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Syntheses, Characterization and Catalytic Application of Palladacycles Containing Phosphane or Phosphane Oxide Functionalities

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The preparation of ligand precursors PhN=C(CMe$_2$)(NPh)-C=N(CH$_2$)$_2$PPh$_2$ (**1**) and PhN=C(CMe$_2$)(NPh)C=N(CH$_2$)$_2$P(O)-Ph$_2$ (**2**) are described. Treatment of **1** or **2** with 1 molequiv. Pd(OAc)$_2$ affords orthometallated palladium(II) complexes [PhN=C(CMe$_2$)(N-η^1-Ph)C=N(CH$_2$)$_2$PPh$_2$]Pd(OAc) (**3**) as a mononuclear complex or {[PhN=C(CMe$_2$)(N-η^1-Ph)C=N-(CH$_2$)$_2$P(O)Ph$_2$]Pd(OAc)}$_2$ (**4**) as an acetate-bridged dinuclear complex, respectively. Reaction of **3** with excess LiCl in methanol affords a mononuclear palladium(II) complex [PhN=C(CMe$_2$)(N-η^1-Ph)C=N(CH$_2$)$_2$PPh$_2$]PdCl (**5**). The crystal and molecular structures are reported for compounds **3**–**5**. Application of these novel palladacyclic complexes to the Suzuki and Heck reactions with aryl halide substrates was examined.

Introduction

Among studies on the palladium-catalyzed cross-coupling reactions palladacycles are likely to serve as a source of highly active but unstable zero-valent palladium species.[1a] They were considered to function as low-ligated and phosphane-free catalysts, which helped toward the evaluation the real potential of these systems.[1] Recently, enhanced catalytic activities are observed with new palladium complexes containing electron-rich and bulky ligands such as phosphanes and carbenes.[1–2] The effectiveness of these systems was attributed to a combination of electronic and steric properties of the ligands that favour both the oxidative addition and reductive elimination steps in the catalytic cycle.

In our previous reports,[3] palladacycles bearing four-membered diimine ligands with pendant functionalities have exhibited comparable catalytic activities towards Suzuki- and Heck-type reactions. Owing to the success in the application of those palladacycles and the advantages of phosphanes involved in the cross-coupling reactions, the enhancement of the catalytic activity might be expected by introducing electron-rich and bulky groups, such as phosphanes, into our four-membered diimine ligands as the pendant functionalities. Therefore, we report here the syntheses and characterization of novel palladacycles supported by four-membered diimine ligands with pendant phosphane or phosphane oxide functionalities. Their catalytic activity toward the Suzuki- and Heck-type reactions was also investigated.

Results and Discussion

Syntheses and Characterization of Ligand Precursors and Palladacycles

The new ligand precursor **1** was synthesized from the reaction of PhN=C(CMe$_2$)(NPh)C=N(CH$_2$)$_2$Cl with KPPh$_2$ in thf.[4] Compound **2** was synthesized by the oxidation of **1** with excess H$_2$O$_2$(aq.) in thf.[5] Both compounds were characterized by NMR spectroscopy and elemental analysis, which indicate four-membered diimine compounds with different functionalities than those reported previously.[3] The ^{31}P{^{1}H} NMR spectrum of the phosphorus(V) species **2** shows a characteristic upfield-shifted singlet at +31.9 ppm, whereas the spectrum of the phosphorus(III) original ligand **1** presents a signal at –18.7 ppm. A summary of the synthetic route and the proposed structures is shown in Scheme 1.

Treatment of **1** or **2** with 1 molequiv. Pd(OAc)$_2$ in thf at room temperature or under reflux conditions yielded complexes **3** or **4** as an orange or a greyish solid, respectively. Both compounds were characterized by NMR spectroscopy and elemental analysis. Similarly to the results reported previously, one more tertiary carbon atom is found in the region of phenyl ring on the basis of the ^{13}C{^{1}H} NMR spectrum in each case, which indicates that the metallated carbon atom is created during the reaction in both compounds. The ^{31}P{^{1}H} NMR spectrum of **3** shows one singlet at +29.5 ppm, which indicates the coordination of the phosphorus(III) group to the palladium centre.[6a] However, the ^{31}P{^{1}H} NMR spectrum of **4** shows one singlet at +29.8 ppm. This indicates that the oxide group is not coordinated to the palladium atom, as a significant downfield shift is expected to occur on coordination as a result of the inductive deshielding effect on the phosphorus atom.[7]

