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FULL PAPER

A series of (NHC)Pd(N^O)(OAc) complexes: synthesis, characterization and catalytic activities towards desulfinative Sonogashira coupling of arylsulfonyl hydrazides with arylalkynes

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A series of well-defined *N*-heterocyclic carbene palladium (II) complexes with general formula (NHC)Pd(N^O)(OAc) were prepared through reaction of Pd(NHC)$(OAc)_2(H_2O)$ with 1-methyl-1*H*-pyrazole-3-carboxylic acid or 1-methyl-1*H*-indazole-3-carboxylic acid in the presence of K_2CO_3. These complexes were then used for desulfinative Sonogashira coupling of arylsulfonyl hydrazides with terminal alkynes. With low catalyst loading, all synthesized palladium compounds exhibited moderate to high catalytic activities for the reactions.

KEYWORDS
Arylsulfonyl hydrazides, NHC–Pd complexes, Sonogashira coupling

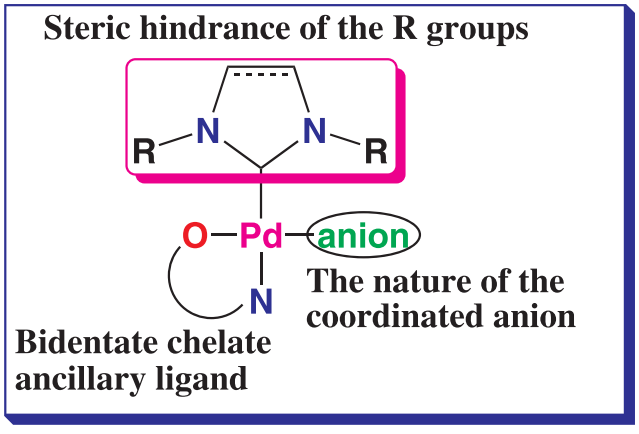
1 | INTRODUCTION

Internal alkynes are important structural units found in bioactive compounds and functional materials, which could be further transformed into multi-functionalized compounds.[1] Recent years, the Pd-catalyzed Sonogashira coupling reaction of terminal alkynes with aryl halides, has represented a convenient access to internal alkynes.[2] Significant efforts have been devoted to the development of efficient Pd-precatalysts for Sonogashira coupling reactions and a series of Pd catalytic systems have been well-established.[3] Although the palladium-catalyzed Sonogashira coupling reactions of terminal alkynes with aryl halides have left an impact in every area of chemistry, the development of air-stable, readily available, and inexpensive arylating reagents that circumvent the need for the aryl halides is still in high demand. Recently, Dong and Zhou have employed arylsulfonyl hydrazides as the aryl sources in Sonogashira coupling reaction *via* desulfitation processes, which avoided the traditionally aryl halides as the aryl sources.[4] Chang has reported decarboxylative-desulfinative coupling of alkynyl carboxylic acids with arylsulfonyl hydrazides.[5] Additionally, the use of sulfonates directly as coupling partners in related reactions has been fully reported.[6]

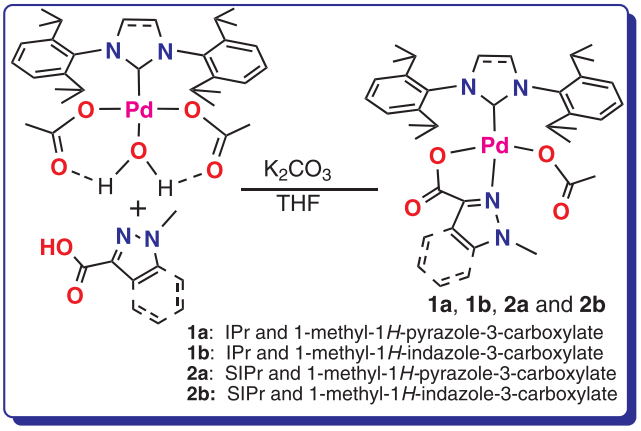
As is well known, high catalyst loading, toxic and air-sensitive phosphanes were commonly used as the ancillary ligands in the Pd-precatalysts for this transformation. Accordingly, Pd-complexes overcoming these limitations are highly desirable. *N*-Heterocyclic carbenes (NHCs) have received increasing attention after their isolation and characterization by Arduengo.[7] Over the past three decades, the use of NHCs as functional ligands in Pd-catalyzed coupling reactions has remained a perennial concern.[8] A number of structurally diverse NHC–Pd complexes have been synthesized and characterized.[9] Due to stronger σ-donor properties of NHCs, the well-defined NHC–Pd complexes have shown considerable catalytic activities in Pd-catalyzed coupling reactions

