMR spectra revealed the appearance of diagnostic carbene carbon doublet peaks (171.0 and 168.9 ppm for **1**, 173.6 and 171.7 ppm for **2**, 171.6 and 169.6 ppm for **3**, 173.7 and 171.7 ppm for **4**, 171.4 and 169.5 ppm for **5**, 173.6 and 171.7 ppm for **6**, respectively), which were splitted by the adjacent P donors. These values were significantly shifted downfield relative to that of the imidazolium NCHN peak of the starting ligand precursors (141.0 ppm for IMes•HCl and 145.0 ppm for IPr•HCl),^{10k} but were as expected close to the values found in the mononuclear *N*-heterocyclic carbene (NHC)/PPh₃ palladium complex PdCl₂(IPr)PPh₃ (169.8 and 172.4 ppm).^{8a} The important ²J_{CP} coupling constant (196.1 to 208.7 Hz) is characteristic of the *trans*-position of the phosphine ligands with respect to the NHCs.^{8a,11} Furthermore, ³¹P NMR spectra of all complexes showed sharp singlet (13.0 to 16.5 ppm) shifted up field when compared to the mononuclear complex PdCl₂(IPr)PPh₃ (20.4 ppm), attributed probably to the more electron-rich of the PPh₃.

Table 1 Selected ¹³C and ³¹P NMR spectral data of **1–6**

Complex	¹³ C NMR ^a (C _{carbene})		³¹ P NMR ^a [(Ph ₂ P(CH ₂) _n) ₂]
	δ_c	² J _{CP}	δ_p
1	170.0	208.7	16.5
2	172.6	196.9	16.5
3	170.6	197.4	13.7
4	172.7	196.1	13.5
5	170.4	197.4	13.5
6	172.7	196.4	13.0

^a ¹³C and ³¹P NMR spectra were recorded in CDCl₃ at 298K (δ in ppm, *J* in Hz)

Crystal structures

The molecular structures of **1–6** have been further characterized by single-crystal X-ray diffraction studies. A summary of the crystallographic data was provided in Table 2 and selected bond lengths and angles were given in Table S1 (ESI).† As expected, the crystal structures of **1–6** showed a dinuclear framework with two palladium(II) centers were held together by a bridging diphosphine ligand. Each palladium center was coordinated by an *N*-heterocyclic carbene ligand, a phosphorus atom and two chloro ions in a *trans*-arrangement, giving rise to a four coordinate environment (Scheme 1). In agreement with the spectral data, the incoming P donors were invariably *trans* to the NHC ligands which are similar to that observed in the mononuclear *N*-heterocyclic carbene palladium complexes. Both of the compounds **1** and **2** crystallize as CH₂Cl₂ solvates. The structure of solvate **1**·2CH₂Cl₂ crystallizes in the monoclinic space group *P2*(1)/*c*, while the *i*-Pr-substituted analogue of the solvate **2**·2CH₂Cl₂ belongs to the triclinic space group *P* $\bar{1}$. There are two independent molecules in a unit cell of the solvate **2**·2CH₂Cl₂, only one molecule is shown in Fig. 2. The molecular structures of **1** and **2** which are composed of P–C–C–P skeletons are quite similar except the substituted groups of the carbene ring. The predominant molecular shape for **1** and **2** is a zigzag chain structure of the P–C–C–P skeleton in which the NHC groups are oriented to an opposite direction for each other. The two carbene planes adopt a parallel but non-coplanar orientation with the vertical separation of 2.62 Å for **1** and 2.31 Å, 2.36 Å for **2**. As shown in Fig. 1 and 2, each Pd center is four-coordinated by an *N*-heterocyclic carbene ligand, a P donor from the diphosphine ligand and two chloro ions in a slightly distorted square planar geometry, with angles between adjacent ligands ranging from 85.73(4)° to 93.83(5)°. The

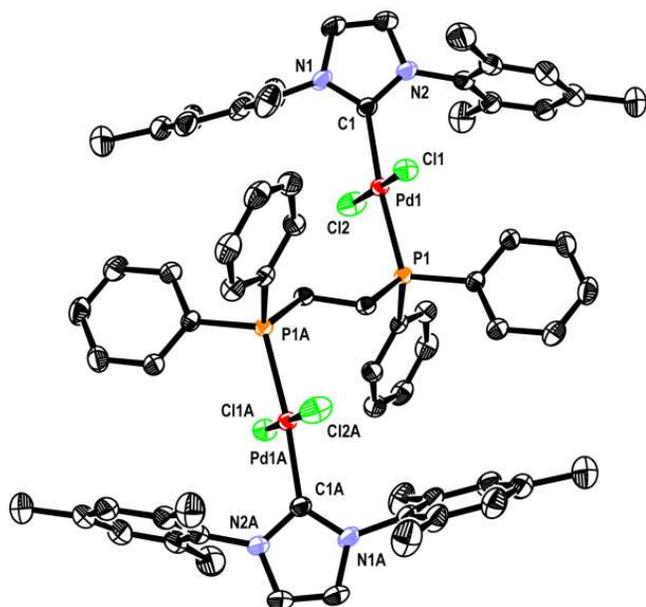


Fig. 1 ORTEP diagram of **1** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms and solvent molecules (CH₂Cl₂) have been omitted for clarity. The suffix A in **1** denotes symmetry operation 1 – *x*, 1 – *y*, 1 – *z*.

dihedral angles between the carbene ring planes and the PdCNCl₂ coordination planes amount to 69.53°, 77.33° and 77.50°, which are typical for NHC complexes to relieve steric congestion. The phosphine ligand acts as bridges, linking the palladium centers to form dinuclear NHC–palladium complexes with Pd···Pd separation of 6.97 Å for **1** and 7.21 Å, 7.24 Å for **2**, respectively. However, there are some minor structural differences between **1** and **2**. The dihedral angle between the carbene ring plane and the plane defined by Pd1P1Pd1A in compound **1** is only 38.34°, which is significantly shorter than that in compound **2** (69.93° and 70.12°), and might be caused by the steric repulsion of the *i*-Pr groups. The corresponding dihedral angle between the PdCNCl₂ coordination plane and the Pd1P1Pd1A plane in compound **1** (72.16°) is significantly larger than that found in **2** (33.52° and 33.57°).