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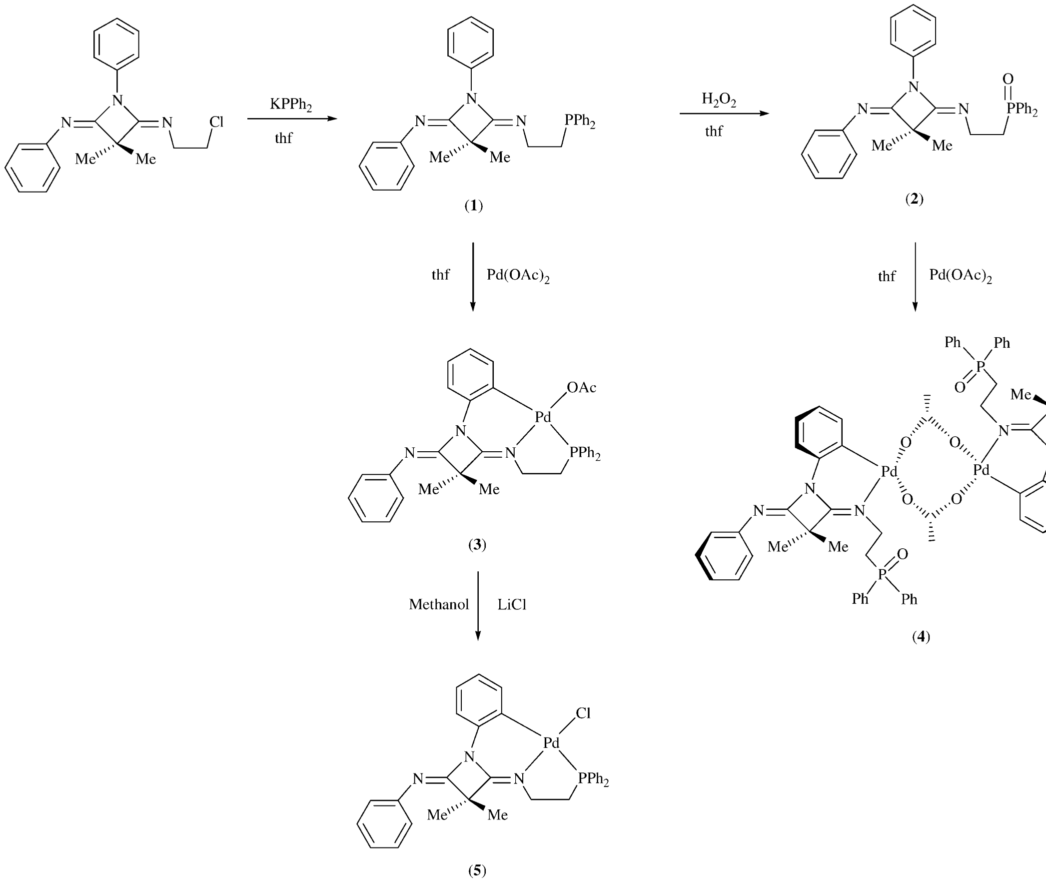


Scheme 1.

Suitable crystals of **3** or **4** for structural determination were obtained from a thf/hexane solution. The molecular structures are depicted in Figures 1 and 2. Compound **3** demonstrates a mononuclear form, whereas compound **4** is formed as a dinuclear species with two acetate groups as bridging ligands. In compound **3**, the bond angles around Pd metal centre [from 83.39(5) to 92.96(8)°] indicate a complex that has a slightly distorted square-planar geometry, in which the palladium metal centre is coordinated to one phenyl carbon atom, one imine nitrogen atom, one phosphorus atom, and one disordered OAc oxygen atom. The bite angles N_{imine}–Pd–$C_{metallated}$ [92.96(8)°] and N_{imine}–Pd–P [83.39(5)°] are similar to those found in our previous work [93.20(10)°, 93.77(8)°, 94.51(10)° and 93.47(12)° resulting from the imino nitrogen and the metallated carbon; 79.89(7)°, 80.06(9)°, 81.86(9)° and 84.62(8)° resulting from the imino nitrogen and pendant functionalities].[3] The bond length Pd–P [2.3129(5) Å] is within the range found for some phosphane-containing palladacycles [2.2091(5)–2.319(2) Å].[8] The bond length Pd–$C_{metallated}$ [2.053(2) Å] is longer than those found for phosphane-containing palladacycles[8] and from our previous reports [1.978(10)–2.025(3) Å].[3] The bond length Pd–N_{imine} [2.0210(17) Å] falls in the range between those found for some palladacycles with a tridentate ligand [1.988(2)–2.000(7) Å][3,8a] and those found for some palladium complexes containing a iminophosphane ligand [2.049(4)–2.224(4) Å].[9] The bond length Pd–O_{OAc} [2.052(7) and 2.085(2) Å disordered] is comparable to those found in the literature [2.036(2)–2.0897(19) Å].[3,8a,8b] In compound **4**, only one signal corresponding to the OAc group is observed in the NMR spectrum, which indicates the *anti* conformation.[6a,6b] This conformation matches that in the solid state. The bond angles around each Pd metal centre [from 82. 9(3) to 93.6(5)° for Pd; from 83.1(4) to 93.4(4)° for PdA] indicate a dinuclear palladium complex that has a slightly distorted square-planar geometry around each Pd metal centre. Each palladium metal centre is coordinated to one phenyl ring carbon atom, one imine nitrogen atom and two bridging acetate oxygen atoms. The bite angles N_{imine}–Pd–$C_{metallated}$ [93.6(5)° and 93.4(4)°] and the bond lengths Pd–$C_{metallated}$ [1.997(12) and 2.012(13) Å] and Pd–N_{imine} [2.015(10) and 2.028(10) Å] are similar to those discussed for **3**. The bond angles O_{OAc}–Pd–O_{OAc} [82.9(3)°and 83.1(4)°] are smaller than and the bond lengths Pd–O_{OAc} [2.058(9), 2.069(9), 2.141(8) and 2.163(8) Å] are comparable to those found for acetate-bridged dinuclear palladacycles [86.5(2)–91.3(1)° and 2.029(2)–2.175(11) Å, respectively].[6] The differing bond lengths exhibited by the two Pd–O_{OAc} bonds around the same Pd metal centre reflect the higher *trans* influence of the aryl carbon atom relative to the imine nitrogen atom.[6a–6e] The distance between Pd and PdA [2.8878(4) Å] is within the range found for acetate-bridged dinuclear palladacycles of the [C,N] coordination type [2.8502(13)–2.929(2) Å].[6]

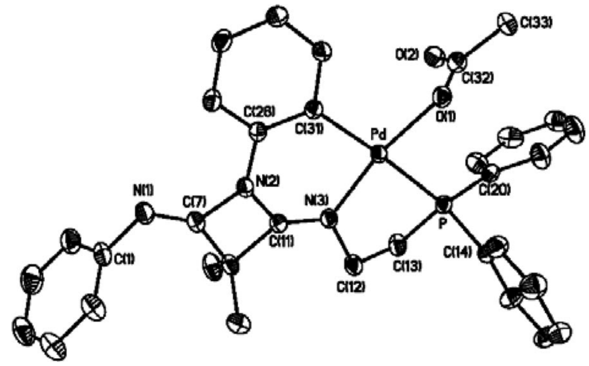


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and bond angles [°]: Pd–N(3), 2.0210(17); Pd–O(1), 2.085(2); Pd–O(1′), 2.052(7), Pd–C(31), 2.053(2); Pd–P, 2.3129(5); N(3)–Pd–C(31), 92.96(8); C(31)–Pd–O(1), 92.51(8), N(3)–Pd–P, 83.39(5); O(1)–Pd–P, 91.29(6); N(3)–Pd–O(1), 168.52(8); C(31)–Pd–P, 176.17(6). Hydrogen atoms on carbon atoms omitted for clarity.