relative to the phosphane/Pd systems.[10] Generally, the well-defined NHC–Pd complexes usually consist of a 1:1 ratio of Pd/NHC which could easily form the active [NHC–Pd^0] species.[11] Studies have suggested that the catalytic activities of NHC–Pd complexes related substantially to the steric hindrance of the *N*-substituents in NHC backbone.[12] Meanwhile, ancillary ligands around the Pd centres also play an important role to their catalytic performance. For example, since Organ first reported the pyridine stabilized NHC–Pd complexes (Pd-PEPPSI-NHC), which demonstrated high activity towards C–C coupling reactions, a great number of *N*-donors were introduced into the coordination with the NHC–Pd units.[13] The different electron donating ability of the *N*-donors certainly influenced their coordination with the Pd centre, which played a fine-tuning role on the catalytic activities.[13b, d] Besides the monodentate *N*-donors, a series of bidentate N^O ligands assisted NHC–Pd complex have also been synthesized and showed high activities towards Pd-catalyzed reactions.[14] As shown in the scheme 1, the former researches mainly concentrated on the modification of the well-defined NHC–Pd complexes with the ancillary ligands, whereas less attention was paid to the coordination of the anions. The coordinated anions can also affect the structures and activities of the well-defined NHC–Pd complexes to some degree.

As part of our ongoing project aimed to explore new types of well-defined NHC–Pd complexes, we envision incorporation of 1-methyl-1*H*-pyrazole-3-carboxylate and 1-methyl-1*H*-indazole-3-carboxylate into the [Pd (NHC)$(OAc)_2(H_2O)$] complexes to form a new class of (NHC)Pd(N^O)(OAc) complexes (Scheme 2). The application of these well-defined NHC-Pd complexes in desulfinative Sonogashira coupling of arylsulfonyl hydrazides with terminal alkynes for the synthesis of internal alkynes was investigated.



SCHEME 1 Modification strategy of the well-defined NHC–Pd complexes



SCHEME 2 Synthesis of the well-defined (NHC)Pd(NO)(OAc) complexes **1a**, **1b**, **2a** and **2b**

2 | RESULTS AND DISCUSSION

Synthesis and characterization of the well-defined (NHC)Pd(N^O)(OAc) complexes.

The (NHC)Pd(N^O)(OAc) complexes (**1a**, **1b**, **2a** and **2b**) were synthesized by reaction of [Pd (NHC)$(OAc)_2(H_2O)$] with an equivalent amount of 1-methyl-1*H*-pyrazole-3-carboxylic acid or 1-methyl-1*H*-indazole-3-carboxylic acid in the presence of K_2CO_3, the desired (NHC)Pd(N^O)(OAc) complexes (**1a**, **1b**, **2a** and **2b**) could be obtained in satisfied yields. In order to completely explore the structural features and catalytic activities of the complexes, herein, the unsaturated and saturated carbene ligands (IPr and SIPr) were all investigated. The structures of all four complexes were fully characterized by means of ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, HRMS and X-ray single-crystal diffraction analyses. The formation of the well-defined NHC-Pd complexes is evident according to the stoichiometric proton signal resonances of NHCs and the ancillary ligands in the ^{1}H NMR spectra. Furthermore, the ^{13}C NMR spectra displayed typical carbene and carbonyl carbon resonances. HRMS analysis confirms the assignment of the complexes by showing their [M–OAc$^-$]$^+$ fragments.

X-ray crystal structures of the obtained complexes.

Suitable crystals of the complexes for single-crystal X-ray diffraction analyses were obtained by diffusion of *n*-hexane into their dichloromethane solution (Table S1). As shown in Figure 1, all complexes were mononuclear structures with each Pd-centers was coordinated by an NHC, a N^O bidentate chelate ligand and an acetate anion, which showed a slightly distorted square plane geometry. In agreement with the common N^O ligands assisted NHC–Pd complexes, the neutral σ-donating nitrogen atoms located *trans* to the NHCs, while the carboxylate oxygen anions are situated in the *cis* position to

