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Full Paper

Synthesis, Solid-state Structures, Solution Behaviour and Catalysis Studies of Nickel Complexes of Bis(benzimidazolin-2-ylidene)pyridine Pincer Ligands*

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N-Heterocyclic carbene–nickel complexes with five- and four-coordinate geometries [(CNC)NiBr₂] and [(CNC)NiBr]X ($X = PF_6$ or BPh₄) have been prepared with the pincer ligands 2,6-bis(*N*-octylbenzimidazolin-2-ylidene)pyridine and 2,6-bis(*N*-butyl-5,6-dimethoxybenzimidazolin-2-ylidene)pyridine. The addition of the *n*-octyl substituent significantly extends the solubility of the complexes and has allowed UV-vis solution studies of the complexes in dichloromethane and methanol. The four- and five-coordinate species exist in equilibrium in solution and this equilibrium has been explored by UV-vis studies. The complexes have also been characterized by NMR studies, and single crystal X-ray diffraction studies have been performed on [(CNC)NiBr₂] (where CNC = 2,6-bis(*N*-octylbenzimidazolin-2-ylidene)pyridine) and [(CNC)NiBr]BPh₄ (where CNC = 2,6-bis(*N*-butyl-5,6-dimethoxybenzimidazolin-2-ylidene)pyridine).

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Introduction

Metal complexes of 'pincer' ligands bearing *N*-heterocyclic carbenes (NHCs) have been studied extensively, involving a range of additional donor types.^[1–3] Within this class of compounds, NHC 'pincer' ligands with a pyridyl core are common (e.g. 1 in Fig. 1). Although there is now an extensive variety of different NHC structural motifs, the pyridyl-core CNC pincer has predominantly been explored with imidazole-derived NHCs. Metal complexes of 2,6-bis(imidazol-2-ylidene)pyridine type ligands cover the majority of the d-block elements, with significant interest in catalysis applications.^[1,2,4–8] By comparison, complexes of the benzimidazole-based 2,6-bis(benzimidazolin-2-ylidene)pyridine ligand system have only been reported with Pd, Ag, Os and recently Ni.^[4,9–14]

In our recent exploration of nickel complexes of the 2,6bis(benzimidazolin-2-ylidene)pyridine ligand system, we identified the formation of the five-coordinate [(CNC)NiX₂] complexes **2** (where CNC = 2,6-bis(3-*n*-butylbenzimidazolin-2-ylidene)pyridine, X = Cl, Br),^[13] an unusual coordination geometry for this CNC ligand system. Other studies of nickel complexes with 2,6-bis(imidazol-2-ylidene)pyridine ligands have predominantly identified only four-coordinate [(CNC)NiX]⁺ geometries,^[7,15–17] with one example of a six-coordinate nickel complex.^[17] The five-coordinate complexes **2** displayed surprisingly low solubility in a range of organic solvents, and our studies suggested dissolution of these purple [(CNC)NiX₂] complexes resulted in formation of yellow solutions containing [(CNC)NiX]⁺ cations **3** (X = Cl, Br).^[13]

In this paper, we report our continued exploration of these nickel complexes bearing 2,6-bis(benzimidazolin-2-ylidene) pyridine ligands, including catalysis studies in Kumada coupling reactions. Incorporation of octyl substituents has allowed us to explore the solution behaviour of these complexes in solvents other than highly polar solvents such as methanol. In addition, we have explored the incorporation of methoxy groups into the periphery of the benzimidazole moiety, because incorporation of these groups in the 5,6-positions should not influence the coordination environment based on sterics, but may influence the electronic properties of the carbene donor atom. Several studies have incorporated methoxy groups onto benzimidazolin-2-ylidenes in an effort to explore the influence they have on metal complexation.^[18–23]

Results and Discussion

The syntheses reported here are derived from the previously reported procedures for the synthesis of 2 (X = Br),

^{*}Dedicated to Professor Allan H. White on the occasion of his 75th birthday.

 $3 \cdot PF_6$ (X = Br) and the bis(benzimidazolium) dibromide salt used as the ligand precursor.^[10,13] Treatment of 5,6-dimethoxybenzimidazole^[24] with sodium hydride and then reaction of the resulting benzimidazolate anion with 2,6dichloropyridine in DMF at 70°C for 24 h and then 140°C for a further 24 h afforded 1,3-bis(5,6-dimethoxybenzimidazol-1-yl) pyridine (4) in good yield (Scheme 1). Alkylation of 4 with a large excess of 1-bromobutane afforded the bis(benzimidazolium) salt 5.2Br. A solution of 5.2Br and nickel acetate tetrahydrate in DMF was heated from room temperature to $\sim 110^{\circ}$ C over the course of ~ 10 min, and then immediately allowed to cool, which resulted in the formation of the five-coordinate nickel complex 6 as a purple precipitate, which could be further purified by recrystallization from nitromethane. Treatment of a mixture 6 and potassium hexafluorophosphate in methanol afforded the four-coordinate complex salt 7.PF₆ as an orange powder in high yield (Scheme 1). Attempts to grow single

provider in high yield (scheme 1). Attempts to grow single crystals of either **6** or $7 \cdot \text{PF}_6$ proved difficult, routinely affording extremely fine needles that were not suitable for single-crystal X-ray studies. Such behaviour was also observed for the previously studied non-methoxy analogues **2** (X = Br) and $3 \cdot \text{PF}_6$ (X = Br).^[13] The salt $7 \cdot \text{BPh}_4$ was prepared similarly to $7 \cdot \text{PF}_6$, using sodium tetraphenylborate instead of potassium hexa-fluorophosphate. Recrystallization of the tetraphenylborate salt $7 \cdot \text{BPh}_4$ afforded single crystals that were suitable for X-ray studies (see *Solid-State Studies*). Dissolution of $7 \cdot \text{PF}_6$ in methanol or dichloromethane afforded bright yellow solutions. In the case of **6**, solutions in methanol are bright yellow whereas solutions in dichloromethane are yellow to orange, depending on concentration.

Our previous solution studies of the five-coordinate complex 2 (X = Br) were restricted to polar solvents owing to the



Fig. 1.

insoluble nature of **2**. In an effort to improve the solubility of such systems, and to further explore the solution behaviour of these complexes, we synthesized the *n*-octyl-substituted bis (benzimidazolium) salt **8**·2Br and the five- and four-coordinate complexes **9** and **10**·PF₆ in good yields using procedures similar to those described above (Fig. 2). As with **2** (X = Br) and **3**·PF₆ (X = Br), attempts to grow crystals of **9** and **10**·PF₆ invariably afforded extremely fine needles; however, we were fortunate that when using THF and methanol as recrystallization solvents, dark purple crystals of **9** suitable for X-ray studies were isolated



7.PF₆ 85 %

Scheme 1. Synthesis of the pyridyl-bis(dimethyoxybenzimidazolium) salt **5**·2Br and the bis(dimethyloxybenzimidazolin-2-ylidene)pyridine nickel complexes **6** and **7**·PF₆.