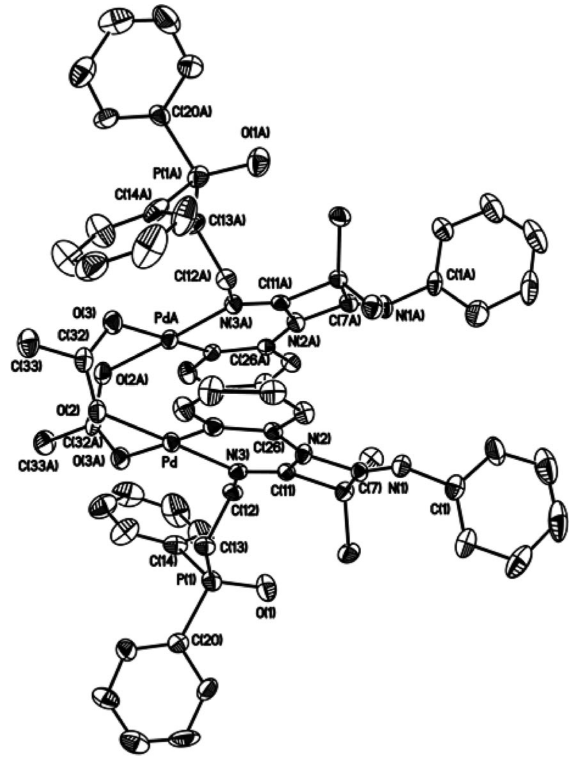


Figure 2. Molecular structure of one of the crystallographically independent molecules of **4**. Selected bond lengths [Å] and bond angles [°]: Pd–C(31), 2.012(13); Pd–N(3), 2.015(10); Pd–O(2), 2.069(9); Pd–O(3A), 2.141(8); Pd–PdA, 2.8878(4); PdA–C(31A), 1.997(12); PdA–N(3A), 2.028(10); PdA–O(2A), 2.058(9); PdA–O(3), 2.163(8); C(31)–Pd–N(3), 93.6(5); C(31)–Pd–O(2), 90.9(5); N(3)–Pd–O(2), 175.4(4); C(31)–Pd–O(3A), 173.2(5); N(3)–Pd–O(3A), 92.6(4); O(2)–Pd–O(3A), 82.9(3); C(31A)–PdA–N(3A), 93.4(4); C(31A)–PdA–O(2A), 91.5(4); N(3A)–PdA–O(2A), 175.1(4); C(31A)–PdA–O(3), 173.2(4); N(3A)–PdA–O(3), 92.1(4); O(2A)–PdA–O(3), 83.1(4). Hydrogen atoms on carbon atoms omitted for clarity.

Reaction of **3** with excess lithium chloride in refluxing methanol yields **5** as a dark green solid.[10] The spectroscopic and elemental analysis data are consistent with a structure similar to **3**, but with a Cl atom coordinated to the metal centre instead of an OAc group. Suitable crystals of **5** for structural determination were obtained from a CH_2Cl_2/hexane solution. The molecular structure is depicted in Figure 3. The bond lengths and angles are similar to those discussed above. The bond length Pd–Cl [2.3124(6) Å] falls towards the lower end of the range of those found for palladacycles containing tridentate ligands [2.3181(8)–2.427(2) Å].[3a,8c–8e] Attempts to synthesize a palladium chloride complex containing ligand **2** by a similar route have been unsuccessful.

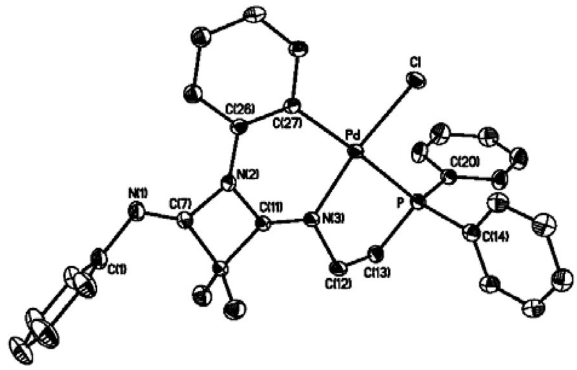


Figure 3. Molecular structure of **5**. Selected bond lengths [Å] and bond angles [°]: Pd–N(3), 2.0321(18); Pd–C(27), 2.078(2); Pd–Cl, 2.3124(6); Pd–P, 2.3129(6); N(3)–Pd–C(27), 92.91(8); N(3)–Pd–Cl, 172.32(5); C(27)–Pd–Cl, 94.22(6); N(3)–Pd–P, 83.81(5); C(27)–Pd–P, 175.95(6); Cl(1)–Pd–P, 89.18(2). Hydrogen atoms on carbon atoms omitted for clarity.