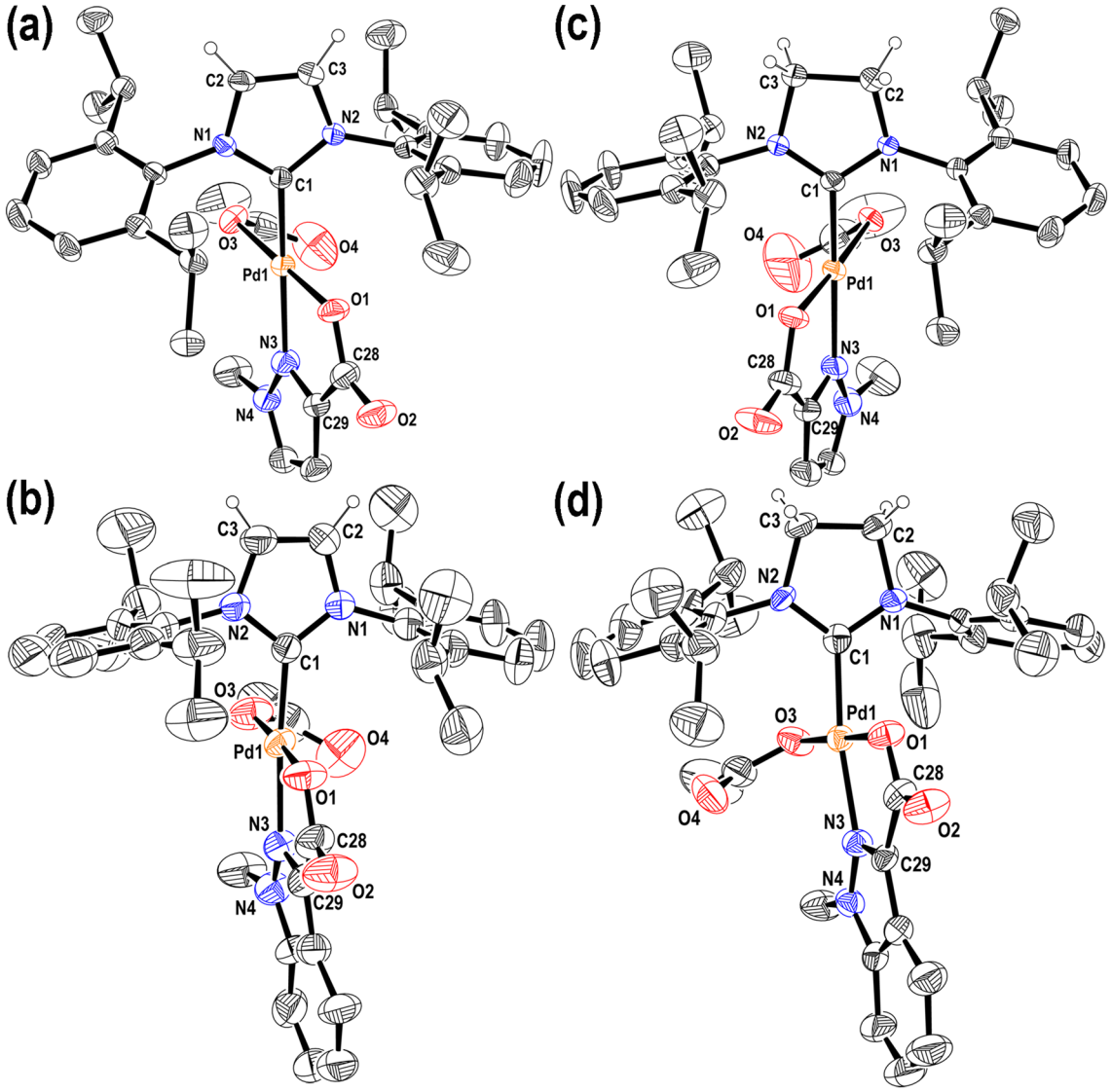


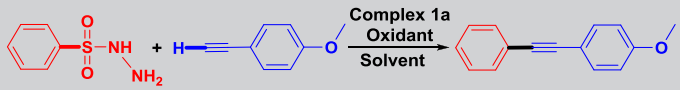
FIGURE 1 ORTEP diagrams of **1a**•CH2Cl2, **1b**•solvent, **2a**•2H2O and **2b** with thermal displacement parameters drawn at 30% probability. Parts of the hydrogen atoms and solvent molecules have been omitted for clarity. There are two independent molecules in a unit cell of (**1b**•solvent)2, only one molecule was shown

the NHCs. The fourth coordination-site of the Pd centers is occupied by the acetate which was in a direction opposite the carboxylate. The $PdCNO_2$ coordination planes are approximately coplanar with the five-membered chelate rings PdC_2NO and the pyrazole (indazole) planes, but are twisted from the carbene ring planes with dihedral angles ranging from 68.74 to 87.04° respectively. As usual in NHC-bearing complexes, the Pd–$C_{carbene}$ distances fall in a range of single bonds [1.947(6)–1.962(6) Å], but were significantly shorter than that in the related complex (IPr)Pd (pyridine-2,6-dicarboxylate) [2.005(2) Å]. Furthermore, the Pd–N bond distances are in a range of 2.087(6)–2.101(7) Å, which were slightly longer than that in (IPr)Pd (pyridine-2,6-dicarboxylate) [1.9430(18) Å]. The Pd–O bond lengths [1.971(6)–2.208(4) Å] are similar to those found in related complexes.[14a]