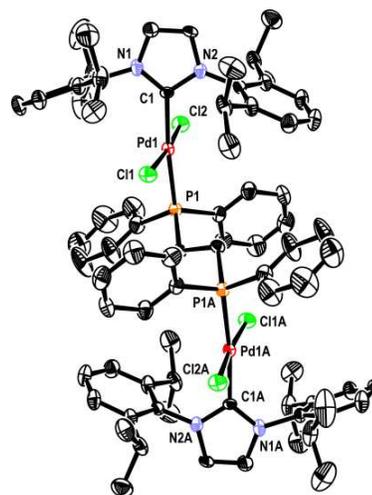


Fig. 2 ORTEP diagram of **2** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms and solvent molecules (CH₂Cl₂) have been omitted for clarity. The suffix A in **2** denotes symmetry operation 1 – *x*, 1 – *y*, 1 – *z*.

The reactions of the dimeric compounds [Pd(μ -Cl)(Cl)(NHC)]₂ with the bridging diphosphine ligand dppb yield the compounds **3** and **4**. The Mes-substituted compound **3** crystallizes in the monoclinic space group *P2*(1)/*c* and the *i*-Pr-substituted analogue **4** crystallizes in the orthorhombic space group *Pna*21. X-Ray structure analysis also shows zigzag chain structures of the dppb with the distances of two corresponding Pd···Pd being 8.52 Å for **3** and 8.93 Å for **4**. The dihedral angles between the carbene ring planes and the PdCNCl₂ coordination planes amount to 82.55° for compound **3**, and 68.69°, 78.51° for **4**, respectively (Fig. 3 and 4). Although compounds **3** and **4** possess the same four hydrocarbon chain of the diphosphine ligand, the vectors of the two NHC–Pd groups for these molecules are significantly different. In compound **3**, the carbene ring planes adopt a parallel orientation (a vertical separation of 4.03 Å) with the opposite direction which is similar with that observed in compounds **1** and **2**. The molecular structure of **4** which possesses the *i*-Pr-substituted ligand is also composed of a zigzag chain structure of the P–C–C–C–P backbone, however, the two carbene ring planes pointed to the same direction and are arranged in a twisted

orientation with a dihedral angle of 33.39° . The two corresponding PdCPCl₂ coordination planes also pointed to the same direction with a dihedral angle of 72.22° . In compound **3**, the Pd1P1APd1A plane is oriented at dihedral angles of 30.89° and 67.23° with respect to the carbene ring plane and the PdCNCl₂ coordination plane. These values are somewhat shorter than that in compound **1** (38.34° and 72.16°). In compound **4**, the Pd1P1APd1A adopt a non-coplanar orientation with a torsion angle of 44.34° .

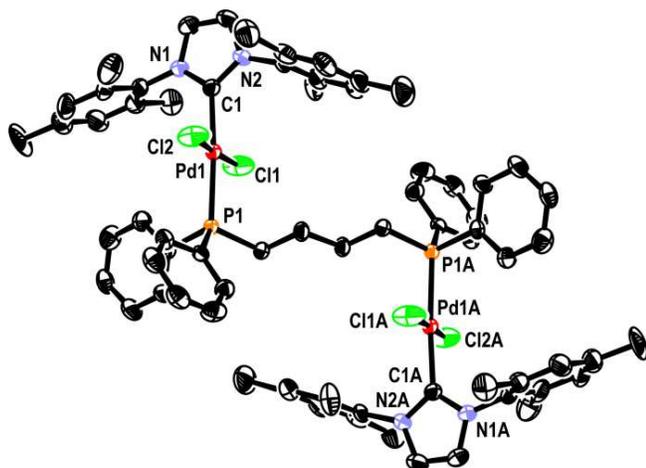


Fig. 3 ORTEP diagram of **3** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms have been omitted for clarity. The suffix A in **3** denotes symmetry operation $1 - x, -y, -z$.

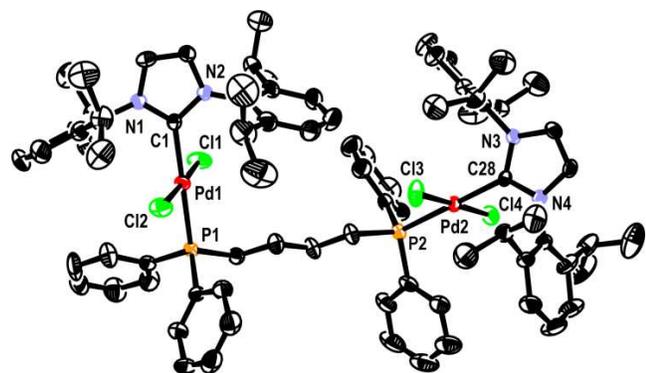


Fig. 4 ORTEP diagram of **4** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