(see *Solid-State Studies*). The addition of the octyl substituents significantly improved the solubility of the complexes, particularly the five-coordinate complex **9**, which proved to be soluble in chlorinated solvents such as dichloromethane, affording purple–brown coloured solutions. This contrasts with the butyl-substituted complex **2** (X = Br), which only displayed appreciable solubility in more polar solvents such as methanol, and on dissolution (of the purple solid) afforded yellow solutions.

All compounds were characterized by ¹H and ¹³C NMR studies. The ¹³C NMR spectra of the nickel complexes were obtained using relatively concentrated solutions of the complexes. Solutions were prepared using [D]chloroform (with a drop of [D₃]methanol) for the five-coordinate complexes **6** (orange in colour) and **9** (dark brown–purple in colour), and [D]chloroform (with [D₆]dimethylsulfoxide) for the four-coordinate materials **7**·PF₆ and **10**·PF₆. Each of the ¹³C NMR spectra displayed a relatively sharp downfield signal attributed to the carbene carbons bound to each nickel centre (δ_C 166.4 (**6**); 172.0 (**9**); 165.6 (**7**·PF₆); 169.8 (**10**·PF₆)). However, at these concentrations the ¹H NMR spectra often displayed broadened signals for the solutions of the five-coordinate complexes **6** and **9**. Dilution of the solutions resulted in sharper spectra from which accurate data could be obtained.







10.PF₆

Fig. 2. *n*-Octyl-substituted compounds reported in this paper.

Solid-State Studies of 9 and 7. BPh₄. Et₂O

Table 1 summarizes selected coordination geometries for the two structures **9** and $7 \cdot \text{BPh}_4 \cdot \text{Et}_2\text{O}$.

The structure for **9** displays a distorted trigonal bipyramidal geometry around the nickel centre, with the two bromide atoms and N21 forming the horizontal plane and the carbene carbons C12 and C32 occupying the axial positions (Fig. 3). The geometry in **9** is similar to that of the crystallographically characterized chlorido complex **2** (X = CI)^[13] and a related [(CNC)PdI₂] complex.^[11] The structure of **9** represents only the third crystallographically characterized example of this unusual five-coordinate geometry for nickel or palladium complexes of this class of pincer ligand system.^[11,13] Group 10 metal complexes of these types of *N*-heterocyclic carbene CNC pincer ligands typically display four-coordinate geometries have been only observed with CNC ligands based on benzimidazolin-2-ylidenes and not the more common imidazol-2-ylidenes.^[11,13]

The cation 7 shows an essentially coplanar molecule with the exception of the pendant butyl chains and methoxy groups (Fig. 4). The most deviant atoms from the plane are C24 $(\delta 0.122(2) \text{ Å})$ and C35 $(\delta 0.166(2) \text{ Å})$. The dihedral angles between the planes of the two benzimidazolin-2-ylidene groups and the pyridyl groups are $3.60(6)^{\circ}$ (between planes 1 and 2) and $5.17(6)^{\circ}$ (between planes 2 and 3). The dihedral angle between the two benzimidazolin-2-ylidene groups (planes 1 and 3) is 1.68(5)°. The unit cell containing 7.BPh₄ also includes one molecule of diethyl ether (solvent) per molecule of compound (Fig. 5). The cations are arranged in the cell as centrosymmetrically related pairs (Figs 6, 7) with the Ni1...Ni1 (1-x), 1-y, 1-z) distance being 3.4767(3) Å and Ni1...N21(1-x, 1 - y, 1 - z 3.583(2)Å. The coordination geometry around the nickel centre is approximately square planar. There is no significant deflection of the bromide atom away from planarity, with an N21-Ni1-Br1 angle of 179.54(5)° and a total deviation of the bromide atom out of the NC₂Ni plane of 0.019(3) Å, compared with 166.68(9)° and 0.528(4) Å for the non-methoxy analogue $3 \cdot PF_6$ (X = Br).^[13] The 'cavity' for the bromido ligand to occupy in the ideal square-planar geometry, as measured by the distance between the two benzimidazole-bound methylene carbons C1...C5, is only slightly larger in the methoxyfunctionalized complex, at 6.594(2)Å, compared with 6.547(6) Å for $3 \cdot PF_6$ (X = Br).^[13] A comparison of the solidstate structures for the cations in 7 and 3 (X = Br) does not reveal any obvious reasons as to why the coordination geometry around the nickel centres should vary so significantly; however, the variation in their geometries appears to correlate with the observed differences in their solution behaviour.

UV-vis Studies

In our earlier studies of the five-coordinate [(CNC)NiBr₂] **2**, the low solubility of the complex in various organic solvents limited

Table 1. Selected bond lengths [Å] and angles [°] for 7 and 9, and relevant literature examples

Complex	C–Ni [Å]	N–Ni [Å]	Ni–X [Å]	C–Ni–C [°]	N-Ni-X[°]	$R{\cdots}R^{A}\left[\mathring{A}\right]$	$NC_2Ni\cdots X^B$ [Å]
$7 \cdot BPh_4$	1.929(2), 1.933(1)	1.866(2)	2.2989(4)	162.73(8)	179.54(5)	6.594(2)	0.019(3)
$3 \cdot PF_6 (X = Br)^{[13]}$	1.924(4), 1.932(4)	1.866(3)	2.2955(6)	163.08(14)	166.68(9)	6.547(6)	0.528(4)
9	1.894(2), 1.890(2)	1.876(2)	2.5177(5), 2.4404(4)	161.7(1)	127.50(6), 132.46(6)	6.341(4)	1.998(3), 1.797(3)
$2 (X = Cl)^{[13]}$	1.897(6), 1.900(7)	1.871(5)	2.2791(18), 2.4324(19)	162.0(3)	141.38(17), 115.64(17)	6.270(10)	2.192(4), 1.424(6)

^AThe distance between the two carbon atoms, of the alkyl substituents, bound to the azolyl nitrogen. ^BThe distance of the halide out of the NC₂Ni plane.



Fig. 3. Molecular structure of 9.