2.1 | Catalytic investigation

With the obtained well-defined NHC–Pd complexes, their catalytic activities in desulfinative Sonogashira coupling reaction were investigated. As previously reported in the literature, Cu $(OAc)_2$ as the oxidant and DMF as the solvent was the best choice for the reaction.[4] Therefore, we initially probed the efficacy of complex **1a** as the catalyst in desulfinative Sonogashira coupling with Cu $(OAc)_2$ as the oxidant and DMF as the solvent (Table 1). Fortunately, complex **1a** successfully carried out the

TABLE 1 Optimization of the reaction conditions for complex 1a[a,b]



Entry	Catalyst	Oxidant	Solvent	Yield(%)[b]
1	**1a** (1%)	$Cu(OAc)_2$	DMF	62
2	-	$Cu(OAc)_2$	DMF	0
3	**1a** (1%)	-	DMF	0
4	**1a** (2%)	$Cu(OAc)_2$	DMF	80
5	**1a** (4%)	$Cu(OAc)_2$	DMF	85
6	**1a** (2%)	$Cu(OAc)_2$	DMAc	68
7	**1a** (2%)	$Cu(OAc)_2$	DMSO	32
8	**1a** (2%)	$Cu(OAc)_2$	THF	trace
9	**1a** (2%)	$Cu(OAc)_2$	CH_3CN	trace
10[c]	**1a** (2%)	$Cu(OAc)_2$	DMF	84
11[d]	**1a** (2%)	$Cu(OAc)_2$	DMF	78
12[e]	**1a** (2%)	$Cu(OAc)_2$	DMF	62
13[f]	**1a** (2%)	$Cu(OAc)_2$	DMF	42
14	**1a** (2%)	O_2	DMF	trace
15	**1a** (2%)	$K_2S_2O_8$	DMF	trace
16	**1a** (2%)	Ag_2CO_3	DMF	trace
17	**1a** (2%)	$CuCl_2$	DMF	trace
18	**1a** (2%)	$CuBr_2$	DMF	trace
19	**1a** (2%)	Cu_2O	DMF	20
20[g]	**1a** (2%)	$Cu(OAc)_2$	DMF	84

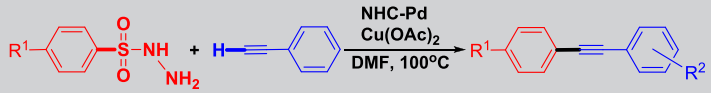
[a]Reaction conditions: benzenesulfonyl hydrazide (0.5 mmol, 86 mg), 4-methoxyphenylacetylene (0.75 mmol, 100 mg), complex **1a** (0.01 mmol, 6.8 mg), $Cu(OAc)_2$ (1.0 mmol, 182 mg), solvent (4.0 ml) at 100 °C for 4 hr.
[b]Isolated yield.
[c]Performed for 6 hr.
[d]Performed at 120 °C.
[e]Performed at 80 °C.
[f]With 1.0 equiv of $Cu(OAc)_2$ (0.5 mmol)
[g]Under nitrogen atmosphere.

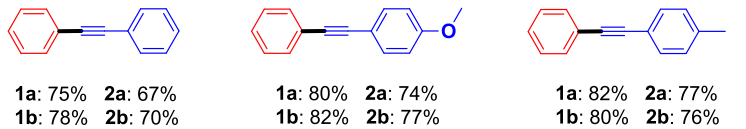
desulfinative Sonogashira coupling of benzenesulfonyl hydrazide with 4-methoxyphenylacetylene giving the desired internal alkyne (Entry 1) and no reaction occurred in the absence of either catalyst or oxidant (Entries 2 and 3). Further evaluation of the conditions for the reaction involved the screening of the catalyst loading, reaction temperature and solvent. An increase in the amount of the catalyst loading employed from 1.0% to 2.0% led to a substantial increase in product yield (Entry 4). However, further increases in the amount of the catalyst loading proved a slightly increase of the yield (Entry 5). The effect of solvents was then investigated and the solvent also played an important role in the coupling reaction. Changing the solvent from DMF to DMAc could be employed with only minor reductions in yield. Meanwhile, other polar aprotic solvents such as DMSO, CH_3CN and THF led to significant reduction in yields (Entries 6–9). On the basis of the screening, 2.0 mol % complex **1a** at 100 °C for 4 hr, thus giving the optimal coupling result. Further prolonging the reaction time to 6 hr could not improve the catalytic performance. To further examine the influence of the reaction temperature, coupling reactions between benzenesulfonyl hydrazide and 4-methoxyphenylacetylene as models with complex **1a** at 2.0 mol % catalyst loading in different reaction temperature were carried out for temperature–conversion study (Figure S1). It's worth noting that the reaction was sensitive to the reaction temperature. Benzenesulfonyl