For the diphosphine ligand with a P–C–C–C–C–C–P backbone, single crystals were obtained for the Mes and *i*-Pr-substituted derivatives **5** and **6**, which confirmed the dinuclear NHC–palladium structures. The Mes-substituted compound **5** crystallizes in the orthorhombic space group *Pccn*, and the *i*-Pr-substituted analogue **6** crystallizes as H₂O solvates **6**·H₂O, which belongs to the monoclinic space group *P2(1)/n*. X-Ray structure analysis also shows zigzag chain structures of the dpph with the distances of two corresponding Pd···Pd being 9.87 \AA for **5** and 11.43 \AA for **6** (Figs. 5 and 6). The two NHC–Pd groups in **5** and **6** are bridged by one dpph ligand and oriented to an opposite direction for each other, respectively, which are similar with that found in compounds **1–3**. The

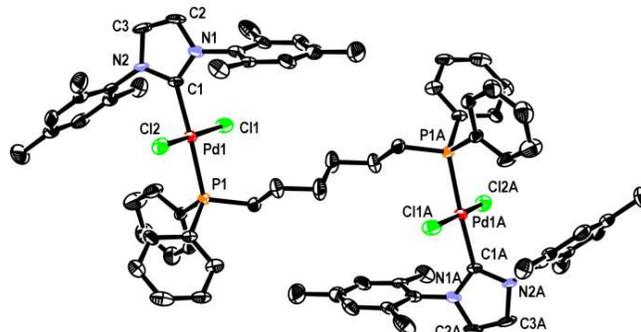


Fig. 5 ORTEP diagram of **5** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms have been omitted for clarity. The suffix A in **5** denotes symmetry operation $-x, -y, 1 - z$.

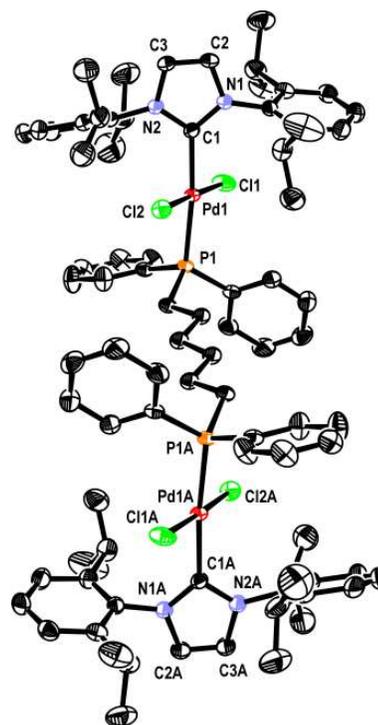


Fig. 6 ORTEP diagram of **6** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms and solvent molecules (H₂O) have been omitted for clarity. The suffix A in **6** denotes symmetry operation $-x, 2 - y, -z$.

vertical distance between the two parallel carbene ring planes in compound **5** (2.40 \AA) is significantly shorter than that in compound **6** (9.42 \AA), which attributed to the more extended dihedral angle between the carbene ring plane and the Pd1P1APd1A plane of compound **6**. In compound **5**, the dihedral angles between the carbene ring plane and the Pd1P1APd1A plane are significantly shorter (14.62°) than that found in the Mes-substituted analogues **1** (38.34°) and **3** (30.89°). However, in compound **6**, the carbene ring plane is oriented approximately perpendicularly to the Pd1P1APd1A plane with the dihedral angle of 89.96° , which is significantly larger than that found in compound **5**. Moreover, the dihedral angle between the PdCNCl₂ coordination plane and the Pd1P1APd1A plane in compound **5** (62.84°) is somewhat

Table 2 Crystallographic data for compounds 1–6

Compound	1•2CH ₂ Cl ₂	2•2CH ₂ Cl ₂	3	4	5	6•H ₂ O
formula	C ₇₀ H ₇₆ Cl ₈ N ₄ P ₂ Pd ₂	C ₈₂ H ₁₀₀ Cl ₈ N ₄ P ₂ Pd ₂	C ₇₀ H ₇₆ Cl ₄ N ₄ P ₂ Pd ₂	C ₈₂ H ₁₀₀ Cl ₄ N ₄ P ₂ Pd ₂	C ₇₂ H ₈₀ Cl ₄ N ₄ P ₂ Pd ₂	C ₈₄ H ₁₀₆ Cl ₄ N ₄ OP ₂ Pd ₂
fw	1531.69	1700.00	1389.89	1558.20	1417.94	1604.27
crystal system	monoclinic	triclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> <i>n</i> a21	<i>P</i> <i>c</i> <i>c</i> <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> /Å	12.0625(11)	13.168(6)	10.996(8)	29.940(3)	11.988(7)	9.8882(16)
<i>b</i> /Å	24.805(2)	13.479(7)	20.067(15)	13.7039(14)	35.97(2)	20.486(3)
<i>c</i> /Å	13.2469(13)	28.285(13)	15.377(11)	21.536(2)	15.244(9)	19.902(3)
α /deg	90.00	99.380(7)	90.00	90.00	90.00	90.00
β /deg	114.600(2)	90.260(8)	104.080(12)	90.00	90.00	94.177(3)
γ /deg	90.00	119.210(7)	90.00	90.00	90.00	90.00
<i>V</i> /Å ³	3603.9(6)	4303(4)	3291(4)	8835.9(15)	6573(7)	4020.8(11)
<i>Z</i>	2	2	2	4	4	2
<i>D</i> _{calc} /g cm ⁻³	1.411	1.312	1.403	1.171	1.433	1.325
<i>F</i> (000)	1564	1756	1428	3240	2920	1672
μ /mm ⁻¹	0.882	0.746	0.801	0.604	0.804	0.666
GOF	1.078	1.146	1.025	1.114	1.176	1.049
reflections collected	17895	21896	15769	55671	30014	20356
independent reflections (<i>R</i> _{int})	6318 (0.0424)	14904 (0.2229)	5729 (0.0480)	15517 (0.0395)	5682 (0.0904)	7060 (0.0284)
observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	4728	10500	4156	13055	4614	5943
refined parameters	410	875	364	863	361	411
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0447	0.0828	0.0582	0.0445	0.1191	0.0334
<i>wR</i> 2(all data)	0.1283	0.2676	0.2064	0.1327	0.2634	0.0860