Fig. 4. Structure of cation 7 projected onto the coordination plane.

our solution studies to polar solvents such as methanol.^[13] In these studies, the UV-vis spectra of solutions of [(CNC)NiBr₂] **2** in methanol were almost identical to those of the four-coordinate [(CNC)NiBr]PF₆ **3**·PF₆ in methanol, which suggested the dissolution of the five-coordinate [(CNC)NiBr₂] **2** afforded solutions of the four-coordinate cation [(CNC)NiBr]⁺.^[13] The improved solubility of the octyl-substituted [(CNC)NiBr₂] **9** in chlorinated solvents compared with the butyl analogue **2** (X = Br) allowed further studies of the solution behaviour of these types of complexes.

Solutions of **9** in dichloromethane were brown–purple (Fig. 8), whereas solutions in methanol were bright yellow. The differences in solution colour are consistent with the dramatically different UV-vis spectra (Fig. 9). The spectrum for a methanol solution of **9** (Fig. 9) is very similar to that of the spectra for solutions of the four-coordinate [(CNC)NiBr] PF_6 **10**·PF₆ in methanol or dichloromethane (Fig. 9), which excludes the possibility that the absorption profile of **9** in methanol originates from the cationic solvato-complex with a

distorted trigonal bipyramidal geometry. These data are consistent with the dissolution of $[(CNC)NiBr]PF_6$ **10**·PF₆ in either methanol or dichloromethane resulting in solutions with the four-coordinate species $[(CNC)NiBr]^+$ **10**, as well as dissolution of **9** in methanol forming the same four-coordinate species. We assume that the spectrum of **9** in dichloromethane (Fig. 9) is a spectrum of the five-coordinate species in solution, based on the stark differences in colour in solution (brown–purple for **9** in dichloromethane; bright yellow for **10** in dichloromethane) that parallel their solid-state appearances (purple powders for **9**; yellow powders for **10**·PF₆) (see Supplementary Material).

The additions of tetrabutylammonium bromide to a dichloromethane solution of [(CNC)NiBr]PF₆ **10**·PF₆ results in a significant change in the UV-vis spectra (Fig. 10). With subsequent additions of tetrabutylammonium bromide, the intensity of the peaks at ~450 and 540 nm increases and at the same time, the intensity the peak at ~395 nm slightly decreases. After the addition of excess bromide (>5 equiv.) the spectrum is similar to that of solutions of the five-coordinate [(CNC)NiBr₂] **9**.



Fig. 5. Unit cell contents of $7 \cdot BPh_4 \cdot Et_2O$ projected along the *a* axis.



Fig. 6. A pair of centrosymmetrically related cations of **7** projected oblique to the coordination plane.

In methanol solutions of [(CNC)NiBr]PF₆10·PF₆, there was no significant change in the spectra on the addition of tetrabutylammonium bromide. This solution behaviour is consistent with an equilibrium existing involving the four- and five-coordinate species (Scheme 2). It would appear that the ability of the solvent to solvate bromide ions is a major contributing factor as to the position of the equilibrium. The isosbestic point at \sim 420 nm in Fig. 10 is consistent with the equilibrium involving only two species that absorb in the visible spectrum, presumably $[(CNC)NiBr_2]$ 9 and $[(CNC)NiBr]^+$ 10. When solutions of 9 in dichloromethane were treated with increasing amounts of water (within solubility limits), the position of the equilibrium shifted away from the five-coordinate 9. This change in the equilibrium position was observed by the decrease of the absorbance peaks at \sim 450 and 550 nm and an increase in the peak at \sim 390 nm (Fig. 11), and is consistent with the increased solvation of the free bromide by water.

The methoxy-functionalized complex 6 appeared to behave differently in dichloromethane solutions compared with 9. The UV-vis spectra for dichloromethane solutions of 6 and

7·PF₆ are remarkably similar (Fig. 12). Although there is an increase in the absorbance at \sim 550 nm in the solution of **6** in dichloromethane, it is not as pronounced as in the spectrum of **9** in dichloromethane. The addition of a large excess of tetrabutylammonium bromide to the solution of **6** in dichloromethane resulted in a small enhancement of the absorbance at 550 nm (Fig. 13). It would appear that in the case of **6**, the addition of the methoxy substituents causes the nickel to favour, though possible not exclusively, a four-coordinate geometry in solution. However, in the solid state, the colour of **6** (dark purple) is consistent with the five-coordinate geometry. This may be a result of the subtle differences in the complex structure (see *Solid-State Studies*) or a result of an electronic influence of the methoxy groups on the carbene donor atoms.

Catalysis Studies

The catalytic activity of complexes 6 and 2 (X = Br) was evaluated in Tamao-Kumada-Corriu coupling reactions against several aryl substrates of varying electronic and steric properties (Table 2). Despite the very low solubility of both complexes in THF, the addition of the Grignard reagent to the mixture afforded a dark red solution, presumably as a result of the dissolution of the complex. The results show that only moderate yields of coupling products were obtained, with complex 2 (X = Br) proving to be the 'better' catalyst (Table 2). Both complexes show little tolerance for sterically hindered substrates. Significant quantities of the homo-coupled products (from the Grignard reagents) were found in all reactions, which has been previously reported for similar systems.^[26] This side reaction is believed to be responsible for lower than expected yields, as the Grignard reagent is consumed in the formation of the homo-coupled product. The catalyst only showed reactivity towards aryl halides. The attempted coupling of alkyl halides (e.g. (4-bromobutoxy)benzene) did not form the desired product; instead, ¹H NMR analysis indicated the formation of alkenes (e.g. 4-phenoxybut-1-ene), suggesting a β-hydride elimination pathway. Without the addition of the nickel



Fig. 7. A pair of centrosymmetrically related cations of 7 projected onto the coordination plane. The molecule at 1-x, 1-y, 1-z is shown with blackened bonds.



Fig. 8. Solutions of 6 and 9 in dichloromethane $(1 \times 10^{-3} \text{ and } 1 \times 10^{-4} \text{ M})$.



Fig. 9. UV-vis spectra of solutions of 9 and $10 \cdot PF_6$ in methanol and dichloromethane ($\sim 10^{-4}$ M).

complexes, there was no reaction between (4-bromobutoxy)benzene and the Grignard reagent. The more soluble complexes $7 \cdot PF_6$ and $3 \cdot PF_6$ were also tested, and found to have similar activity to their parent compounds. In comparison with the imidazole-based analogue $1 \cdot Br$, the benzimidazolin-2-ylidene pincer complexes studied here proved to be less efficient catalysts in Tamao–Kumada–Corriu coupling reactions.^[26] The complexes also displayed less activity than a benzimidazolin-2ylidene nickel complex of the type [(NHC)₂NiBr₂] bearing a *cis*-chelating dibenzimidazolin-2-ylidene ligand.^[27]



Fig. 10. UV-vis spectra of a solution of 10-PF₆ in dichloromethane (~10⁻⁴ M) with successive additions of tetrabutylammonium bromide.