hydrazide would undergo loss of N_2 and SO_2 gas at 100 °C to generate the aryl source and further increase in reaction temperature proved detrimental. The oxidant proved to be critical for coupling reaction to occur. Among the various oxidants examined, the Cu $(OAc)_2$ (2.0 equiv) gave the best results. The use of less amount of Cu $(OAc)_2$ substantially reduced the yield. Moreover, the use of other oxidants and additives such as molecular oxygen, $K_2S_2O_8$, Ag_2CO_3, $CuCl_2$, $CuBr_2$ and Cu_2O were examined for this direct reaction, and 2.0 equiv. of Cu $(OAc)_2$ displayed the highest reactivity. Molecular oxygen, $K_2S_2O_8$, Ag_2CO_3, $CuCl_2$, $CuBr_2$ were ineffective in the reaction and did not yield any coupling product. Cu_2O were no longer the effective additives in the reaction and only about 20% yield of the product was achieved (Entries 14–19). Herein, the desulfitative oxidation of arylsulfonyl hydrazide was indeed a copper-mediated process. Moreover, the model reaction was performed in the presence of a nitrogen atmosphere, complex **1a** showed a slightly better performance of the reaction as that in air atmosphere. The use of nitrogen atmosphere seems to be not the necessary conditions for the precatalyst reported herein.

With the optimized reaction conditions in hand, we next tested the scope of arylacetylenes (Table 2). As expected, phenylacetylene and phenylacetylenes with a

TABLE 2 Desulfinative Sonogashira coupling of arylsulfonyl hydrazides with alkynes[a,b]

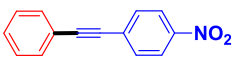




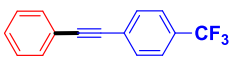
1a: 75% **2a**: 67%
1b: 78% **2b**: 70%

1a: 80% **2a**: 74%
1b: 82% **2b**: 77%

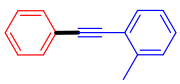
1a: 82% **2a**: 77%
1b: 80% **2b**: 76%



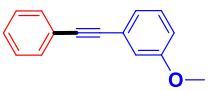
1a: 80% **2a**: 72%
1b: 80% **2b**: 75%



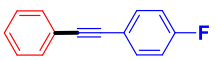
1a: 75% **2a**: 72%
1b: 78% **2b**: 70%



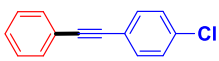
1a: 72% **2a**: 66%
1b: 74% **2b**: 70%



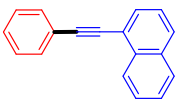
1a: 80% **2a**: 75%
1b: 78% **2b**: 72%



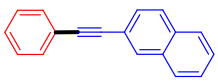
1a: 82% **2a**: 77%
1b: 84% **2b**: 79%



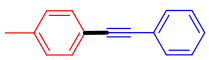
1a: 85% **2a**: 80%
1b: 85% **2b**: 78%



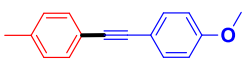
1a: 77% **2a**: 66%
1b: 75% **2b**: 68%



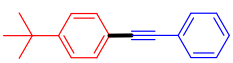
1a: 86% **2a**: 80%
1b: 86% **2b**: 82%



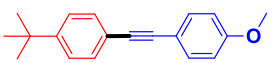
1a: 80% **2a**: 75%
1b: 80% **2b**: 75%



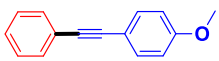
1a: 85% **2a**: 80%
1b: 82% **2b**: 78%



1a: 82% **2a**: 78%
1b: 82% **2b**: 75%



1a: 87% **2a**: 80%
1b: 85% **2b**: 80%



Pd(IPr)(OAc)$_2$(H$_2$O): 63%
Pd(SIPr)(OAc)$_2$(H$_2$O): 58%

[a]Reaction conditions: alkynes (0.5 mmol), arylsulfonyl hydrazides (0.75 mmol), [NHC − Pd] (0.01 mmol), Cu $(OAc)_2$ (1.0 mmol, 2.0 equiv), DMF (4.0 ml), 100 °C, 4 hr.
[b]Isolated yields.

series of electron-donating and withdrawing substituted groups, such as methoxy, methyl, nitro and trifluoromethyl were compatible under this procedure, and the products were isolated in good yields. Encouraged by these promising results, we further applied the optimized reaction conditions to examine the substrate scope of arylacetylenes with halogen substituents. Gratifyingly, fluoro and chloro groups functionalities on the phenyl ring of phenylacetylenes, also afforded the desired products in good yields. Moreover, the coupling reaction of sterically hindered 2-methylphenylacetylene and 3-methoxyphenylacetylene with benzenesulfonyl hydrazide proceeded smoothly and moderate product yields were observed. The coupling reactions could be extended to naphthylacetylenes, and therefore, the coupling products between 1-naphthylacetylene and 2-naphthylacetylene with benzenesulfonyl hydrazide was achieved. Apart from benzenesulfonyl hydrazide, other arylsulfonyl hydrazides were applicable. 4-Methyl and 4-(*tert*-butyl) substituted benzenesulfonyl hydrazide could be applied in this catalytic system and are able to undergo the coupling reactions smoothly with phenylacetylene and 4-methoxyphenylacetylene, respectively, which generated the corresponding products in good yields.