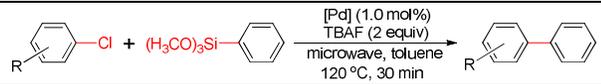
shorter than that found in compounds **1** and **3**, but is significantly larger than found in compound **6** (30.46°) and as mentioned above, these differences might be attributed to the larger steric hindrance of the *ortho iso*-propyl groups in **6** than the methyl groups in analogue **5**.

The detailed structural analysis indicates that the structural parameters around the palladium centers, such as the bond angles and bond distances, are in a range similar to those for mononuclear NHC–palladium complexes. The Pd–C_{carbene} bonds [2.043(5) Å for **1**, 2.032(10), 2.036(9) Å for **2**, 2.031(6) Å for **3**, 2.047(5), 2.041(5) Å for **4**, 1.992(11) Å for **5**, and 2.038(3) Å for **6**] and Pd–P bonds [2.3177(12) Å for **1**, 2.288(3), 2.307(3) Å for **2**, 2.317(2) Å for **3**, 2.3107(15) Å, 2.3067(15) Å for **4**, 2.278(3) Å for **5**, and 2.3004(8) Å for **6**] in compounds **1–6** are comparable to those found in mononuclear phosphine/*N*-heterocyclic carbene–palladium complexes PdCl₂(NHC)PPh₃ [e.g., Pd–C_{carbene}: 2.028(5) Å and Pd–P: 2.3137(6) Å for PdCl₂(SImes)PPh₃ (SImes = *N,N'*-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene)^{11b} and Pd–C_{carbene}: 2.032(5) Å and Pd–P: 2.3054(13) Å for PdCl₂(IPr)PPh₃].^{7a} The Pd–Cl bonds fall in a narrow range of 2.193(4)–2.309(3) Å and are comparable to those found in the *N*-heterocyclic carbene–palladium complexes.⁸ Furthermore, the carbene ring planes of all complexes are twisted out of the adjacent PdCPCl₂ coordination planes with the dihedral angles ranging from 59.73° to 82.55° in order to avoid intra-ligand repulsion. However, compared to the mononuclear complexes, there was no clear trend for the steric hindrance influence in dinuclear complexes **1–6**. For example, the dihedral angle of 69.53° between the carbene ring plane and the PdCNCl₂ plane in compound **1** is somewhat shorter than that in the mononuclear complex PdCl₂(SImes)PPh₃ (74.91°).^{11b} With the same Mes-

substituent, the PdCPCl₂ coordination plane of the compound **3** is oriented approximately perpendicularly to the carbene ring plane with a dihedral angle of 82.55°, which is significantly larger than the mononuclear complex PdCl₂(SImes)PPh₃. In compound **5**, the dihedral angle between the carbene ring plane and the PdCNCl₂ plane (76.96°) is slightly larger than that in the mononuclear complex PdCl₂(SImes)PPh₃. With the *i*-Pr-substituent NHC–palladium complexes, the dihedral angles between the PdCPCl₂ coordination plane and the carbene ring are significantly different, for example, the dihedral angles between the carbene ring plane and the PdCNCl₂ plane in compound **2** (77.33° and 77.50°), which are fall in the range of **1** (69.53°) and **3** (82.55°), but are significantly larger than that in the mononuclear *i*-Pr-substituent NHC–palladium complex PdCl₂(IPr)PPh₃ (67.78°).^{7a} In compound **4**, although the two carbene ring segments have seemingly identical chemical environments, the coordination geometries of the two Pd atoms are slightly different, with the dihedral angles between carbene ring planes and the coordination planes amount to 68.69° and 78.51°, respectively. For the compound **6**, the dihedral angle between the carbene ring plane and the PdCNCl₂ plane (59.73°) is shorter than all the above mentioned mono- and di-nuclear complexes.

Catalytic tests

The palladium-catalyzed Hiyama coupling reaction is one of the most powerful methods for the preparation of biaryl derivatives. Many efforts have been directed towards the development of efficient catalytic systems for the Hiyama reaction.¹² Recently, some *N*-heterocyclic carbene palladium complexes have been used in the Hiyama coupling reaction

Table 3 Hiyama reaction of trimethoxyphenylsilane with aryl chlorides catalyzed by **1–6**^a


Entry	Aryl chloride	[Pd]	Cat. loading [mol%]	Yield (%) ^b
1	R = NO ₂	1	1	84
2	R = NO ₂	2	1	88
3	R = NO ₂	3	1	83
4	R = NO ₂	4	1	90
5	R = NO ₂	5	1	87
6	R = NO ₂	6	1	89
7	R = NO ₂	1 ^c	1	92
8	R = CN	1	1	82
9	R = CN	2	1	85
10	R = CN	3	1	84
11	R = CN	4	1	88
12	R = CN	5	1	87
13	R = CN	6	1	88
14	R = CN	1 ^c	1	90
15	R = COCH ₃	1	1	78
16	R = COCH ₃	2	1	83
17	R = COCH ₃	3	1	80
18	R = COCH ₃	4	1	82
19	R = COCH ₃	5	1	84
20	R = COCH ₃	6	1	83
21	R = H	1	2	67
22	R = H	2	2	70
23	R = H	3	2	65
24	R = H	4	2	73
25	R = H	5	2	63
26	R = H	6	2	69
27	R = CH ₃	1	2	55
28	R = CH ₃	2	2	60
29	R = CH ₃	3	2	63
30	R = CH ₃	4	2	62
31	R = CH ₃	5	2	57
32	R = CH ₃	6	2	60

^a Reaction conditions: trimethoxyphenylsilane (0.30 mmol), aryl chloride (0.25 mmol), [Pd] catalyst (containing 1.0 mol% Pd), TBAF (0.50 mmol) in toluene (1.0 mL) at 120 °C under microwave irradiation for 30 min.