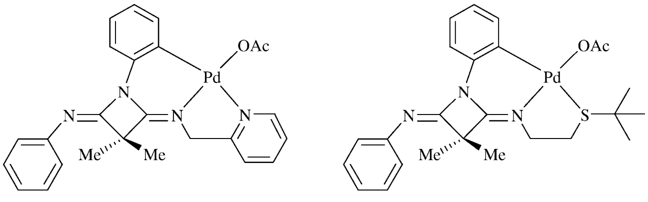
Catalytic Studies

Because of the success of some phosphane-containing or CN-type palladacycles in catalyzing cross-coupling reactions,[1] these palladacycles are expected to catalyze carbon–carbon coupling reactions. For the purpose of comparing the reactivity with other corresponding palladacycles, Suzuki and Heck reactions were chosen to demonstrate the catalytic activities. Potential candidates **3**–**5** as catalyst precursors were introduced in the Suzuki coupling reaction of 4-bromoacetophenone with phenylboronic acid at 50 °C with a 0.5 mol-% Pd, as shown in Scheme 2. Selected results are listed in Table 1. The optimum base/solvent mixture for the reaction was found to be K_3PO_4/toluene after several trials with a combination of bases (KF, K_3PO_4 and Cs_2CO_3) and solvents [*N*,*N*-dimethylacetamide (dma), thf and toluene]. A higher reactivity was observed for **4** with a conversion of up to 99% in 10 min (Entries 1–3). A similar trend was observed by using electron-rich 4-bromoanisole as the substrate (Entries 4, 5 and 7). The coupling activities were higher when KF was used as the base (Entries 6 and 8). Therefore KF/toluene was introduced to examine the performance of **4** in the coupling reactions involving poor-coupling partners, at room temperature. The conversion was up to 92% over 6 h when 2 mol-% Pd was used (Entries 10 and 11). Compound **4** also exhibited an excellent conversion over 4 h with 4-bromoacetophenone under the optimized conditions and at room temperature when 1 mol-% Pd was used (Entry 9). Because of the higher activity and solubility of **4**, lower catalyst concentrations were investigated with 4-bromoanisole as the substrate; catalyst/substrate ratios from 5×10^{-4} to 5×10^{-6} were investigated. The reactions gave a conversion of 95% over 2.5 h at 70 °C for the 5×10^{-4} ratio, 96% over 1 h at 100 °C for the 5×10^{-5} ratio and 74% over 48 h at 100 °C for the 5×10^{-6} ratio (Entries 12–14). The same conditions were applied to examine the catalytic activity of **4** with methyl 4-bromobenzoate as the substrate with a catalyst/substrate ratio of 5×10^{-6}. The reaction gave a conversion of 97% over 12 h at 100 °C (Entry 15). Catalyst productivities were observed with a turnover of up to 1.4×10^5 during a 48-h period for the coupling of the electronically deactivated aryl bromide and with a turnover of up to 1.9×10^5 during a 12-h period for the coupling of the electronically activated aryl bromide. These values are comparable to those for palladacycles bearing C,N-type or C,P-type ligands.[11] Complex **4** was tested with 4-chloroacetophenone and phenylboronic acid, and 1 mol-% Pd and K_3PO_4/toluene at 100 °C. The reaction gave a conversion of 55% over 24 h (Entry 16). Better conversions were found by adding tetra-*n*-butylamine bromide ($n$$Bu_4NBr$, TBAB) as cocatalyst (70% conversion for 20 mol-% TBAB in Entry 17; 99% conversion for 50 mol-% TBAB in Entry 18).[12] A poor conversion was observed when 4-chloroanisole was used as the substrate under the optimum conditions (Entry 19). In order to determine the influence of the pendant functionality on the catalytic activity,[3] the OAc-containing palladacycles **3**, **6**[3a] and **7**[3b] (as shown in Scheme 3) were examined as catalysts with 4-bromoanisole as the substrate and 1 mol-% Pd under optimized conditions at 70 °C (Entries 20–22). In comparison with other CNX-type palladacycles of four-membered diimine systems,[3] a higher reactivity was observed for the palladacycle containing the pendant PPh_2 moiety. However, the CN-type palladacycle **4** demonstrates a higher catalytic activity for the Suzuki reaction (Entries 4, 6, 7, 21 and 22).

$$\text{Ar-X} + \text{Ph-B(OH)}_2 \xrightarrow[T\ (^{o}\text{C})\ /\ \text{solvent}]{\text{[cat] / base}} \text{Ph-Ar}$$

[cat] = Palladacycles

Scheme 2. Application of the palladacycles in the Suzuki reaction.



(**6**)[3a]

(**7**)[3b]

Scheme 3. The palladacycles with terdentate [C,N,N] or [C,N,S] ligands.

Compounds **3**–**5** were also examined as catalysts in the Heck coupling reaction of 4-bromoacetophenone with styrene at 135 °C over a period of 1.5 h with 1 mol-% Pd and under optimum conditions (KF/dma), as shown in Scheme 4. Selected results are listed in Table 2. Excellent activities under the optimum conditions (Entries 1–3) were obtained. A higher activity was observed for **3** when using a less reactive substrate in the presence of 20 mol-% TBAB over 12 h (Entries 4–6). The same conditions were applied to examine the other electronically deactivated aryl bromide, however, with lower conversions (Entries 7 and 8).