Conclusions

Solution studies of the octyl-substituted bis(benzimidazolin-2ylidene)pyridyl pincer five-coordinate nickel complex [(CNC) NiBr₂] suggest that the complex, with a five-coordinate geometry, can exist in solution, unlike what was observed in earlier studies.^[13] The five-coordinate species is in an equilibrium with the four-coordinate species [(CNC)NiBr]⁺, and the equilibrium is strongly influenced by the nature of the solvent system, in addition to ligand variations (pincer and halide), as reported previously.^[13] The addition of methoxy groups to the periphery of the benzimidazolin-2-ylidene appears to result in the favouring of the four-coordinate geometry in solution, though the exact reason for this preference is unknown. The nickel complexes displayed only moderate activity in Tamao– Kumada–Corriu coupling reactions.

Experimental

Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AV400N (400.13 MHz for ¹H, 100.61 MHz for ¹³C) spectrometer at 300 K. ¹H and ¹³C chemical shifts were referenced to the residual solvent resonances. Assignments of NMR spectra were made with the aid of DEPT, ¹H–¹H COSY, HSQC (one-bond ¹H–¹³C correlations) and HMBC (two- and



Scheme 2. Equilibria involving 9 and 10 in solution.



Fig. 11. UV-vis spectra of a solution of 9 in dichloromethane ($\sim 10^{-4}$ M) with successive additions of water.



Fig. 12. UV-vis spectra of 6 and 7 (7·PF₆, 7·BPh₄) in dichloromethane and methanol solutions ($\sim 10^{-4}$ M).

three-bond ¹H–¹³C correlations) experiments. Coupling reactions were analysed using an HP 5890A gas chromatograph with a flame ionization detector (FID). Microanalyses were performed by the Central Science Laboratory, University of Tasmania, or locally using a Perkin Elmer 2400 CHNS/O Analyser. UV-vis spectra were collected using Perkin–Elmer Lambda 35 or GBC 916 UV-vis spectrophotometers. Quoted peak maxima are for the range 350–700 nm. 5,6-Dimethoxybenzimidazole,^[24]1,3-bis(benzimidazol-1-yl) pyridine,^[10] the five-coordinate [(CNC)NiBr₂] complex **2**^[13] and the four-coordinate [(CNC)NiBr]PF₆ salt **3**·PF₆^[13] were synthesized by literature procedures.



Fig. 13. UV-vis spectra of solution of 6 and $7 \cdot PF_6$ in dichloromethane ($\sim 10^{-4}$ M), with the addition of tetrabutylammonium bromide.

1,3-Bis(5,6-dimethoxybenzimidazol-1-yl)pyridine 4

A solution of 5,6-dimethoxybenzimidazole (2.0 g, 11 mmol) in dimethylformamide (10 mL) was added dropwise to a cooled (ice-bath) suspension of sodium hydride (60 % dispersion in oil, 0.50 g, 12 mmol) in dimethylformamide (10 mL). The reaction mixture was warmed to room temperature and stirred for 1 h, and then 2,6-dichloropyridine (0.68 g, 4.6 mmol) was added. The resulting mixture was then heated at 70°C for 24 h, and then at 140°C for a further 24 h. The mixture was cooled and then diluted with water (20 mL). The resulting precipitate was collected, washed with diethyl ether $(2 \times 10 \text{ mL})$ and recrystallized from toluene (\sim 50 mL) to produce a light-pink powder (1.62 g, 65 %). δ_{H} (CDCl₃) 3.76 (s, 6H, 2 × OCH₃), 3.97 (s, 6H, $2 \times \text{OCH}_3$, 7.34 (s, 2H, 2 × benzimidazolyl CH), 7.50 (d, J 8.0, 2H, pyridyl H3 and H5), 7.80 (s, 2H, $2 \times$ benzimidazolyl CH), 8.11 (t, J 8.0, 1H, pyridyl H4), 8.46 (s, 2H, 2 × benzimidazolyl CH). δ_C (CDCl₃) 56.3 (OCH₃), 56.3 (OCH₃), 96.7 (CH, benzimidazolyl C4 or C7), 102.4 (CH, benzimidazolyl C7 or C4), 110.3 (CH, pyridyl C3/C5), 125.7 (C, benzimidazolyl C8 or C9), 138.3 (C, benzimidazolyl C9 or C8), 139.1 (benzimidazole C2), 141.9 (CH, pyridyl C4), 147.6 (C, benzimidazolyl C5 or C6), 148.2 (C, benzimidazolyl C6 or C5), 149.7 (C, pyridyl C2/C6). Anal. calc. for C₂₃H₂₁N₅O₄: C 64.03, H 4.91, N 16.23. Found: C 63.99, H 4.78, N 16.08 %.

1,1'-(2,6-Pyridyl)bis(3-n-butyl-5,6-

dimethoxybenzimidazolium) Dibromide 5.2Br

A mixture of 1-bromobutane (5.0 mL, 29 mmol) and 4 (0.84 g, 1.9 mmol) in dimethylformamide (10 mL) was sealed in a screw-capped flask and then heated at 100°C for 48 h. The mixture was cooled and a precipitate was collected. The filtrate

	+ R ₁ +	$RMgX \xrightarrow{6 \text{ or } 2} \qquad $		
ArX	RMgX	Product	Catalyst	Yield [%] ^A
Br	PhMgBr		2 6	58 54
Br			2	53
Br			2 6	38 17
MeO		<i>—</i> ———————————————————————————————————	2 6	51 33
Br OMe		MeO	2	18
Br		_	2	0^{B}
CI			2 6	53 33
CI			2	27
MeO		OMe	2	27
Cl		MeO	2	6
MeO	4-MePhMgCl		2	44
Br OMe		MeO	2	6
MeO		ОМе	2	20
Cl		MeO	2	5

Table 2.Tamao–Kumada–Corriu coupling reactions catalyzed by complexes 6 and 2 (X = Br)Conditions: aryl halide (1.0 mmol), ArMgX (1.5 mmol) and catalyst (0.05 mmol) in THF (1.5 mL); 24 h, 30°C under Ar