^b Isolated yield.

^c The reaction was carried out with an oil-bath heating at 120 °C and stirred for 6 h.

with high activities.¹³ Microwave-assisted organic synthesis is advantageous for enabling rapid, reproducible, and scalable chemistry development, which has been extensively used for carrying out chemical reactions.¹⁴ It was envisaged that the microwave irradiation would enhance the rate of reaction, thereby reducing the reaction time. Herein, the catalytic activities of the dinuclear NHC–Pd complexes for the Hiyama coupling reaction were examined. The compounds **1–6** are catalytically active towards the Hiyama coupling reaction of aryl chloride with trimethoxyphenylsilane in the presence of TBAF (*tetra*-butylammonium fluoride) in toluene under microwave irradiation conditions, yielding the corresponding biphenyl products were given in Table 3. In general, all of the compounds give rise to highly active catalysts for the aryl chloride substrates with electron-withdrawing groups, such as 4-chloronitrobenzene giving good yields within 30 min at 120 °C under microwave irradiation (Table 3, entries 1–6). When the reaction was carried out with oil-bath heating at 120 °C, a slightly higher yield (92%) yield was obtained, however, the

reaction time must be prolonging to more than 6 h (Table 3, entry 7). For the activated substrate 4-chlorobenzonitrile and 4-chloroacetophenone, as expected, gave better coupling yields (78–88%) than chlorobenzene (63–73%) (Table 3, entries 8–26). For the less active electron-donating 4-chlorotoluene, the yields of the products dropped to 55–63% (Table 3, entries 27–32). It has to be pointed out that the difference in yields according to the substrates results from the electrophilic character of the aryl chlorides. Highest yields are achieved for the aryl chlorides with electron-withdrawing groups. In addition, the sterically bulky di(*iso*-propyl) derivatives (compounds **2**, **4** and **6**) consistently performed better with higher yields than their trimethyl counterparts (compounds **1**, **3** and **5**), which is in agree with the result reported in the literature.¹⁵

Conclusions

In summary, a series of dinuclear *N*-heterocyclic carbene (NHC)–palladium complexes **1–6** bridged by the diphosphine ligands have been prepared by reacting the chloro-bridged dimeric carbene complexes with the respective bridging ligand. The catalytic behaviors of the diphosphine-bridged dinuclear NHC–palladium complexes in Hiyama coupling reaction were investigated and generated the corresponding products in moderate to good yields. As a derivative of the NHC–palladium complexes, this kind of dinuclear complexes would have potential uses in catalysis.

Experimental

General considerations

The dimeric palladium complexes [Pd(μ -Cl)(Cl)(NHC)]₂ were prepared using a method previously reported in the literature.¹⁶ The chemicals were purchased from commercial suppliers and were used without purification prior to use except where otherwise indicated. All ¹H, ¹³C and ³¹P NMR were performed in CDCl₃ and recorded on a Bruker Avance 400 NMR spectrometer with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Bruker IFS 120 HR spectrometer as KBr disks. Elemental analyses were performed on a Vario El III elemental. Flash column chromatography was carried out using 300–400 mesh silica gel.

Synthesis

[PdCl₂(IMes)]₂(μ -dppe) (**1**)

A mixture of the dimeric complex [Pd(μ -Cl)(Cl)(IMes)]₂ (96 mg, 0.10 mmol) and dppe (40 mg, 0.10 mmol) was dissolved in CH₂Cl₂ (5 mL) and stirred at ambient temperature overnight. The reaction mixture was filtered over Celite, the solvent was reduced under vacuum and the yellow precipitate formed by addition of *n*-hexane (10 mL). The solid was filtered off, washed with *n*-hexane, and dried under vacuum, yield 117 mg (86%). Crystals suitable for X-ray analysis were obtained by a slow diffusion of *n*-hexane into a dichloromethane solution of the product. ¹H NMR (400 MHz, CDCl₃): δ = 7.31–7.24 (m,

12H), 7.17 (t, $J = 7.2$ Hz, 8H), 7.02 (s, 4H), 6.96 (s, 8H), 2.29–2.28 (m, 40H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 170.0$ (d, $^2J_{\text{C,P}} = 208.7$ Hz, $\text{C}_{\text{carbene}}$), 138.4 (*o*- CH_3 -CAr), 136.2 (N-CAr), 135.4 (*p*- CH_3 -CAr), 133.6 (d, $^2J_{\text{C,P}} = 10.4$ Hz, CH Ph), 130.3 (d, $^1J_{\text{C,P}} = 42.4$ Hz, CPh), 129.4 (CH Ph), 128.8 (CH Ph), 127.5 (d, $^2J_{\text{C,P}} = 9.9$ Hz, CH Ph), 123.0 (d, $^4J_{\text{C,P}} = 5.6$ Hz, N-CH=CH-N), 21.6 (*p*- CH_3), 18.9 (*o*- CH_3), 15.2 (PCH₂). ^{31}P NMR (121.5 MHz, CDCl_3): $\delta = 16.5$. IR (KBr, cm^{-1}): 2920, 2858, 1488, 1435, 1406, 1330, 1280, 1230, 1106, 914, 854, 727. Anal. Calc. for $[\text{PdCl}_2(\text{IMes})]_2(\mu\text{-dppe})$ ($\text{C}_{68}\text{H}_{72}\text{Cl}_4\text{N}_4\text{P}_2\text{Pd}_2$): C, 59.97; H, 5.33; N, 4.11%. Found: C, 59.72; H, 5.07; N, 4.18%.