Table 1. Suzuki coupling reaction catalyzed by new palladium complexes.[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] [mol-%]	T [°C]	t [h]	Conversion [%][b]	Yield [%][c]
1	**3**	4-bromoacetophenone	K_3PO_4	toluene	0.5	50	1.5	97	95
2	**4**	4-bromoacetophenone	K_3PO_4	toluene	0.5	50	0.16	99	92
3	**5**	4-bromoacetophenone	K_3PO_4	toluene	0.5	50	1.5	98	94
4	**3**	4-bromoanisole	K_3PO_4	toluene	0.5	50	6	92	85
5	**4**	4-bromoanisole	K_3PO_4	toluene	0.5	50	0.75	87	84
6	**4**	4-bromoanisole	KF	toluene	0.5	50	0.75	93	91
7	**5**	4-bromoanisole	K_3PO_4	toluene	0.5	50	6.5	90	86
8	**4**	4-*tert*-butyl-bromobenzene	KF	toluene	0.5	50	1.25	95	92
9	**4**	4-bromoacetophenone	K_3PO_4	toluene	1	room temp.	4	99	95
10	**4**	4-bromoanisole	KF	toluene	1	room temp.	3	56	–
11	**4**	4-bromoanisole	KF	toluene	2	room temp.	6	92	84
12	**4**	4-bromoanisole	KF	toluene	0.05	70	2.5	95	92
13	**4**	4-bromoanisole	KF	toluene	0.005	100	1	96	94
14	**4**	4-bromoanisole	KF	toluene	0.0005	100	48	74	70
15	**4**	Methyl 4-bromobenzoate	KF	toluene	0.0005	100	12	97	95
16	**4**	4-chloroacetophenone	K_3PO_4	toluene	1	100	24	55	–
17[d]	**4**	4-chloroacetophenone	K_3PO_4	toluene	1	100	24	70	–
18[e]	**4**	4-chloroacetophenone	K_3PO_4	toluene	1	100	24	99	95
19[e]	**4**	4-chloroanisole	KF	toluene	1	100	72	<5	–
20	**3**	4-bromoanisole	K_3PO_4	toluene	1	70	1	96	91
21	**6**	4-bromoanisole	KF	thf	1	70	12	94	91
22	**7**	4-bromoanisole	K_3PO_4	toluene	1	70	4	97	90

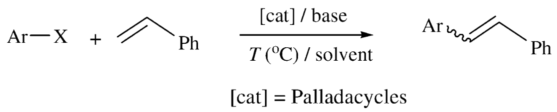
[a] Reaction conditions: 1.0 mmol aryl halide, 1.5 mmol phenylboronic acid, 2.0 mmol base, 2 mL solvent. [b] Determined by ^1H NMR spectroscopy. [c] Isolated yield (average of two experiments). [d] Addition of 20 mol-% TBAB. [e] Addition of 50 mol-% TBAB.

Table 2. Heck coupling reaction catalyzed by new palladium complexes.[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] [mol-%]	T [°C]	t [h]	Conversion [%][b]	Yield [%][c]
1	**3**	4-bromoacetophenone	KF	dma	1	135	1.5	91	84
2	**4**	4-bromoacetophenone	KF	dma	1	135	1.5	94	89
3	**5**	4-bromoacetophenone	KF	dma	1	135	1.5	93	90
4[d]	**3**	4-bromoanisole	KF	dma	1	135	12	96	91
5[d]	**4**	4-bromoanisole	KF	dma	1	135	12	80	77
6[d]	**5**	4-bromoanisole	KF	dma	1	135	12	92	88
7[d]	**3**	4-bromotoluene	KF	dma	1	135	12	73	–
8[d]	**3**	4-*tert*-butyl-bromobenzene	KF	dma	1	135	12	68	–
9	**3**	4-bromoacetophenone	KF	dma	0.1	135	2.75	99	92
10	**3**	4-bromoacetophenone	KF	dma	0.01	135	8	95	90
11	**3**	4-bromoacetophenone	KF	dma	0.001	135	36	97	91
12[d]	**3**	4-chloroacetophenone	KF	dma	1	135	24	29	–
13[e]	**3**	4-chloroacetophenone	KF	dma	3	135	36	38	–
14[d]	**6**	4-bromoanisole	KF	dma	1	135	12	80	71
15	**7**	4-bromoanisole	K_3PO_4	dmf	1	135	12	96	91
16	**3**	4-bromoacetophenone	K_3PO_4	thf	1	70	1.5	<5	–
17	**4**	4-bromoacetophenone	K_3PO_4	thf	1	70	1.5	49	–
18	**5**	4-bromoacetophenone	K_3PO_4	thf	1	70	1.5	<5	–
19	**4**	4-bromoacetophenone	K_3PO_4	thf	1	70	12	63	–
20[d]	**4**	4-bromoacetophenone	K_3PO_4	thf	1	70	12	90	82
21[d]	**4**	Methyl 4-bromobenzoate	K_3PO_4	thf	1	70	10	97	92
22[d]	**4**	4-bromobenzaldehyde	K_3PO_4	thf	1	70	12	99	94
23[d]	**4**	4-bromoanisole	K_3PO_4	thf	1	70	30	85	77
24[e]	**4**	4-bromoanisole	K_3PO_4	thf	1	70	18	90	84
25[e]	**4**	4-bromotoluene	K_3PO_4	thf	1	70	24	81	77
26[e]	**4**	4-*tert*-butyl-bromobenzene	K_3PO_4	thf	1	70	24	70	–

[a] Reaction conditions: 1.0 mmol aryl halide, 1.3 mmol styrene, 1.5 mmol base, 2 mL solvent. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield (average of two experiments). [d] Addition of 20 mol-% TBAB. [e] Addition of 50 mol-% TBAB.

Lower catalyst concentrations were loaded with catalyst/substrate ratios of 10^{-3} to 10^{-5}, which led to conversions above 95 % over periods of 2.75 to 36 h (Entries 9–11). Catalyst productivity was observed with a turnover of up to 9.1×10^4 during a 36-h period for the coupling of the electronically activated aryl bromide; the TOF is comparable to those found in the literature.[13] Complex **3** exhibited a poor activity in the reaction with the electronically activated aryl chloride even with higher catalyst and TBAB loadings (Entries 12 and 13). Compounds **6** and **7** were examined under optimized conditions with 4-bromoanisole as the substrate. The catalytic activities fall in the order **3** = **7** > **6** (Entries 4, 14 and 15). A higher activity was observed with the palladacycle containing a pendant PPh_2 moiety for the Heck reaction.



Scheme 4. Application of the palladacycles in the Heck reaction.