^AYield determined by GC-FID using bis(ethyleneglycol) dibutyl ether as an internal standard from an average of two runs. ^BYield determined by ¹H NMR.

was diluted with diethyl ether (50 mL) and the resulting precipitate collected. The solids were combined, and then recrystallized from 1-propanol (~10 mL) to afford a colourless powder (0.79 g, 57 %). $\delta_{\rm H}$ (CDCl₃) 1.04 (t, J7.36, 6H, 2 × CH₃), 1.56 (m, 4H, $2 \times CH_2$), 2.14 (m, 4H, $2 \times CH_2$), 4.03 (s, 6H, OCH₃), 4.08 (s, 6 H, OCH₃), 4.86 (t, J 7.34, 4H, 2 × NCH₂), 7.17 (s, 2H, 2 × benzimidazolyl H4 or H7), 7.93 (s, 2H, $2 \times$ benzimidazolyl H7 or H4), 8.45 (t, J 8.10, 1H, pyridyl H4), 8.67 (d, J 8.0, 2H, pyridyl H3 and H5), 11.88 (s, 2H, NCHN). $\delta_{\rm C}$ (CDCl₃) 13.6 (CH₃), 19.9 (CH₂), 31.4 (CH₂), 48.1 (NCH₂), 57.0 (OCH₃), 57.9 (OCH₃), 94.7 (CH, benzimidazolyl C4 or C7), 97.3 (CH, benzimidazolyl C7 or C4), 117.6 (CH, pyridyl C3/ C5), 123.5 (C, benzimidazolyl C8), 125.7 (C, benzimidazolyl C9), 139.7 (CH, benzimidazolyl C2), 146.1 (CH, pyridyl C4), 146.3 (C, pyridyl C2/C6), 150.1 (C, benzimidazolyl C6 or C5), 151.6 (C, benzimidazolyl C5 or C6). Anal. calc. for C31H39Br2N5O4 · 0.6CH3CH2CH2OH · 1.5H2O: C 51.26, H 6.14, N 9.11. Found: C 51.44, H 5.92, N 8.99%.

1,1'-(2,6-Pyridyl)bis(3-n-octylbenzimidazolium) Dibromide **8**·2Br

A mixture of 1,3-bis(benzimidazol-1-yl)pyridine (8.0 g. 25 mmol) and 1-bromooctane (50 mL, 0.29 mol) in dimethylformamide (70 mL) was heated at 120°C for 24 h and then at 140°C for 48 h. The reaction mixture was cooled and the resulting precipitate was collected and washed with diethyl ether $(2 \times 20 \text{ mL})$ to afford a colourless powder (11.4 g, 63 %). $\delta_{\rm H}$ ((CD₃)₂SO) 0.86 (m, 6H, $2 \times CH_3$), 1.27–1.47 (m, 20H, $10 \times$ CH_2), 2.07 (m, 4H, 2 × CH_2), 4.70 (t, J7.6, 4H, 2 × NCH_2), 7.80 (m, 2H, benzimidazolyl H5 or H6), 7.82 (m, 2H, benzimidazolyl H6 or H5), 8.30 (d, J8.0, 2H, benzimidazolyl H4 or H7), 8.41 (d, J 8.0, 2H, benzimidazolyl H7 or H4), 8.48 (d, J 8.4, 2H, pyridyl H3 and H5), 8.78 (t, J 8.0, 1H, pyridyl H4), 10.90 (s, 2H, NCHN). δ_C ((CD₃)₂SO) 13.9 (CH₃), 22.0 (CH₂), 25.8 (CH₂), 28.5 $(2 \times CH_2)$, 31.2 $(2 \times CH_2)$, 47.4 (NCH₂), 114.3 (CH, benzimidazolyl C7 or C4), 115.7 (CH, benzimidazolyl C4 or C7), 117.9 (CH, pyridyl C3/C5), 127.3 (CH, benzimidazolyl C5 or C6), 127.9 (CH, benzimidazolyl C6 or C5), 129.5 (C, benzimidazolyl C8 or C9), 131.6 (C, benzimidazolyl C9 or C8), 142.9 (CH, benzimidazolyl C2), 144.5 (CH, pyridyl C4), 146.4 (C, pyridyl C2/C6). Anal. calc. for C₃₅H₄₇Br₂N₅: C 60.26, H 6.79, N 10.04. Found: C 59.97, H 6.77, N 9.81 %.

Dibromido[1,1'-(2,6-pyridyl)bis(3-n-butyl-5,6dimethoxybenzimidazolin-2-ylidene)]nickel(II) **6**

A mixture of nickel acetate tetrahydrate (0.52 g, 2.1 mmol) and 5.2Br (1.0 g, 1.4 mmol) in dimethylformamide (4 mL) was heated from room temperature to 110°C over the course of ~ 10 min and then immediately allowed to cool. The resulting precipitate was collected, washed with diethyl ether (10 mL) and recrystallized from nitromethane ($\sim 150 \,\mathrm{mL}$) to yield a purple fine crystalline solid (0.58 g, 54 %). $\lambda_{\text{max}}/\text{nm}$ (ϵ/M^{-1} cm⁻¹) (CH₂Cl₂) 462 (3300); (CH₃OH) 455 (3600). $\delta_{\rm H}$ (CDCl₃ +1 drop CD₃OD) 0.97 (t, J 7.2, 2×6 H, CH₃), 1.48 (m, 4H, $2 \times$ CH₂), 1.85 (m, 4H, 2 × CH₂), 3.92 (s, 6H, OCH₃), 4.11 (s, 6H, OCH_3), 4.80 (t, J 7.6, 4H, 2 × NCH₂), 6.98 (s, 2H, benzimidazolyl H4 or H7), 7.62 (s, 2H, benzimidazolyl H7 or H4), 8.23 (d, J 8.4, 2H, pyridyl H3 and H5), 8.72 (t, J 8.4, 1H, pyridyl H4). $\delta_{\rm C}$ (CDCl₃ + 1 drop CD₃OD) 13.8 (CH₃), 19.9 (CH₂), 32.4 (CH₂), 47.0 (NCH₂), 57.4 (OCH₃), 57.8 (OCH₃), 95.0 (CH, benzimidazolyl C4 or C7), 95.9 (CH, benzimidazolyl C7 or C4), 108.9 (CH, pyridyl C3/C5), 122.4 (C, benzimidazolyl C8), 129.2 (C, benzimidazolyl C9), 147.7 (CH, pyridyl C4), 149.2 (C, benzimidazolyl C5 or C6), 149.7 (C, benzimidazolyl C6 or C5), 150.4 (C, pyridyl C2/C6) 166.4 (C, C–Ni). Anal. calc. for $C_{31}H_{37}Br_2N_5NiO_4$ ·H₂O: C 47.72, H 5.04, N 8.98. Found: C 47.63, H 5.12, N, 8.99 %.