Besides, by the horizontal comparison of these four complexes, under our test conditions, it is clear that unsaturated NHC–Pd complexes **1a** and **2a** demonstrated higher catalytic activities than their saturated analogues **1b** and **2b** in all cases. We still do not have a satisfactory interpretation for this anomalous result. The saturated NHC − Pd complexes are commonly more effective than their corresponding unsaturated analogues due to the greater steric demand of the saturated ligands,[15] but there were still some exceptions.[16] Finally, the comparison of the catalytic activities between the obtained Pd-complexes with the reactants [Pd (NHC) $(OAc)_2(H_2O)$] was also investigated under the same conditions. All reactions were carried out in the presence of 2.0 mol% catalyst loading and 2.0 equiv of Cu $(OAc)_2$, using benzenesulfonyl hydrazide and 4-methoxyphenylacetylene as the substrates. As shown in Table 2, the well-defined NHC − Pd complexes showed higher catalytic activities when compared to the [Pd (NHC)$(OAc)_2(H_2O)$] complexes. The fact was reasoned to be due to the dissociation and recoordination of the ancillary ligands in the heteroleptic NHC − Pd complexes easily form and stabilize the active [NHC–Pd^0] species, which might be beneficial for improving the catalytic performance. Meanwhile, as ancillary ligands (1-methyl-1*H*-pyrazole-3-carboxylate and 1-methyl-1*H*-indazole-3-carboxylate), there seems to be little difference in catalytic activities between the two kinds of catalytic systems due to the same coordination abilities of the N^O donors to the Pd-centres. Although the product yields and reaction time of our catalytic system did not have distinctive advantage in comparation to the related literature, our system also showed an improvement of the reaction conditions, as it can be done with low catalyst loading (2.0 mol%) and without using the phosphorus ligands.

3 | CONCLUSIONS

In summary, we have prepared a new class of (NHC) Pd(N^O)(OAc) complexes *via* incorporating (NHC) Pd(N^O)(OAc) complexes with 1-methyl-1*H*-pyrazole-3-carboxylic acid or 1-methyl-1*H*-indazole-3-carboxylic acid. The obtained complexes exhibited good catalytic activities in desulfinative Sonogashira coupling of arylsulfonyl hydrazides with arylalkynes. This protocol offers a new Pd-catalyzed system for accessing various internal alkynes with good yields and is a complement to the traditional Sonogashira coupling reactions. Further studies aimed at exploring the activity of these NHC–Pd catalysts are currently ongoing in our laboratories.

4 | EXPERIMENTAL

4.1 | General remarks

The chemicals were purchased from commercial suppliers and were used without further purification. NMR spectra were recorded at 400 or 600 MHz (for ^{1}H NMR) and 100 or 150 MHz (for ^{13}C NMR) on Bruker Avance NMR spectrometers. ^{1}H, and ^{13}C NMR were performed in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. The C, H, and N analyses were performed with a Vario El III elementar. Flash column chromatography was carried out using 300–400 mesh silica gel. The requisite [Pd (NHC)$(OAc)_2(H_2O)$] were prepared according to the report in the literature.[17]

4.2 | Synthesis of complexes 1a, 1b, 2a and 2b

A mixture of the complex [Pd (NHC)$(OAc)_2(H_2O)$] (1.0 mmol, 630 mg), 1-methyl-1*H*-pyrazole-3-carboxylic acid or 1-methyl-1*H*-indazole-3-carboxylic acid (1.0 mmol) and K_2CO_3 (1.2 mmol, 165 mg) were dissolved in THF (10.0 ml). After stirring for 12 hr at 50 °C, the reaction mixture was purified by flash column

chromatography on short silica gel with THF as eluent, the residue was reduced under vacuum and recrystallized from *n*-hexane/CH_2Cl_2 solutions to afford the products.