The reaction of 4-bromoacetophenone with styrene can also be performed under mild reaction conditions with 1 mol-% Pd.[14] Compound **4** exhibits a higher activity with K_3PO_4/thf when using **3**–**5** as candidates for the precatalysts at 70 °C (Entries 16–18), whereas compounds **3** and **5** demonstrate higher activities at high temperature (Entries 1 and 3). Better conversions were achieved by extending the reaction time or by adding 20 mol-% TBAB (Entries 19 and 20). Similar conversions were observed when using methyl 4-bromobenzoate or 4-bromobenzaldehyde as substrates (Entries 21 and 22). Similar conditions were applied when investigating the electronically deactivated aryl bromide, with 85 % conversion over 30 h (Entry 23). Higher activities were observed over 18 h by increasing the loading of TBAB up to 50 mol-% (Entry 24). These conditions were applied when investigating the other electronically deactivated aryl bromides, however, with lower conversions over 24 h (Entries 25 and 26).

Conclusion

Three novel palladacycles bearing phosphane or phosphane oxide functionalities have been prepared and their catalytic activity toward the Suzuki and Heck C–C coupling reactions has been demonstrated. Under optimized conditions, palladacycle **4** exhibits a comparable activity to those of existing CN-type palladacyclic systems for both the Suzuki and Heck coupling reactions. For those CNP-type palladacycles, the OAc-containing complex **3** exhibits a slightly higher activity than the Cl-containing complex **5** for both coupling reactions. Although complex **3** is more active in catalyzing the Heck reaction with aryl bromides containing electron-donating groups at higher temperatures, complex **4** seems to be more active in catalyzing both coupling reactions under relatively mild conditions. In the case of the four-membered diimine palladacyclic system, the phosphane-containing palladacycles exhibit a higher activity for both the Suzuki and Heck coupling reactions than those reported in our previous work. In some cases, the CN-type palladacycle **4** demonstrates a higher catalytic activity than those with dative groups. Preliminary studies on the fine-tuning of the ligands and further application of metal complexes to the catalytic reactions are currently underway.

Experimental Section

General Procedure: All manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk-line or dry-box techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Methanol and dma were used as supplied. Deuterated solvents were dried with molecular sieves. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on a Varian Mercury-400 (400 MHz) or on a Varian Inova-600 (600 MHz) spectrometer in [D]chloroform at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. ^{31}P{^{1}H} NMR spectra are referenced externally using 85% H_3PO_4 at δ = 0 ppm. Elemental analyses were performed with an Elementar Vario ELIV instrument. $KPPh_2$ (0.5 M in thf, Aldrich), H_2O_2 (Showa, 30% in H_2O), $Pd(OAc)_2$ (Acros), styrene (Acros), K_3PO_4 (Lancaster), KF (Acros), Cs_2CO_3 (Aldrich), TBAB (TCI) and LiCl (Lancaster) were used as supplied. $PhN{=}C(CMe_2)(NPh)C{=}N(CH_2)_2Cl$ was prepared by the literature method.[3b]

$PhN{=}C^{A}(C^{B}Me_2)(N^{B}Ph)C^{C}{=}N(CH_2)_2PPh_2(C^{A}–N^{B})(C^{B}–C^{C})$ (1): To a flask containing $PhN{=}C(CMe_2)(NPh)C{=}N(CH_2)_2Cl$ (0.583 g, 1.79 mmol) in thf (25 mL) was added $KPPh_2$ (3.6 mL, 0.5 M in thf, 1.79 mmol) at room temperature. After 3 h of stirring, the volatiles were removed under reduced pressure. The residue was triturated with hexane (10 mL), followed by extraction with toluene (10 mL) and washing with hexane (10 mL) to afford a pale-yellow solid. Yield: 0.73 g, 86.0%. ^{1}H NMR (600 MHz): δ = 1.24 [s, 6 H, $C(CH_3)_2$], 2.41 (m, 2 H, CH_2), 3.50 (m, 2 H, CH_2), 6.89 (d, J = 7.2 Hz, 2 H, *o*-Ph), 7.05 (t, J = 7.2 Hz, 1 H, *p*-Ph), 7.12 (t, J = 7.2 Hz, 1 H, *p*-Ph), 7.26 (t, J = 7.8 Hz, 2 H, *m*-Ph), 7.31 (m, 6 H, C*H*-Ph), 7.35 (t, J = 7.8 Hz, 2 H, *m*-Ph), 7.45 (m, 4 H, C*H*-Ph), 8.21 (d, J = 7.8 Hz, 2 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 21.4 [s, $C(CH_3)_2$], 30.9 (d, J_{CP} = 12.2 Hz, CH_2), 45.9 (d, J_{CP} = 23.8 Hz, CH_2), 57.9 [s, $C(CH_3)_2$], 119.4, 121.5, 123.2, 124.3, 128.4 (d, J_{CP} = 6.6 Hz), 128.63, 128.65, 132.68, 132.81 (CH-C_6H_5), 137.2, 138.28, 138.36, 146.8, 157.9 (*tert-C*) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = –18.7 ppm. $C_{31}H_{30}N_3P$ (475.57): calcd. C 78.29, H 6.36, N 8.84; found C 78.28, H 6.32, N 8.89.

$PhN{=}C^{A}(C^{B}Me_2)(N^{B}Ph)C^{C}{=}N(CH_2)_2P(O)Ph_2(C^{A}–N^{B})(C^{B}–C^{C})$ (2): To a flask containing **1** (1.035 g, 2.18 mmol) in thf (20 mL) was added H_2O_2 (0.28 mL, 30% in water, 2.4 mmol) at room temperature. After 2 h of stirring, the reaction mixture was dried with $MgSO_4$ for 1 h. The suspension was filtered, and the filtrate was pumped to dryness to afford an off-white solid. Yield: 0.90 g, 84.0%. ^{1}H NMR (600 MHz): δ = 1.32 [s, 6 H, $C(CH_3)_2$], 2.69 (m, 2 H, CH_2), 3.75 (m, 2 H, CH_2), 6.89 (d, J = 7.2 Hz, 2 H, *o*-Ph), 7.06 (t, J = 7.2 Hz, 1 H, *p*-Ph), 7.12 (t, J = 7.2 Hz, 1 H, *p*-Ph), 7.27 (t, J = 7.8 Hz, 2 H, *m*-Ph), 7.32 (t, J = 7.8 Hz, 2 H, *m*-Ph), 7.44–7.46 (m, 4 H, overlap), 7.50 (m, 2 H, overlap), 7.78 (m, 4 H, overlap), 8.10 (d, J = 7.8 Hz, 2 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 21.3 [s, $C(CH_3)_2$], 32.4 (d, J_{CP} = 69.9 Hz, CH_2), 41.8 (s, CH_2), 58.0 [s, $C(CH_3)_2$], 119.3, 121.4, 123.3, 124.4, 128.58, 128.62, 128.69, 130.69, 130.75, 131.8 (CH-C_6H_5), 132.8, 133.4, 137.1, 146.7, 157.9, 158.7 (*tert-C*) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = 31.9 ppm. $C_{31}H_{30}N_3OP$ (491.57): calcd. C 75.74, H 6.15, N 8.55; found C 74.96, H 5.83, N 8.22.

