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A highly efficient memantine-modified palladium catalyst for Suzuki–Miyaura cross-coupling reaction

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ABSTRACT

A new simple Pd(memantine)$_2$Cl$_2$ complex was synthesized and characterized by ^{1}H NMR, ^{13}C NMR and X-ray single crystal structure determination. The Suzuki–Miyaura reaction of aryl bromides catalyzed by Pd(memantine)$_2$Cl$_2$ complex was investigated in air with different temperature. The high turnover numbers of 650,000 have been obtained in the reaction of 4-bromonitrobenzene with phenylboronic acid at 80 °C. At room temperature, the complex also showed high activity for Suzuki–Miyaura cross-coupling reaction of aryl bromides with a wide range of functional groups under air, and the turnover number of up to 99,000 was achieved. The catalytic system also gives good yields toward the reaction of several heteroaryl bromides with thiophenylboronic acid.

1. Introduction

Palladium-catalyzed C–C bond forming reactions continues to be the most important method to synthesize the biaryls,[1,2] which are ubiquitous motifs found in conducting polymers,[3] bioactive compounds,[4] catalyst ligands,[5] and natural products.[6] Among these reactions, the Suzuki–Miyaura cross-coupling reaction have received extensive attention due to the advantages, such as a good functional group tolerance, mild reaction conditions, and easy handling of by-products.[7] In general, an active and selective Suzuki reaction catalyst could be achieved by using an appropriate supporting ligand[8] and the phosphines have proved to be the most common[9] and efficient ligands.[10] However, the phosphorous-based ligands are often air- and/or moisture-sensitive, hence require an inert-atmosphere technology during operation, and in some cases, it was plagued by the degradation caused by P–C bond cleavage.[11] To address these problems, many non-phosphorous C- or N-based ligands have been developed.[12–15] Particularly, given the fact that the atoms N and P are in the same column of Periodic Table, the N-based ligand exhibited similar properties with the P-based ligand to some extent, but relatively insensitive to air and moisture. Therefore, in the past decades, the N-type ligands including aryl-2-oxazolines,[8] aryloximes,[16] arylimines,[17] and diazabutadine derivatives,[18] pyridine-piperidine bidentate ligands[19] and so on have been extensively explored in this reaction as an alternative to phosphine. In most cases, a high active catalyst could be achieved. For example, an oxime-derived palladacycle (containing a N-donor) proved to be a high efficient Suzuki–Miyaura coupling reaction catalyst for challenging substrate arylchloride, which can enable a set of (hetero) aryl chlorides to undergo the reaction in air.[20] A palladium precatalyst based on a piperazine-derived diaminodiol also proved to be an excellent catalyst for both bromide and chloride derivatives, and a high TON of 548,400 for 4-bromobenzonitriles could be achieved.[21]

However, the commercially available simple amine have been under-developed as supporting ligand in Suzuki reaction.[8] The first successful example was reported by D. W. Boykin and co-workers in 2004, which demonstrated that the bulky secondary amine Cy$_2$NH modified catalyst *trans*-(Cy$_2$NH)$_2$Pd(OAc)$_2$ could catalyzed Suzuki cross-coupling of 4-bromoanisole at room temperature with 2 mol % catalyst loading. Following that work, J. H. Li et al. reported that an in situ generated Pd(OAc)$_2$/Dabco (Dabco: 4-diazabicyclo [2.2.2]octane) catalyst exhibited an extremely high activity for Suzuki reaction, and up to 950,000 TONs could be achieved for the coupling reaction of PhI with *p*-chlorophenylboronic acid.[22] Recently, another simple amine, 2,2′-diamino-6,6′-dimethylbiphenyl (L) was also found a useful ligand for this reaction. Even the less active aryl chlorides could readily react with arylboronic acid in

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DMF at 110 °C with 5 mol % of palladium loading.[23] According to the literature, a bulky and electronically rich ligand is beneficial for improving the catalyst activity and selectivity of these palladium catalysts.[24] As our continuous effort to develop high efficient and robust catalyst for Suzuki reaction, herein we first report our result on catalytic properties of complex **1**(Pd(memantine)$_2$Cl$_2$) in Suzuki–Miyaura cross-coupling reaction.