$[\text{PdCl}_2(\text{IPr})]_2(\mu\text{-dppe})$ (2)

A mixture of the dimeric complex $[\text{Pd}(\mu\text{-Cl})(\text{Cl})(\text{IPr})]_2$ (113 mg, 0.10 mmol) and dppe (40 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (5 mL) and stirred at ambient temperature overnight. The reaction mixture was filtered over Celite, the solvent was reduced under vacuum and a yellow precipitate formed by addition of *n*-hexane (10 mL). The solid was filtered off, washed with *n*-hexane, and dried under vacuum, yield 130 mg (85%). Crystals suitable for X-ray analysis were obtained by a slow diffusion of *n*-hexane into a dichloromethane solution of the product. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.39$ (t, $J = 7.6$ Hz, 4H), 7.27–7.19 (m, 20H), 7.14 (t, $J = 7.2$ Hz, 8H), 7.06 (s, 4H), 3.12 (sept, $J = 6.4$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 2.00 (br, 4H, CH_2), 1.20 (d, $J = 6.4$ Hz, 24H, CH_3), 1.03 (d, $J = 6.8$ Hz, 24H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 172.6$ (d, $^2J_{\text{C,P}} = 196.9$ Hz, $\text{C}_{\text{carbene}}$), 146.6 (*iPr*-CAr), 135.3 (N-CAr), 133.9 (d, $^2J_{\text{C,P}} = 10.5$ Hz, CH Ph), 130.3 (d, $^1J_{\text{C,P}} = 42.8$ Hz, CPh), 130.1 (d, $^4J_{\text{C,P}} = 1.8$ Hz, CH Ph), 129.4 (d, $^4J_{\text{C,P}} = 5.5$ Hz, CH Ph), 127.4 (d, $^4J_{\text{C,P}} = 9.9$ Hz, CH Ph), 123.8 (d, $^4J_{\text{C,P}} = 5.5$ Hz, N-CH=CH-N), 123.4 (CH Ar), 28.4 ($\text{CH}(\text{CH}_3)_2$), 26.2 ($\text{CH}(\text{CH}_3)_2$), 22.8 ($\text{CH}(\text{CH}_3)_2$), 19.2 (PCH₂). ^{31}P NMR (121.5 MHz, CDCl_3): $\delta = 16.5$. IR (KBr, cm^{-1}): 2919, 2857, 1484, 1435, 1407, 1329, 1275, 1229, 1103, 1028, 910, 853, 732. Anal. Calc. for $[\text{PdCl}_2(\text{IPr})]_2(\mu\text{-dppe})$ ($\text{C}_{80}\text{H}_{96}\text{Cl}_4\text{N}_4\text{P}_2\text{Pd}_2$): C, 62.79; H, 6.32; N, 3.66%. Found: C, 62.58; H, 6.17; N, 3.34%.

$[\text{PdCl}_2(\text{IMes})]_2(\mu\text{-dppb})$ (3)

Compound **3** was synthesized by a similar method for the synthesis of **1** except that dppb was used instead of dppe. Yield: 125 mg (90%). Crystals for X-ray diffraction was obtained by a slow diffusion of diethyl ether into a dichloromethane solution of the product. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.35$ –7.31 (m, 12H), 7.23–7.19 (m, 8H), 7.03–7.00 (m, 12H), 2.36 (s, 12H, *p*- CH_3), 2.30 (s, 24H, *o*- CH_3), 2.19 (br, 4H, CH_2), 1.94 (br, 4H, CH_2). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 170.6$ (d, $^2J_{\text{C,P}} = 197.4$ Hz, $\text{C}_{\text{carbene}}$), 138.5 (*o*- CH_3 -C Ar), 136.3 (d, $^4J_{\text{C,P}} = 3.4$ Hz, N-CAr), 135.5 (*p*- CH_3 -C Ar), 133.6 (d, $^2J_{\text{C,P}} = 10.2$ Hz, CH Ph), 130.8 (d, $^1J_{\text{C,P}} = 42.5$ Hz, CPh), 129.6 (d, $^4J_{\text{C,P}} = 2.1$ Hz, CH Ph), 128.9 (CH Ph), 127.7 (d, $^4J_{\text{C,P}} = 10.0$ Hz, CH Ph), 123.1 (d, $^4J_{\text{C,P}} = 5.8$ Hz, N-CH=CH-N), 30.9 (PCH₂CH₂), 21.2 (*p*- CH_3), 19.0 (*o*- CH_3), 14.1 (PCH₂CH₂). ^{31}P NMR (121.5 MHz, CDCl_3): $\delta = 13.7$. IR (KBr, cm^{-1}): 2964, 2867, 1486, 1433, 1403, 1380, 1331, 1276, 1179, 1105, 1058, 1025, 945, 909, 849, 799. Anal.

Calc. for $[\text{PdCl}_2(\text{IMes})]_2(\mu\text{-dppb})$ ($\text{C}_{70}\text{H}_{76}\text{Cl}_4\text{N}_4\text{P}_2\text{Pd}_2$): C, 60.49; H, 5.51; N, 4.03%. Found: C, 60.74; H, 5.17; N, 4.15%.