Bromido[1,1'-(2,6-pyridyl)bis(3-n-butyl-5,6dimethoxybenzimidazolin-2-ylidene)]nickel(11) Hexafluorophosphate 7·PF₆

A mixture 6 (0.11 g, 0.17 mmol) and potassium hexafluorophosphate (60 mg, 0.33 mmol) in methanol (20 mL) was warmed for 5 min until an orange precipitate developed. The solid was collected, washed with water (5 mL) and diethyl ether $(2 \times 10 \text{ mL})$, and dried to afford an orange powder (0.10 g), 85%). $\lambda_{max}/nm (\epsilon/M^{-1} cm^{-1}) (CH_2Cl_2) 464 (3200). \delta_H (90\%)$ CDCl₃, 10% (CD₃)₂SO) 0.95 (t, *J* 7.2, 6H, 2 × CH₃), 1.45 (m, $4H, 2 \times CH_2$), 1.82 (m, $4H, 2 \times CH_2$), 3.92 (s, $6H, OCH_3$), 3.97 (s, 6H, OCH₃), 4.76 (m, 4H, $2 \times \text{NCH}_2$), 7.04 (s, 2H, $2 \times$ benzimidazolyl H4 or H7), 7.43 (s, 2H, 2 × benzimidazolyl H7 or H4), 7.97 (d, J 8.4, 2H, pyridyl H3 and H5), 8.40 (t, J 8.4, 1H, pyridyl H4). δ_C (90 % CDCl₃, 10 % (CD₃)₂SO) 13.0 (CH₃), 18.8 (CH₂), 31.5 (CH₂), 45.9 (CH₂), 55.8 (OCH₃), 56.2 (OCH₃), 94.2 (CH, benzimidazolyl C4 or C7), 94.6 (CH, benzimidazolyl C7 or C4), 107.3 (CH, pyridyl C3/C5), 121.5 (C, benzimidazolyl C8 or C9), 128.6 (C, benzimidazolyl C9 or C8), 146.0 (CH, pyridyl C4), 148.4 (C, benzimidazolyl C5 or C6), 148.8 (C, benzimidazolyl C6 or C5), 150.1 (C, pyridyl C2/C6), 165.6 (C, C-Ni). Anal. calc. for C31H37BrN5NiO4PF6·H2O: C 44.05, H 4.65, N 8.29. Found: C 44.04, H 4.61, N 8.26 %.

Bromido[1,1'-(2,6-pyridyl)bis(3-n-butyl-5,6dimethoxybenzimidazolin-2-ylidene)]nickel(11) Tetraphenylborate (7·BPh₄)

A mixture of 6 (0.15 g, 0.19 mmol) and sodium tetraphenylborate (0.14 g, 0.40 mmol) in methanol (10 mL) was warmed for 5 min. The mixture was then diluted with water (10 mL) and the resulting precipitate was collected. The solid was washed with water (10 mL) and methanol (10 mL) to afford an orange solid. The solid was recrystallized by the diffusion of vapours between a diethyl ether solution and a solution of the salt in dichloromethane to afford orange crystals (0.14 g, 71 %). λ_{max}/nm $(\epsilon/M^{-1}\,cm^{-1})$ (CH₃OH) 456 (3000). $\delta_{\rm H}$ (90% CDCl₃, 10% (CD₃)₂SO) 0.90 (t, 6H, J7.2, 2 × CH₃), 1.41 (m, 4H, CH₂), 1.79 (m, 4H, CH₂), 3.82 (s, 6H, OCH₃), 3.86 (s, 6H, OCH₃), 4.72 (t, J 7.6, 4H, NCH₂), 6.67 (t, 4H, J 7.0, 4 × BPh₄ p-ArH), 6.79–6.85 (m, 10H, $8 \times BPh_4$ *m*-ArH, $2 \times benzimidazolyl C4 or C7$), 7.07 (s, 2H, 2 \times benzimidazolyl C4 or C7), 7.13 (d, J 8.3, 2H, pyridyl H3 and H5), 7.23 (br s, 8H, 8 × BPh₄ *o*-ArH), 7.36 (t, *J* 8.2, 1H, pyridyl H4). δ_C (90 % CDCl₃, 10 % (CD₃)₂SO) 13.6 (CH₃), 19.6 (CH₂), 32.2 (CH₂), 46.7 (CH₂), 56.5 (OCH₃), 56.9 (OCH₃), 94.6 (CH, benzimidazolyl C4 or C7), 95.1 (CH, benzimidazolyl C7 or C4), 107.1 (CH, pyridyl C3/C5), 121.5 (CH, BPh₄ C4), 122.3 (C, benzimidazolyl C8), 125.4 (CH, BPh₄ C3/C5), 129.3 (C, benzimidazolyl C9), 135.8 (CH, BPh₄ C2/C6), 146.7 (CH, pyridyl C4), 149.2 (C, benzimidazolyl C5 or C6), 149.6 (benzimidazolyl C6 or C5), 150.6 (C, pyridyl C2/C6), 163.8 (C, q, J49, BPh₄ ipso-Ar) 166.6 (C, C-Ni). Anal. calc. for C₅₅H₅₇BBrN₅NiO₄; C 65.96, H 5.74, N 6.99. Found: C 66.26, H 5.72, N 6.89%. Crystals suitable for X-ray studies were grown by the diffusion of vapours between a diethyl ether solution and a solution of the salt in dichloromethane.