2. Results and discussion

2.1. The properties and molecular structure of complex 1

The new simple complex Pd(memantine)$_2$Cl$_2$ was synthesized by the reaction of Pd(OAc)$_2$ with memantine hydrochloride, and a single crystal of complex **1** was grown by slow evaporation of CH$_2$Cl$_2$/*n*-Hexane solvent system, allowing for structural elucidation by X-ray single crystal analysis. The molecular structure is illustrated in Fig. 1. Crystal data are presented in Table 1. The acetate was replaced by chloride ion based on the X-ray single crystal determined. Selected bond lengths and angles are given in Table 2. The bond lengths and angles are all within the expected range, without distorted square-planar geometry (the dihedral angle between the plane of Cl(1)–Pd(1)–Cl(2) and the plane of N(1)–Pd(1)–N(2) is 90°). The Pd–Cl(1) and Pd–Cl(2) bond distances (2.3001(10) nm and 2.3001(10) nm, respectively) are identical.

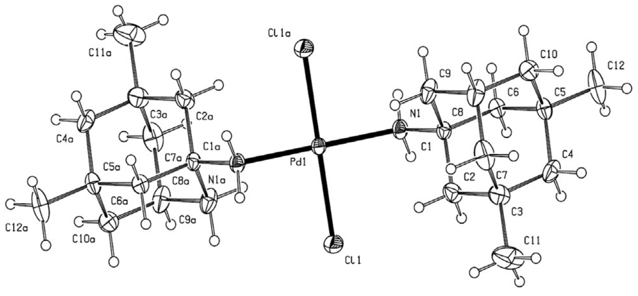


Fig. 1. The molecular structure and ORTEP representation of complex **1**.

Table 1
Crystal and refinement data for complex **1**

Empirical formula	C$_{24}$H$_{42}$Cl$_2$N$_2$Pd
Formula weight	535.89
Temperature/K	293.15
Crystal system	Triclinic
Space group	P-1
a/Å	6.6333(7)
b/Å	7.6678(8)
c/Å	12.507(3)
α/°	85.124(14)
β/°	79.886(15)
γ/°	75.155(9)
Volume/Å^3	604.80(16)
Z	1
ρ calcd mg/mm^3	1.471
m/mm^{-1}	1.002
F(000)	280.0
Crystal size/mm^3	0.2×0.15×0.1
Radiation	Mo K*α* (*λ*=0.7107)
2*Θ* range for data collection	6.302–52.734°
Index ranges	$-8\leq h\leq 8$, $-9\leq k\leq 9$, $-15\leq l\leq 15$
Reflections collected	5265
Independent reflections	5265[*R*(int)=?]
Data/restraints/parameters	5265/0/144
Goodness-of-fit on F^2	1.047
Final *R* indexes [$I\geq 2\sigma(I)$]	*R*1=0.0358, *wR*2=0.0877
Final *R* indexes [all data]	*R*1=0.0382, *wR*2=0.0890
Largest diff. peak/hole/e Å^{-3}	0.68/−0.68

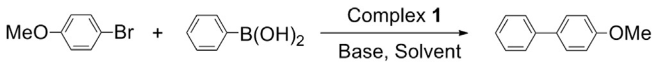
Table 2
Selected bond lengths (nm) and angles (°) for complex **1**

Pd(1)–Cl(1)1	2.3001(10)	Pd(1)–N(1)1	2.051(3)
Pd(1)–Cl(1)	2.3001(10)	N(1)–C(1)	1.497(5)
Pd(1)–N(1)	2.051(3)	Cl(1)1–Pd–Cl(1)	180
N(1)1–Pd–Cl(1)1	90.08(10)	C(1)–N(1)–Pd(1)	123.7(2)
N(1)–Pd–Cl(1)1	89.92(10)	N(1)–C(1)–C(2)	110.1(3)
N(1)–Pd–Cl(1)	90.08(10)	N(1)–C(1)–C(6)	107.7(3)
N(1)1–Pd–Cl(1)	89.92(10)	N(1)–C(1)–C(9)	110.8(3)
N(1)–Pd–N(1)1	180		