$[\text{PdCl}_2(\text{IPr})]_2(\mu\text{-dppb})$ (4)

Compound **4** was synthesized by a similar method for the synthesis of **2** except that dppb was used instead of dppe. Yield: 134 mg (86%). Crystals suitable for X-ray analysis were obtained by a slow diffusion of *n*-hexane into a dichloromethane solution of the product. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.37$ –7.24 (m, 24H), 7.20 (t, $J = 7.2$ Hz, 8H), 7.11 (s, 4H), 3.52–3.47 (m, 4H, PCH₂CH₂), 3.12 (sept, $J = 6.4$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 1.83 (br, 4H, PCH₂CH₂), 1.27 (d, $J = 6.4$ Hz, 24H, CH_3), 1.07 (d, $J = 6.8$ Hz, 24H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 172.7$ (d, $^2J_{\text{C,P}} = 196.1$ Hz, $\text{C}_{\text{carbene}}$), 146.6 (*iPr*-CAr), 135.3 (N-CAr), 133.5 (d, $^2J_{\text{C,P}} = 10.0$ Hz, CH Ph), 130.8 (d, $^1J_{\text{C,P}} = 42.4$ Hz, CPh), 129.6 (CH Ph), 129.4 (d, $^4J_{\text{C,P}} = 2.1$ Hz, CH Ph), 127.6 (CH Ph), 127.5 (CH Ph), 123.9 (d, $^4J_{\text{C,P}} = 5.8$ Hz, N-CH=CH-N), 123.5 (CH Ar), 28.5 ($\text{CH}(\text{CH}_3)_2$), 26.2 ($\text{CH}(\text{CH}_3)_2$), 22.8 ($\text{CH}(\text{CH}_3)_2$), 15.2 (PCH₂CH₂). ^{31}P NMR (121.5 MHz, CDCl_3): $\delta = 13.5$. IR (KBr, cm^{-1}): 2964, 2864, 1466, 1433, 1406, 1380, 1364, 1274, 1120, 1100, 1058, 942, 908, 800, 755, 736. Anal. Calc. for $[\text{PdCl}_2(\text{IPr})]_2(\mu\text{-dppb})$ ($\text{C}_{82}\text{H}_{100}\text{Cl}_4\text{N}_4\text{P}_2\text{Pd}_2$): C, 63.20; H, 6.47; N, 3.60%. Found: C, 62.97; H, 6.72; N, 3.43%.

$[\text{PdCl}_2(\text{IMes})]_2(\mu\text{-dpph})$ (5)

Compound **5** was synthesized by a similar method for the synthesis of **1** except that dpph was used instead of dppe. Yield: 128 mg (91%). Crystals suitable for X-ray analysis were obtained by a slow diffusion of *n*-hexane into a dichloromethane solution of the product. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.39$ –7.37 (m, 12H), 7.24 (t, $J = 7.2$ Hz, 8H), 7.05–7.03 (m, 12H), 2.41 (s, 12H, *p*- CH_3), 2.32 (s, 24H, *o*- CH_3), 2.07–2.00 (m, 4H, PCH₂CH₂CH₂), 1.22 (br, 4H, PCH₂CH₂CH₂), 1.10 (br, 4H, PCH₂CH₂CH₂). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 170.4$ (d, $^2J_{\text{C,P}} = 197.4$ Hz, $\text{C}_{\text{carbene}}$), 138.4 (*o*- CH_3 -CAr), 136.2 (N-CAr), 135.5 (*p*- CH_3 -CAr), 133.5 (d, $^2J_{\text{C,P}} = 10.1$ Hz, CH Ph), 130.9 (d, $^1J_{\text{C,P}} = 42.4$ Hz, CPh), 129.5 (d, $^4J_{\text{C,P}} = 2.4$ Hz, CH Ph), 128.8 (CH Ph), 127.5 (d, $^2J_{\text{C,P}} = 9.8$ Hz, CH Ph), 123.0 (d, $^4J_{\text{C,P}} = 5.7$ Hz, N-CH=CH-N), 30.5 (PCH₂CH₂CH₂), 22.6 (PCH₂CH₂CH₂), 21.2 (*p*- CH_3), 18.9 (*o*- CH_3), 14.0 (PCH₂CH₂CH₂). ^{31}P NMR (121.5 MHz, CDCl_3): $\delta = 13.5$. IR (KBr, cm^{-1}): 2964, 2868, 1465, 1431, 1380, 1331, 1278, 1170, 1125, 1069, 946, 819, 802, 736. Anal. Calc. for $[\text{PdCl}_2(\text{IMes})]_2(\mu\text{-dpph})$ ($\text{C}_{72}\text{H}_{80}\text{Cl}_4\text{N}_4\text{P}_2\text{Pd}_2$): C, 60.98; H, 5.69; N, 3.95%. Found: C, 60.63; H, 5.47; N, 4.04%.