4.3 | [(IPr)Pd(1-methyl-1*H*-pyrazole-3-carboxylate)(OAc)] (1a)

The procedure yielded 510 mg (75%) of the pure complex **1a** as a yellow powder. M.p.: 198 °C (decomposed). ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 7.51 (t, J = 7.8 Hz, 2H, *p*-C*H*-phenyl), 7.36 (d, J = 7.8 Hz, 4H, *m*-C*H*-phenyl), 7.15 (s, 2H, NC*H*=C*H*N), 7.06 (d, J = 2.4 Hz, 1H, C*H*-pyrazole), 6.41 (d, J = 2.4 Hz, 1H, C*H*-pyrazole), 3.48 (s, 3H, N-CH_3), 2.81 (sept, J = 6.6 Hz, 4H, C*H* (CH_3)$_2$), 1.70 (s, 3H, CH_3COO$^-$), 1.38 (d, J = 7.2 Hz, 12H, CH (CH_3)$_2$), 1.10 (d, J = 6.6 Hz, 12H, CH (CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm): 177.28 (CH_3*C*OO$^-$), 168.76 (pyrazole-*C*OO$^-$), 153.74 ($C_{carbene}$), 148.22 (pyrazole-N=*C*), 146.52 (N-$C_{aniline}$), 134.49 (*o*-$C_{aniline}$), 132.74 (pyrazole-*C*-N-CH_3), 130.36 (*p*-$C_{aniline}$), 125.10 (NC*H*=*C*HN), 124.08 (*m*-$C_{aniline}$), 106.78 (pyrazole-*C*=C-N-CH_3), 37.52 (N-*C*H_3), 28.47 (*C*H (CH_3)$_2$), 26.09 (CH (*C*H_3)$_2$), 23.12 (*C*H_3COO$^-$), 22.76 (CH (*C*H_3)$_2$). HR-MS (ESI): calcd for $C_{32}H_{41}N_4O_2Pd$ [M–OAc$^-$]$^+$ 619.2264; found 619.2279. Calcd. for (IPr) Pd(1-methyl-1*H*-pyrazole-3-carboxylate)(OAc) ($C_{34}H_{44}N_4O_4Pd$): C, 60.13; H, 6.53; N, 8.25%. Found: C, 60.39; H, 6.81; N, 8.52%.

4.4 | [(IPr)Pd(1-methyl-1*H*-indazole-3-carboxylate)(OAc)] (1b)

The procedure yielded 560 mg (77%) of the pure complex **2a** as a yellow powder. M.p.: 233 °C (decomposed). ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.15 (d, J = 8.4 Hz, 1H, C*H*-indazole), 7.50 (t, J = 7.8 Hz, 2H, *p*-C*H*-phenyl), 7.37 (d, J = 7.8 Hz, 4H, *m*-C*H*-phenyl), 7.18 (s, 2H, NC*H*=C*H*N), 7.17–7.14 (m, 3H, C*H*-indazole), 3.66 (s, 3H, N-CH_3), 2.89 (sept, J = 6.6 Hz, 4H, C*H* (CH_3)$_2$), 1.75 (s, 3H, CH_3COO$^-$), 1.44 (d, J = 6.4 Hz, 12H, CH (CH_3)$_2$), 1.14 (d, J = 6.6 Hz, 12H, CH (CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm): 177.22 (CH_3*C*OO$^-$), 169.18 (*C*OO$^-$-indazole), 153.54 ($C_{carbene}$), 146.49 (N-$C_{aniline}$), 140.71 (indazole-N=*C*), 139.70 (indazole-*C*-N-CH_3), 134.47 (*o*-$C_{aniline}$), 130.38 (*p*-$C_{aniline}$), 128.62 ($C_{indazole}$), 125.06 (NC*H*=*C*HN), 124.10 (*m*-$C_{aniline}$), 123.06 ($C_{indazole}$), 122.10 ($C_{indazole}$), 120.80 ($C_{indazole}$), 108.81 ($C_{indazole}$), 33.88 (N-*C*H_3), 28.57 (*C*H (CH_3)$_2$), 26.15 (CH (*C*H_3)$_2$), 23.16 (*C*H_3COO$^-$), 22.83 (CH (*C*H_3)$_2$). HR-MS (ESI): calcd for $C_{36}H_{43}N_4O_2Pd$ [M–OAc$^-$]$^+$ 669.2421; found 669.2437. Calcd. for (IPr) Pd(1-methyl-1*H*-indazole-3-carboxylate)(OAc) ($C_{38}H_{46}N_4O_4Pd$): C, 62.59; H, 6.36; N, 7.68%. Found: C, 62.87; H, 6.62; N, 7.41%.

4.5 | [(SIPr)Pd(1-methyl-1*H*-pyrazole-3-carboxylate)(OAc)] (2a)