2.2. The Suzuki–Miyaura cross-coupling reaction

The Suzuki-Miyaura coupling reactions of aryl bromides with phenylboronic acid were investigated by employing the complex **1** as catalyst. Firstly, the coupling of 4-bromoanisole with 1.5 equiv of phenylboronic acid in the presence of 1.5 equiv of base at 80 °C was chosen as a model reaction to evaluate the catalytic properties of complex **1** in the Suzuki-Miyaura coupling reactions (Table 3, entries 1–15). Satisfyingly, a moderate GC yield (62%) of desired product was obtained in EtOH with KOH as base, upon 0.0002 mol % Pd loading (Table 3, entry 1). Increasing the catalyst loading to 0.002 mol % could improve the yield to 80%. Subsequently, several bases including NaOH, K$_3$PO$_4$, Na$_2$CO$_3$, NaHCO$_3$ and Cs$_2$CO$_3$ were scanned for this system, and NaOH proved to be the best. The product could be obtained in 91% yield (Table 3, entry 7), which could be further increased to 96% by decreasing the NaOH amount to 1.2 equiv (Table 3, entry 8). Solvent also plays a crucial role in the reaction rate of Suzuki coupling reactions. Polar protic solvents, such as EtOH, *i*-PrOH and *n*-BuOH afforded higher activity than either polar aprotic solvents, such as DMF, DMA, and dioxane, or nonpolar solvent toluene. It was worthy of note that the complex **1** could also be operated in green solvent water, although the yield (50%) is lower than that in ethanol (Table 3, entry 15).

Table 3
Effect of reaction conditions on the Suzuki coupling reaction catalyzed by complex **1**



Entry	Catalyst loading (mol %)	Solvent	Base	Yield (%)[a]
1	0.0002	EtOH	KOH	62
2	0.002	EtOH	KOH	80
3	0.002	EtOH	K$_3$PO$_4$	72
4	0.002	EtOH	Na$_2$CO$_3$	76
5	0.002	EtOH	NaHCO$_3$	24
6	0.002	EtOH	NaOH	91
7	0.002[b]	EtOH	NaOH	96
8	0.002	EtOH	CsCO$_3$	Trace
9	0.002	*i*-PrOH	NaOH	90
10	0.002	*n*-BuOH	NaOH	93
11	0.002	Toluene	NaOH	61
12	0.002	DMF	NaOH	0
13	0.002	DMA	NaOH	10
14	0.002	Dioxane	NaOH	3
15	0.002	H$_2$O	NaOH	50

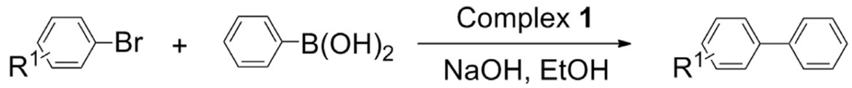
Reaction conditions: catalyst: complex **1**, 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), base (0.75 mmol), solvent (3 mL), 24 h, 80 °C.

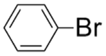
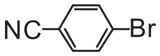
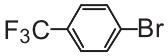
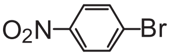
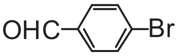
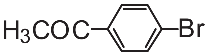
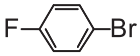
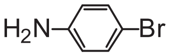
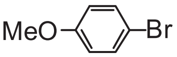
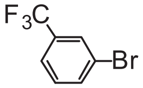
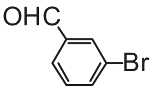
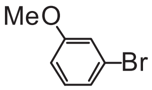
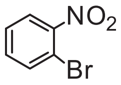
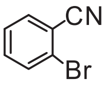
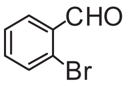
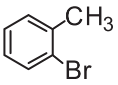
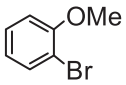
[a] GC yield.

[b] Base: 0.6 mmol.