$[\text{PdCl}_2(\text{IPr})]_2(\mu\text{-dpph})$ (6)

Compound **6** was synthesized by a similar method for the synthesis of **2** except that dpph was used instead of dppe. Yield: 141 mg (89%). Crystals suitable for X-ray analysis were obtained by a slow diffusion of diethyl ether into a dichloromethane solution of the product. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.50$ (t, $J = 7.6$ Hz, 4H), 7.35–7.31 (m, 20H), 7.19 (t, $J = 7.2$ Hz, 8H), 7.13 (s, 4H), 3.12 (sept, $J = 6.8$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 2.00–1.93 (m, 4H, PCH₂CH₂CH₂), 1.30 (d, $J = 6.8$

Hz, 24H, CH₃), 1.10 (d, $J = 7.2$ Hz, 24H, CH₃), 0.95–0.90 (m, 8H, PCH₂CH₂CH₂). ¹³C NMR (100 MHz, CDCl₃): $\delta = 172.7$ (d, $^2J_{C,P} = 196.4$ Hz, C_{carbene}), 146.6 (*i*Pr-CAr), 135.4 (N-CAr), 133.5 (d, $^3J_{C,P} = 9.9$ Hz, CH Ph), 130.9 (d, $^1J_{C,P} = 42.2$ Hz, CPh), 129.6 (CH Ph), 129.4 (d, $^4J_{C,P} = 2.4$ Hz, CH Ph), 127.5 (d, $^2J_{C,P} = 9.8$ Hz, CH Ph), 123.9 (d, $^4J_{C,P} = 5.9$ Hz, N-CH=CH-N), 123.5 (CH Ar), 31.5 (PCH₂CH₂CH₂), 28.5(CH(CH₃)₂), 26.2(CH(CH₃)₂), 22.8 (PCH₂CH₂CH₂), 22.6 (CH(CH₃)₂), 14.0(PCH₂CH₂CH₂). ³¹P NMR (121.5 MHz, CDCl₃): $\delta = 13.0$. IR (KBr, cm⁻¹): 2964, 2866, 1487, 1435, 1405, 1331, 1276, 1105, 1058, 1025, 945, 914, 849, 799. Anal. Calc. for [PdCl₂(IPr)]₂(μ -dpph) (C₈₄H₁₀₄Cl₄N₄P₂Pd₂): C, 63.60; H, 6.61; N, 3.53%. Found: C, 63.77; H, 6.42; N, 3.34%.

General procedure for the NHC–Pd catalyzed Hiyama reaction

The aryl chloride (0.25 mmol), trimethoxyphenylsilane (0.30 mmol), NHC–Pd complex (containing 1.0 mol% Pd), TBAF (0.50 mmol) and dry toluene (1.0 mL) were added into oven-dried microwave vial. The reaction mixture was irradiated in a microwave apparatus at 120 °C for 30 min. After the reaction mixture was cooled to ambient temperature, the product was filtered over Celite and washed with ethyl acetate. Then the filtrate was concentrated with a rotary evaporator, and the residue was then subjected to purification via flash column chromatography with petroleum ether–EtOAc (10:1) as eluent to give the corresponding pure products.

X-Ray crystallography

Data collection was performed on a Bruker-AXS SMART CCD area detector diffractometer at 296 K using ω rotation scans with a scan width of 0.3° and Mo-K α radiation ($\lambda = 0.71073$ Å). Multi-scan corrections were applied using SADABS.¹⁷ Structure solutions and refinements were performed with the SHELX-97 package.¹⁸ All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 . The hydrogen atoms to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of carbon atoms. In compound **1**, a disordered co-crystallized solvent molecule CH₂Cl₂ was refined over two positions with occupancies of 0.57/0.43. In compound **4**, the crystal lattice contains solvent accessible voids of 327 Å³, however, the final difference electron density map contained no chemically significant peaks, the highest peak being 0.90 e/Å³ at a distance of 0.89 Å from the Pd atom and no model for any solvent could be found. In compound **6**, the unit cell includes disordered solvent water molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent water molecules and, thereby, to produce a set of solvent-free diffraction intensities.¹⁹ The SQUEEZE calculations showed a total solvent accessible area volume of 200.3 Å³ and the residual electron density amounted to 20 e per unit cell, corresponding to nearly 2 molecules of H₂O. A summary of the crystallographic data, data collection, and refinement parameters for complexes **1–6** were provided in Table 2.

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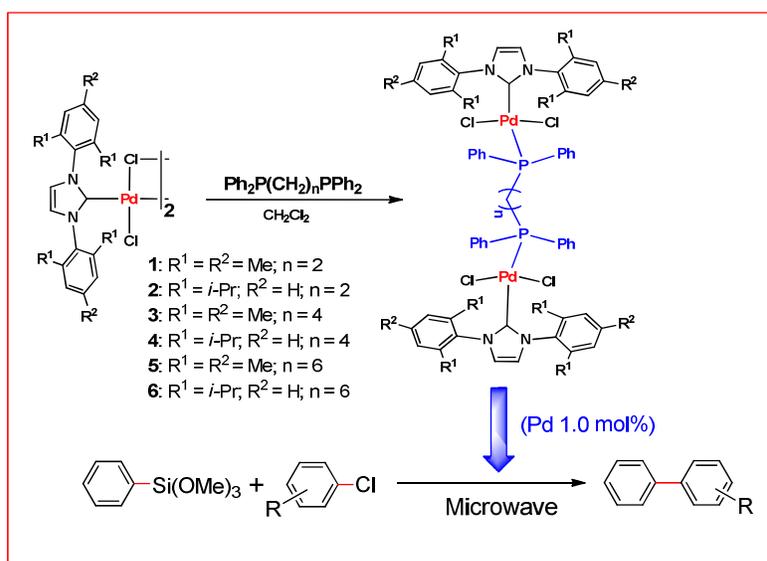
Abstract

Dinuclear NHC–Palladium Complexes Containing Phosphine Spacers: Synthesis, X-Ray Structures and Their Catalytic Activities towards Hiyama Coupling ReactionJin Yang,^a Pinhua Li,^a Yicheng Zhang,^a and Lei Wang^{*a,b}

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Six dinuclear *N*-heterocyclic carbene-palladium complexes were synthesized from $[\text{Pd}(\mu\text{-Cl})(\text{Cl})(\text{NHC})]_2$ and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, and their catalytic activities towards Hiyama reaction were investigated.

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