$[PhN{=}C^{A}(C^{B}Me_2)(N^{B}\text{-}\eta^{1}\text{-}C_6H_4)C^{C}{=}N(CH_2)_2PPh_2(C^{A}–N^{B})(C^{B}–C^{C})]Pd(OAc)$ (3): To a flask containing $Pd(OAc)_2$ (0.45 g, 2.0 mmol) and **1** (0.95 g, 2.0 mmol) was added thf (30 mL) at room temperature. After 18 h of stirring, the volatiles were removed under reduced pressure. The residue was washed with toluene (10 mL) followed by hexane (10 mL) to afford an orange solid. Yield: 1.05 g, 82.0%. ^{1}H NMR (600 MHz): δ = 1.46 [s, 6 H, $C(CH_3)_2$], 1.98 [s, 3 H, $OC(=O)CH_3$], 2.285 (t, J = 6.6 Hz, 1 H, CH_2), 2.296 (t, J = 6.6 Hz, 1 H, CH_2), 3.50 (t, J = 7.2 Hz, 1 H, CH_2), 3.54 (t, J = 6.0 Hz, 1 H, CH_2), 6.95 (d, J = 5.4 Hz, 2 H, C*H*-Ph), 7.10–7.16 (m, 2 H, C*H*-Ph), 7.21 (t, J = 7.8 Hz, 1 H, *p*-Ph), 7.32 (t, J = 8.4 Hz, 2 H, *p*-Ph), 7.44–7.47 (m, 6 H, C*H*-Ph), 7.85 (t, J = 8.4 Hz, 1 H, *p*-Ph), 7.92 (m, 4 H, C*H*-Ph), 8.20 (d, J = 6.0 Hz, 1 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 21.0 [s, $C(CH_3)_2$], 24.0 [s, $OC(=O)CH_3$], 30.5 (d, J_{CP} = 21.9 Hz, CH_2), 50.9 (d, J_{CP} = 13.4 Hz, CH_2), 57.0 [s, $C(CH_3)_3$], 116.6 (d, J_{CP} = 6.0 Hz), 120.9, 124.0, 124.9 (d, J_{CP} = 7.8 Hz), 125.7, 128.80, 128.86, 128.94, 130.8, 133.51, 133.59, 134.8 (CH-C_6H_5), 130.25, 130.48, 131.15, 138.1, 139.0, 145.8, 153.5, 159.0, 176.4 (*tert-C*) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = 29.5 ppm. $C_{33}H_{32}N_3O_2PPd$ (640.02): calcd. C 61.93, H 5.04, N 6.57; found C 61.68, H 4.72, N 6.68.

$\{[PhN{=}C^{A}(C^{B}Me_2)(N^{B}\text{-}\eta^{1}\text{-}C_6H_4)C^{C}{=}N(CH_2)_2P(O)Ph_2(C^{A}–N^{B})\text{-}(C^{B}–C^{C})]Pd(OAc)\}_2$ (4): To a flask containing $Pd(OAc)_2$ (0.33 g, 1.47 mmol) and **2** (0.72 g, 1.47 mmol) was added thf (30 mL) at room temperature. This mixture was heated at reflux for 3 h. The resulting mixture was filtered, and the filtrate was pumped to dryness. The crude product was washed with toluene (15 mL) at 0 °C to afford a grey solid. A second portion of product was isolated by filtering the suspension produced from the addition of hexane to the resulting toluene solution. Yield: 0.73 g, 76.0%. ^{1}H NMR (600 MHz): δ = 1.02 [s, 6 H, $C(CH_3)_2$], 1.24 [s, 6 H, $C(CH_3)_2$], 2.00 [s, 6 H, $OC(=O)CH_3$], 2.07 (m, 2 H, CH_2), 2.84 (m, 2 H, CH_2), 3.00 (m, 2 H, CH_2), 3.48 (m, 2 H, CH_2), 6.60 (m, 2 H, C*H*-Ph), 6.87 (m, 4 H, C*H*-Ph), 6.96 (m, 2 H, C*H*-Ph), 7.05 (m, 2 H, C*H*-Ph), 7.11 (m, 2 H, C*H*-Ph), 7.29 (m, 4 H, C*H*-Ph), 7.40 (m, 4 H, C*H*-Ph), 7.47 (m, 2 H, C*H*-Ph), 7.49 (m, 4 H, C*H*-Ph), 7.57 (m, 2 H, C*H*-Ph), 7.63–7.58 (m, 8 H, C*H*-Ph), 7.99 (m, 2 H, C*H*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 20.69 [s, $C(CH_3)_2$], 20.84 [s, $C(CH_3)_2$], 24.8 [s, $OC(=O)CH_3$], 32.9 (d, J_{CP} = 66.8 Hz, CH_2), 116.2, 120.9, 124.15 (d, J_{CP} = 11.6 Hz), 124.8, 128.6 (m), 128.94, 130.52 (d, J_{CP} = 9.15 Hz), 130.88 (d, J_{CP} = 9.75 Hz), 131.9, 134.5 (CH-C_6H_5), 120.0, 132.59, 132.66, 133.33, 145.4, 154.2, 158.7, 181.4 (*tert-C*) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = 29.8 ppm. $C_{66}H_{64}N_6O_6P_2Pd_2$ (1314.05): calcd. C 60.42, H 4.92, N 6.41; found C 60.15, H 4.54, N 6.12.