With the optimal conditions in hand, the scope and limitations of the present catalytic system was investigated for Suzuki–Miyaura reaction. Firstly, the substrate scope and limitations regard to the aryl bromide were tested. As shown in Table 4, the established complex **1** catalytic system displayed high activity in this cross-coupling reaction. Various aryl bromides, regardless of electronically rich, neutral and deficient properties, reacted

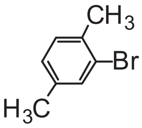
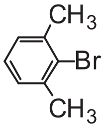
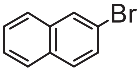
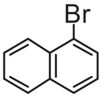
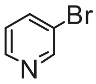
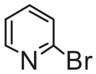
Table 4
Suzuki reaction of various aryl bromides with phenylboronic acid catalyzed by complex **1**



Entry	Aryl bromide	Catalyst loading (mol %)	Time (h)	Yield (%)[a]
1		0.002	24	98
2		0.0002	24	91
3		0.001	6	99
		0.0002	24	96
4		0.0002	6	97
		0.0001	48	65
5		0.001	6	98
6		0.001	6	99
7		0.002	24	96
8		0.002	24	85
9		0.002	24	90
10		0.002	24	94
11		0.002	24	99
12		0.001	6	51
13		0.002	24	90
14		0.002	24	15[b]
15		0.002	24	55
16		0.001	6	18
17		0.002	24	90
18		0.002	24	46

(*continued on next page*)

Table 4 (*continued*)

Entry	Aryl bromide	Catalyst loading (mol %)	Time (h)	Yield (%)[a]
19		0.002	24	80
20		0.002	24	25[b]
21		0.002	24	94
22		0.002	24	97
23		0.01	6	91
24		0.01	6	40

Reaction conditions: catalyst: complex **1**, aryl bromide 0.5 mmol, phenylboronic acid 0.75 mmol, NaOH 0.75 mmol, EtOH 3 mL, 80 °C.

[a] Isolated yield.

[b] GC yield.

smoothly with phenylboronic acid to afford the corresponding coupling products in excellent isolated yields (80–99%, Table 4, entries 1–23). Additionally, the system proved to be compatible with a wide range of functional groups, such as −CN, $-\mathrm{CF_3}$, $-\mathrm{NO_2}$, −CHO, $-\mathrm{COCH_3}$, −F, $-\mathrm{NMe_2}$ and $-\mathrm{NH_2}$ etc. although a relatively strong basic conditions was employed. The position of substituent on the aryl bromide was also influenced the activity. Generally, the activity of different aryl bromides followed a sequence: *para*->*meta*->*ortho*-. For example, 4-bromobenzaldehyde, 3-bromobenzaldehyde and 2-bromo- benzaldehyde gave the product in 98%, 51% and 18% yield, respectively (Table 4, entries 5, 12 and 16). This substituent-position-dependent activity is presumably related to the congested coordinative environment around the palladium centre, which was created by large volume of ligand memantine. This trend was again observed in disubstituted aryl bromides. A satisfying yield of 80% was obtained in case of 2-bromo-1,4-dimethylbenzene as substrate, while only a low GC yield 25% was obtained from 2-bromo-1,3-dimethylbenzene (Table 4, entries 19 and 20). The 1-naphthyl and 2-naphthyl bromides also reacted with phenylboronic acid smoothly. In both cases, almost a quantitative yield can be reached after 24 h. Moreover, the heteroaryl bromides, such as 2- and 3-bromopyridine also proved to be viable for the present catalytic system and proceed nicely to give product 2-phenylpyridine and 3-phenylpyridine in 40% and 91% yield, respectively (Table 4, entries 21–24).

Encouraged by the excellent catalytic activity of complex **1** in the Suzuki coupling reaction of aryl bromides with phenylboric acid, the reaction of electron-deficient aryl chlorides with phenylboronic acid catalyzed by complex **1** was investigated. In the case of 4-chloronitrobenzene, 4-chlorobenzotrifluoride and 4-chloroacetophenone as substrate, the cross-coupling products could be obtained in isolated yields of 42%, 60% and 66%, respectively, when the catalyst loading increased to 1 mol % and the reaction temperature was elevated to 110 °C for 24 h in *n*-butanol. Meanwhile, the homo-coupling product of phenylboronic acid was also observed with about 20% GC yield.

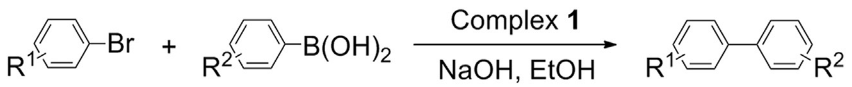
Subsequently, the scope of complex **1** catalytic system was further explored with respect to arylboronic acids (Table 5, entries 1–3). Electron-deficient and sterically hindered boronic acids led to a significant decrease in yields even with increased catalyst loading, however, in the case of the electron-rich 4-methoxyphenyl-boronic acid, 4-bromoanisole could be converted to the desired product with yield of 96% even the catalyst loading was low as 0.001 mol % (Table 5, entry 3).