Dibromido[1,1'-(2,6-pyridyl)bis(3-n-octylbenzimidazolin-2-ylidene)]nickel(II), [(CNC)NiBr₂] **9**

A mixture of 8.2Br (1.9 g, 2.8 mmol) and nickel acetate tetrahydrate (0.88 g, 3.1 mmol) in dimethylsulfoxide (11 mL) was heated to 120°C for \sim 30 min and then allowed to cool. The mixture was diluted with diethyl ether (20 mL) and then stirred overnight. The resulting solid was collected and dried under vacuum to afford dark purple crystals (2.5 g, 81 %). λ_{max}/nm $(\varepsilon/M^{-1} \text{ cm}^{-1})$ (CH₂Cl₂) 538 (1600), 453 (3700); (CH₃OH) 434 (2100), 392 (3500). $\delta_{\rm H}$ (CDCl₃ + 1 drop CD₃OD) 0.90 (m, 6H, $2 \times CH_3$), 1.25–1.37 (m, 16H, $8 \times CH_2$), 1.61 (m, 4H, $2 \times CH_2$), 2.10 (m, 4H, 2 × CH₂), 4.82 (m, 4H, 2 × NCH₂), 7.47–7.52 (m, 4H, benzimidazolyl H5 and H6), 7.53 (m, 2H, benzimidazolyl H7), 7.87 (d, J 8.4, 2H, pyridyl H3 and H5), 8.02 (m, 2H, benzimidazolyl H4), 8.40 (t, J 8.4, 1H, pyridyl H4). $\delta_{\rm C}$ (CDCl₃ + 1 drop CD₃OD) 13.9 (CH₃), 22.5 (CH₂), 26.5 (CH₂), 29.1 (CH₂), 29.1 (CH₂), 30.0 (CH₂), 31.7 (CH₂), 47.8 (NCH₂), 108.0 (CH, pyridyl C3/C5), 112.2 (CH, benzimidazolyl C4 or C7), 112.5 (CH, benzimidazolyl C7 or C4), 125.9 (CH, benzimidazolyl C5 or C6), 126.7 (CH, benzimidazolyl C6 or C5), 128.8 (C, benzimidazolyl C8), 135.6 (C, benzimidazolyl C9), 145.8 (CH, pyridyl C4), 150.6 (C, pyridyl C2/C6), 171.9 (C, C-Ni). Anal. calc. for C35H45Br2N5Ni: C 55.73, H 6.01, N 9.28. Found: C 55.42, H 6.24, N, 9.11 %. Crystals suitable for X-ray studies were grown by the diffusion of vapours between a solution of THF and a solution of the complex in methanol.

Bromido[1,1'-(2,6-pyridyl)bis(3-n-octylbenzimidazolin-2-ylidene)]nickel(11) Hexafluorophosphate, [(CNC)NiBr]PF₆ **10**·PF₆

A mixture of 9 (0.16 g, 0.22 mmol) and potassium hexafluorophosphate (0.68 g, 3.7 mmol) in methanol (10 mL) was heated at reflux for 5 min. Water (9 mL) was added and the mixture was heated for a further 5 min. The reaction was allowed to cooled to room temperature, and then cooled in an ice-bath. The resulting precipitate was collected, washed with methanol (10 mL) and water (10 mL), and dried to afford a yellow solid (0.078 g, 43 %). $\lambda_{\text{max}}/\text{nm} (\epsilon/\text{M}^{-1} \text{ cm}^{-1}) (\text{CH}_2\text{Cl}_2) 432 (1700)$, 387 (2900); (CH₃OH) 440 (1400), 394 (2400). δ_H (90 % CDCl₃, 10% (CD₃)₂SO) 0.57 (m, 6H, 2 × CH₃), 1.0–1.21 (m, 20H, $10 \times CH_2$, 1.65 (m, 4H, 2 × CH₂), 4.60 (m, 4H, 2 × NCH₂), 7.26-7.34 (m, 4H, benzimidazolyl H5 and H6), 7.38 (d, J 7.2, 2H, benzimidazolyl H4 or H7), 7.73 (d, J8.0, 2H, pyridyl H3 and H5) 7.85 (d, J7.6, 2H, H7 or H4), 8.20 (t, J 8.4, 1H, pyridyl H4). δ_C (90 % CDCl₃, 10 % (CD₃)₂SO) 13.4 (CH₃), 21.6 (CH₂), 25.8 (CH₂), 27.4 (CH₂), 28.3 (CH₂), 29.6 (CH₂), 30.8 (CH₂), 46.7 (NCH₂), 107.6 (CH, pyridyl C3/C5), 111.8 (CH, benzimidazolyl C4 or C7), 111.9 (CH, benzimidazolyl C7 or C4), 125.7 (CH, benzimidazolyl C5 or C6), 126.3 (CH, benzimidazolyl C6 or C5), 128.0 (C, benzimidazolyl C8), 135.0 (C, benzimidazolyl C9), 145.9 (CH, pyridyl C4), 150.4 (C, pyridyl C2/C6), 169.8 (C, C–Ni). Anal. calc. for $C_{35}H_{45}BrN_5NiPF_6$: C 51.31, H 5.54, N 8.55. Found: C 51.55, H 5.36, N, 8.42 %.

Catalysis Studies

Typical procedure for nickel-catalyzed Tamao–Kumada– Corriu coupling reaction: Grignard reagent (1.5 mL, 1 M in tetrahydrofuran) was added to a mixture of aryl halide (1 mmol), nickel complex (5 mol %, 0.05 mmol) and bis(ethyleneglycol) dibutyl ether (45 mg) in an argon-purged tube. The reaction was heated at 30°C for 24 h in a Radleys parallel synthesizer. After cooling, the reaction mixture was quenched with HCl (2 mL, 1 M) and extracted with ethyl acetate $(2 \times 5 \text{ mL})$ and dried with CaCl₂. Product yields were determined by GC.

X-Ray Structure Determinations

The crystal data for 9 and 7.BPh₄ ·Et₂O are summarized below, with the structures depicted in Figs 3 and 4, where ellipsoids have been drawn at the 50% probability level, and also in Figs 5-7. Selected coordination geometries are shown in Table 1. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Xcalibur diffractometer (for 9) or an Oxford Diffraction Gemini diffractometer (for 7.BPh₄), both fitted with Mo Ka radiation. Following analytical absorption corrections and solution by direct methods, the structures were refined against F^2 with full-matrix least-squares using the program *SHELXL-97*.^[28] Anisotropic displacement parameters were employed for the non-hydrogen atoms. All H atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atom. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (http://www.ccdc.cam.ac.uk), CCDC No. 862648 (9) and 862649 (7·BPh₄·Et₂O).