The procedure yielded 480 mg (70%) of the pure complex **2a** as a yellow powder. M.p.: 193 °C (decomposed). ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 7.43 (t, J = 7.8 Hz, 2H, *p*-C*H*-phenyl), 7.31 (d, J = 7.8 Hz, 4H, *m*-C*H*-phenyl), 7.06 (d, J = 2.4 Hz, 1H, C*H*-pyrazole), 6.44 (d, J = 2.4 Hz, 1H, C*H*-pyrazole), 4.07 (s, 4H, N-CH_2CH_2-N), 3.46 (s, 3H, N-CH_3), 3.35 (br, 4H, C*H* (CH_3)$_2$), 1.60 (s, 3H, CH_3COO$^-$), 1.46 (d, J = 6.6 Hz, 12H, CH (CH_3)$_2$), 1.26 (d, J = 7.2 Hz, 12H, CH (CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm): 184.80 ($C_{carbene}$), 176.46 (CH_3*C*OO$^-$), 168.99 (pyazole-*C*OO$^-$), 147.98 (pyrazole-N=*C*), 147.44 (N-$C_{aniline}$), 134.55 (*o*-$C_{aniline}$), 132.58 (pyrazole-*C*-N-CH_3), 129.45 (*p*-$C_{aniline}$), 124.60 (*m*-$C_{aniline}$), 106.84 (pyrazole-*C*=C-N-CH_3), 53.56 (N-*C*H_2CH_2-N), 37.51 (N-*C*H_3), 28.59 (*C*H (CH_3)$_2$), 26.38 (CH (*C*H_3)$_2$), 23.64 (CH (*C*H_3)$_2$), 23.16 (*C*H_3COO$^-$). HR-MS (ESI): calcd for $C_{32}H_{43}N_4O_2Pd$ [M–OAc$^-$]$^+$ 621.2421; found 621.2433. Calcd. for (SIPr)Pd(1-methyl-1*H*-pyrazole-3-carboxylate) (OAc) ($C_{34}H_{46}N_4O_4Pd$): C, 59.95; H, 6.81; N, 8.23%. Found: C, 60.22; H, 6.97; N, 8.50%.

4.6 | [(SIPr)Pd(1-methyl-1*H*-indazole-3-carboxylate)(OAc)] (2b)

The procedure yielded 530 mg (72%) of the pure complex **2b** as a yellow powder. M.p. 210 °C (decomposed). ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm): 8.18 (d, J = 8.4 Hz, 1H, C*H*-indazole), 7.40 (t, J = 7.8 Hz, 2H, *p*-C*H*-phenyl), 7.38 (t, J = 7.2 Hz, 1H, C*H*-indazole), 7.30 (d, J = 7.8 Hz, 4H, *m*-C*H*-phenyl), 7.20–7.17 (m, 2H, C*H*-indazole), 4.11 (s, 4H, N-CH_2CH_2-N), 3.66 (s, 3H, N-CH_3), 3.41 (sept, J = 6.6 Hz, 4H, C*H* (CH_3)$_2$), 1.65 (s, 3H, CH_3COO$^-$), 1.52 (d, J = 6.0 Hz, 12H, CH (CH_3)$_2$), 1.28 (d, J = 6.6 Hz, 12H, CH (CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm): 184.33 ($C_{carbene}$), 176.42 (CH_3*C*OO$^-$), 169.30 (indazole-*C*OO$^-$), 147.39 (N-$C_{aniline}$), 140.70 (indazole-N=*C*), 139.46 (indazole-*C*-N-CH_3), 134.52 (*o*-$C_{aniline}$), 129.44 (*p*-$C_{aniline}$), 128.55 ($C_{indazole}$), 124.60 (*m*-$C_{aniline}$), 123.05 ($C_{indazole}$), 122.23 ($C_{indazole}$), 120.84 ($C_{indazole}$), 108.85 ($C_{indazole}$), 53.64 (N-*C*H_2CH_2-N), 33.95 (N-*C*H_3), 28.66 (*C*H (CH_3)$_2$), 26.46 (CH (*C*H_3)$_2$), 23.71 (CH (*C*H_3)$_2$), 23.14 (*C*H_3COO$^-$). HR-MS (ESI): calcd for $C_{36}H_{45}N_4O_2Pd$ [M–OAc$^-$]$^+$ 671.2577; found 671.2591. Calcd. for (IPr)Pd(1-methyl-1*H*-indazole-3-carboxylate)(OAc) ($C_{38}H_{46}N_4O_4Pd$): C,

62.42; H, 6.62; N, 7.66%. Found: C, 62.70; H, 6.88; N, 7.38%.

4.7 | General procedure for NHC–Pd catalyzed desulfinative Sonogashira coupling of arylsulfonyl hydrazides with aryl alkynes

A sealable reaction tube with a magnetic stirring bar was charged with arylsulfonyl hydrazide (0.50 mmol), terminal alkyne (0.75 mmol), Cu $(OAc)_2$ (1.0 mmol, 182 mg), NHC–Pd catalyst (0.01 mmol, 6.8 mg for **1a**, **2a** and 7.3 mg for **1b**, **2b**), and DMF (4.0 ml). The reaction mixture was stirred at 100 °C for 4 hr. After cooling to room temperature, EtOAc (ca. 10 ml) and H_2O (ca. 10 ml) were added to the reaction vial, the crude product in the organic layer was extracted, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The desired product was isolated by column chromatography over silica gel to afford the products.

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