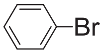
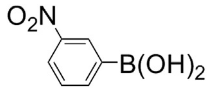
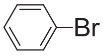
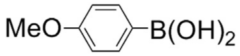
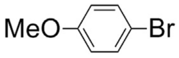
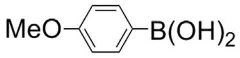
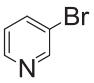
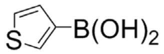
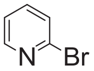
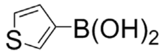
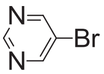
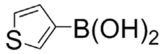
We were happy to discover that the scope of the protocol could be extended to the Suzuki coupling reaction of heteroaryl bromides with heteroarylboronic acid, and so the products of heteroaryl-aryl and biheteroaryls could be obtained with good yield when EtOH was employed as the media (Table 5, entries 4, 5 and 6). Although phosphine ligands, palladacycles, and Pd−NHC catalysts have been successfully used for the Suzuki reaction of heteroaryl bromides with heteroarylboronic acids,[25–27] to the best of our knowledge, the efficiency of simple N-ligands for such couplings has not been demonstrated. And thiophene is an important motif, which can be found in a variety of natural products as well as pharmaceutically interesting compounds. Thiophenylboronic acids are prone to decomposition under polar solvents, possibly by undergoing the protodeboronation,[28] which becomes the limitation plaguing the reactions involving these substrates. We were pleased to find that Suzuki reaction of thiophenylboronic acid could be performed well in the present catalytic system. And a moderate to excellent yield of desired products could be obtained by using 1 mol % catalyst (Table 5, entries 4–6).

Based on the above efficient results, the catalyst system was investigated at room temperature. The desired coupling products were still obtained in excellent isolated yields (Table 6, entries 1–13). And compared to Boykin's reported system of DAPCy (*trans*-$(\mathrm{Cy_2NH})_2\mathrm{Pd(OAc)_2}$) in room temperature, the desired product of the

Table 5

Suzuki reaction of aryl bromides with arylboronic acids catalyzed by complex **1**



Entry	Aryl bromide	Arylbonoric acid	Catalyst loading (mol %)	Yield (%)[a]
1			0.002	53
2			0.001	86
3			0.001	96
4			1	92
5			1	50
6			1	90

Reaction conditions: catalyst: complex **1**, aryl bromide 0.5 mmol, arylboronic acid 0.75 mmol, NaOH 0.75 mmol, EtOH 3 ml, 80 °C, 24 h.

[a] Isolated yield.

4-Bromoanisole with phenylboronic acid could not be obtained even in the presence of 2 mol % DAPCy at room temperature for 30 h. However, the reaction could perform smoothly in our catalytic system and 82% yield of desired product was obtained in the presence of 0.01 mol % catalyst **1** with 24 h (Table 6, entry 8). When catalyst loading reduced to 0.001 mol %, the reaction of 4-bromonitrobenzene, 4-bromobenzotrifluoride and 4-bromobenzonitrile with phenylboronic acid also gave the desired products in high yields of 99%, 88% and 97% in 24 h, respectively (Table 6, entries 1–3). A high TON of up to 99,000 was achieved. Thus, the results indicated that the complex **1** was still efficient in the catalytic process at room temperature.

3. Conclusions

An easy-to-handle catalytic system was reported for the Suzuki-Miyaura coupling reaction using a new simple Pd(memantine)$_2$Cl$_2$ complex as catalyst. The new catalytic system provided a mild and aerial condition for the coupling reaction of aryl bromides with arylboronic acid. A wide range of substrates could be coupled with arylboronic acids to afford the desired products in good to excellent yields. Furthermore, the catalytic system also gives excellent yields toward several heteroaryls. The catalytic reaction results demonstrated that the complex **1** is a highly efficient catalyst in Suzuki cross-coupling reaction.