$[PhN{=}C^{A}(C^{B}Me_2)(N^{B}\text{-}\eta^{1}\text{-}C_6H_4)C^{C}{=}N(CH_2)_2PPh_2(C^{A}–N^{B})(C^{B}–C^{C})]PdCl$ (5): To a flask containing **3** (0.64 g, 1.0 mmol) and LiCl (0.25 g, 6.0 mmol) was added methanol (20 mL) at room temperature. The reaction mixture was heated at reflux for 3 h. The resulting mixture was filtered, and the filtrate was pumped to dryness. The residue was washed with methanol (10 mL), followed by triturating with hexane (10 mL) to afford a dark green solid. Yield: 0.56 g, 90.0%. ^{1}H NMR (600 MHz): δ = 1.50 [s, 6 H, $C(CH_3)_2$], 2.345 (t, J = 7.8 Hz, 1 H, CH_2), 2.354 (t, J = 7.8 Hz, 1 H, CH_2), 3.67 (t, J = 7.2 Hz, 1 H, CH_2), 3.71 (t, J = 7.2 Hz, 1 H, CH_2), 6.95 (d, J = 7.2 Hz, 2 H, *o*-Ph), 7.13 (t, J = 7.8 Hz, 1 H, *p*-Ph), 7.17 (m, 1 H, C*H*-Ph), 7.21 (m, 1 H, C*H*-Ph), 7.33 (t, J = 7.2 Hz, 2 H, *p*-

Ph), 7.42–7.47 (m, 6 H, C*H*-Ph), 7.93–7.96 (m, 4 H, C*H*-Ph), 8.25 (d, J = 4.8 Hz, 1 H, *o*-Ph), 8.66 (m, 1 H, C*H*-Ph) ppm. ^{13}C{^{1}H} NMR (150 MHz): δ = 21.1 [s, C(CH$_3$)$_2$], 29.7 (d, J_{CP} = 22.5 Hz, CH$_2$), 52.0 (d, J_{CP} = 13.95 Hz, CH$_2$), 57.0 [s, C(CH$_3$)$_3$], 116.8 (d, J_{CP} = 6.6 Hz), 120.9, 124.0, 125.1 (d, J_{CP} = 7.2 Hz), 125.7, 128.91, 128.97, 131.0, 133.39, 133.47, 137.8 (CH-C_6H$_5$), 129.67, 129.91, 131.45, 139.2, 140.1, 145.7, 153.5, 159.1 (*tert-C*) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ = 31.1 ppm. $C_{31}H_{29}ClN_3PPd$ (616.34): calcd. C 60.40, H 4.74, N 6.82; found C 59.99, H 4.25, N 6.98.

General Procedure for the Suzuki-Type Coupling Reaction: A prescribed amount of catalyst, base (2 equiv.), phenylboronic acid (1.5 equiv.), and aryl halides (1 equiv., solids) were placed in a Schlenk tube under nitrogen. The solvent (2 mL) and aryl halides (1 equiv., liquids) were added by syringe, and the reaction mixture was heated to the prescribed temperature for the prescribed time.

General Procedure for the Heck Reaction: A prescribed amount of catalyst, base (1.5 equiv.) and aryl halides (1 equiv., solids) were placed in a Schlenk tube under nitrogen. The solvent (2 mL), styrene (1.3 equiv.) and aryl halides (1 equiv., liquids) were added by syringe, and the reaction mixture was heated to the prescribed temperature for the prescribed time.

Crystal Structure Data: Crystals were grown from a thf/hexane solution (**3** or **4**) or a CH_2Cl_2/hexane solution (**5**) and isolated by filtration. Suitable crystals of **3**, **4** or **5** were sealed in thin-walled glass capillaries under nitrogen and mounted on a Bruker AXS SMART 1000 diffractometer. The absorption correction was based on the symmetry equivalent reflections by using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed by using the structure solution. The structure was solved by direct methods with a SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined by using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 3. CCDC-661014, -661015, -661016 for compounds **3**–**5** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Summary of crystal data for compounds **3**–**5**.

	3	**4**	**5**
Formula	$PdC_{33}H_{33}N_3O_2P$	$Pd_4C_{132}H_{128}N_{12}O_{12}P_4$	$PdC_{31}H_{29}ClN_3P$
F_w	640.99	2623.94	616.39
T [K]	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$	$P2_1/c$
a [Å]	14.7944(11)	19.3975(12)	15.7977(11)
b [Å]	10.4423(8)	13.6855(9)	12.1228(8)
c [Å]	19.4410(15)	24.7493(16)	14.9392(10)
α [°]	90	90	90
β [°]	94.4190(10)	110.2110(10)	105.6600(10)
γ [°]	90	90	90
V [Å^3]	2994.5(4)	6165.5(7)	2754.8(3)
Z	4	2	4
$\rho_{calcd.}$ [Mg/m^3]	1.422	1.413	1.486
μ(Mo-K_α) [mm^{-1}]	0.707	0.691	0.854
Reflections collected	16331	34883	14978
No. of parameters	379	1477	324
R_1[a]	0.0276	0.0295	0.0283
wR_2[a]	0.0863	0.0594	0.1047
GoF[b]	1.010	0.999	0.999

[a] $R_1 = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$; w = 0.10. [b] GoF = $[\Sigma w(F_o{}^2 - F_c{}^2)^2/(N_{\text{rflns}} - N_{\text{params}})]^{1/2}$.

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