Crystal Data for 9

 $\begin{array}{l} C_{35}H_{45}Br_2N_5Ni, M=754.29, \mbox{triclinic, space group } P\bar{1}, a=\\ 9.6767(4), b=12.7864(6), c=13.9272(7) \mbox{Å}; \alpha=90.991(4),\\ \beta=99.678(4), \gamma=102.541(4)^\circ; V=1655.57(13) \mbox{Å}^3; Z=2;\\ D_c=1.513 \mbox{ Mg m}^{-3}; \mu=3.032 \mbox{ mm}^{-1}; \mbox{ specimen: } 0.26\times0.12 \\ \times 0.02 \mbox{ mm}^3; \mbox{$\theta_{max}=33.0^\circ$; 20784 reflections collected; 11527} \\ \mbox{ unique } (R_{\rm int}=0.0338); T_{\rm max/min}=0.95/0.65; GoF=1.085;\\ R_1=0.0486, wR_2=0.0824 \ [I>2\sigma(I)]. \end{array}$

Crystal Data for $7 \cdot BPh_4 \cdot Et_2O$

 $\begin{array}{l} C_{59}H_{67}BBrN_5NiO_5, \ M = 1075.61, \ triclinic, \ space \ group \ P\bar{1}, \\ a = 13.3548(4), \ b = 13.9625(4), \ c = 17.3927(5) \ \text{\AA}; \ \alpha = 91.903 \\ (2), \ \beta = 110.563(3), \ \gamma = 117.055(3)^\circ; \ V = 2630.82(18) \ \text{\AA}^3; \\ Z = 2; \ D_c = 1.358 \ \text{Mg m}^{-3}; \ \mu = 1.183 \ \text{mm}^{-1}; \ \text{specimen:} \\ 0.52 \times 0.15 \times 0.12 \ \text{mm}^3; \ \theta_{\text{max}} = 35.0^\circ; \ 63735 \ \text{reflections collected}; \ 21593 \ \text{unique} \ (R_{\text{int}} = 0.0451); \ T_{\text{max/min}} = 0.468/0.329; \\ GoF = 0.903; \ R_1 = 0.0414, \ wR_2 = 0.0970 \ [I > 2\sigma(I)]. \end{array}$

Supplementary Material

Images of 6, 9, $7 \cdot PF_6$ and $10 \cdot PF_6$ in the solid-state form are provided in Supplementary Material.

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References

- D. Pugh, A. A. Danopoulos, Coord. Chem. Rev. 2007, 251, 610. doi:10.1016/J.CCR.2006.08.001
- [2] M. Poyatos, J. A. Mata, E. Peris, *Chem. Rev.* 2009, 109, 3677. doi:10.1021/CR800501S
- [3] D. Yuan, H. Tang, L. Xiao, H. V. Huynh, *Dalton Trans.* 2011, 40, 8788. doi:10.1039/C1DT10269A

- [4] C. Y. Wong, L. M. Lai, P. K. Pat, L. H. Chung, Organometallics 2010, 29, 2533. doi:10.1021/OM100183A
- [5] C.-S. Lee, S. Sabiah, J.-C. Wang, W.-S. Hwang, I. J. B. Lin, Organometallics 2010, 29, 286. doi:10.1021/OM9008247
- [6] F. Jean-Baptiste dit Dominique, H. Gornitzka, A. Sournia-Saquet, C. Hemmert, *Dalton Trans.* 2009, 340.
- [7] A. Mrutu, K. I. Goldberg, R. A. Kemp, *Inorg. Chim. Acta* 2010, 364, 115. doi:10.1016/J.ICA.2010.08.049
- [8] A. Mrutu, D. A. Dickie, K. I. Goldberg, R. A. Kemp, *Inorg. Chem.* 2011, 50, 2729. doi:10.1021/IC200029C
- [9] T. Tu, J. Malineni, K. H. Dötz, Adv. Synth. Catal. 2008, 350, 1791. doi:10.1002/ADSC.200800244
- [10] D. H. Brown, G. L. Nealon, P. V. Simpson, B. W. Skelton, Z. Wang, Organometallics 2009, 28, 1965. doi:10.1021/OM801144M
- [11] T. Tu, X. Bao, W. Assenmacher, H. Peterlik, J. Daniels, K. H. Dötz, *Chemistry* 2009, 15, 1853. doi:10.1002/CHEM.200802116
- [12] T. Tu, X. Feng, Z. Wang, X. Liu, Dalton Trans. 2010, 10598. doi:10.1039/C0DT01083A
- [13] D. H. Brown, B. W. Skelton, *Dalton Trans.* 2011, 8849. doi:10.1039/ C1DT10928F
- [14] T. Tu, H. Mao, C. Herbert, M. Z. Xu, K. H. Dötz, *Chem. Commun.* 2010, 7796. doi:10.1039/C0CC03107K
- [15] K. Inamoto, J.-i. Kuroda, K. Hiroya, Y. Noda, M. Watanabe, T. Sakamoto, Organometallics 2006, 25, 3095. doi:10.1021/OM060043+
- [16] K. Inamoto, J.-i. Kuroda, E. Kwon, K. Hiroya, T. Doi, J. Organomet. Chem. 2009, 694, 389. doi:10.1016/J.JORGANCHEM.2008.11.003

- [17] D. Pugh, A. Boyle, A. A. Danopoulos, *Dalton Trans.* 2008, 1087. doi:10.1039/B715769J
- [18] M. V. Baker, D. H. Brown, P. V. Simpson, B. W. Skelton, A. H. White, *Dalton Trans.* 2009, 7294. doi:10.1039/B908613G
- [19] M. V. Baker, D. H. Brown, P. V. Simpson, B. W. Skelton, A. H. White, *Eur. J. Inorg. Chem.* **2009**, 1977. doi:10.1002/EJIC.200801154
- [20] G. Zou, W. Huang, Y. Xiao, J. Tang, New J. Chem. 2006, 30, 803. doi:10.1039/B601833E
- [21] P. V. Simpson, B. W. Skelton, D. H. Brown, M. V. Baker, *Eur. J. Inorg. Chem.* 2011, 1937. doi:10.1002/EJIC.201001318
- [22] J. Nasielski, N. Hadei, G. Achonduh, E. A. B. Kantchev, C. J. O'Brien, A. Lough, M. G. Organ, *Chemistry* **2010**, *16*, 10844. doi:10.1002/ CHEM.201000138
- [23] N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, Org. Lett. 2005, 7, 1991. doi:10.1021/OL050471W
- [24] D. T. Rosa, R. A. Reynolds III, S. M. Malinak, D. Coucouvanis, *Inorg. Synth.* 2002, 33, 112.
- [25] J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, Organometallics 2002, 21, 700. doi:10.1021/OM010852N
- [26] K. Inamoto, J.-i. Kuroda, T. Sakamoto, K. Hiroya, Synthesis 2007, 2853. doi:10.1055/S-2007-983845
- [27] H. V. Huynh, R. Jothibasu, Eur. J. Inorg. Chem. 2009, 1926. doi:10.1002/EJIC.200801149
- [28] G. M. Sheldrick, Acta Crystallogr. A 2008, 64, 112. doi:10.1107/ S0108767307043930