4. Experiment section

4.1. General information

All the chemicals received from commercial suppliers were used without further purifications unless noted. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer using TMS as the internal standard. Gas chromatographic analyses were performed on an Agilent 6890N GC System equipped with a SE-30 GC column (30 m×0.32 mm×0.25 μm). The GC yields of the cross-coupling reactions were determined from normalized peak areas using an internal standard.

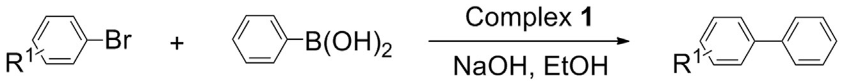
4.2. General procedure for the Suzuki reaction

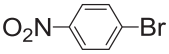
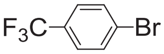
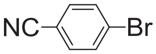
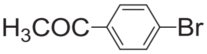
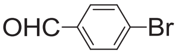
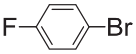
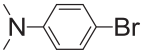
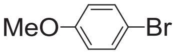
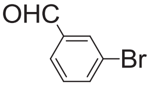
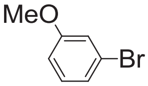
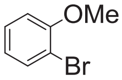
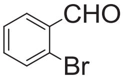
In the reaction tube with a magnetic bar was added the solution of aryl bromides (0.5 mmol) and phenylboronic acid (91 mg, 0.75 mmol), NaOH (24 mg, 0.6 mmol), complex **1** (0.0001–0.02 mol %, dissolved in DMA) and ethanol (3 mL). After stirred for the required time in the preset conditions, the reaction mixture was cooled to room temperature, and then quenched by 1 mL brine and 3 mL water, and extracted with ethyl acetate (3×5 mL). The combined organic layer was dried over anhydrous MgSO$_4$ and the filtrate was concentrated to dryness under reduced pressure. The crude products were purified by column chromatography (petroleum ether, ethyl acetate) on silica gel.

4.3. Preparation of complex 1

A solution of memantine hydrochloride (86.3 mg, 0.4 mmol) in dichloromethane (20 mL) was added dropwise to the 50 mL bottom flask charged with Pd(OAc)$_2$ (44.9 mg, 0.2 mmol) in dichloromethane (5 mL) at room temperature. After the reaction mixture was stirred for 4 h at room temperature, the solvent was evaporated in the reduced pressure to give a pale yellow solid. The crude product was purified by column chromatography (petroleum ether/ethyl acetate=1:3 v/v) on silica gel. Yield: 50% (53.6 mg, 0.1 mmol) (mp>250 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.67 (s, 4H, NH$_2$); 2.22–2.24 (m, 2H, CH); 1.86 (s, 4H, CH$_2$); 1.64–1.74 (m, 8H, CH$_2$); 1.28–1.39 (M, 8H, CH$_2$); 1.17 (s, 4H, CH$_2$); 0.92 (s, 12H, CH$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 55.67, 51.09, 50.12, 43.43, 42.17, 33.04, 30.42, 29.95. HRMS-ESI. calcd for $C_{24}H_{42}Cl_2N_2Pd$ $(M+Na)^+=557.1658$, found 557.1661.

Table 6
Suzuki reaction of various aryl bromides with phenylboronic acids catalyzed by complex **1** at room temperature



Entry	Aryl bromide	Pd (mol %)	Time (h)	Yield (%)[a]
1		0.001	24	99
2		0.001	24	88
3		0.001	24	97
4		0.01	24	95
5		0.01	24	95
6		0.01	24	97
7		0.01	24	71
8		0.01	24	82
9		0.01	24	94
10		0.01	24	81
11		0.01	24	73
12		0.01	24	65

Reaction conditions: catalyst: complex **1**, aryl bromide 0.5 mmol, phenylboronic acid 0.75 mmol, NaOH 0.75 mmol, EtOH 3 ml, 25 °C.

[a] Isolated yield.

4.4. Crystal structure determination of complex 1

A single crystal of complex **1** was grown by slow evaporation of CH_2Cl_2/n-Hexane solvent system, the X-ray intensity data were measured at 293 K on a Xcalibur, Eos diffractometer using graphite monochromated Mo Kα radiation (0.071070 nm). Using Olex2,[29] the structure was solved with the Superflip[30] structure solution program using Charge Flipping and refined with the ShelXL-2012[31] refinement package using Least Squares minimisation.

CCDC 968898 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from the Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.03.064.

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