Organic & Biomolecular Chemistry

www.rsc.org/obc

PAPER

Well-defined [Rh(NHC)(OH)] complexes enabling the conjugate addition of arylboronic acids to α,β-unsaturated ketones†

Byron J. Truscott, George C. Fortman, Alexandra M. Z. Slawin and Steven P. Nolan*

The synthesis and catalytic activity of three well-defined monomeric rhodium(I) hydroxide complexes bearing *N*-heterocyclic carbene (NHC) ligands are reported. [Rh(cod)(ICy)(OH)] promoted the 1,4-addition of arylboronic acids to cyclic enones, with TONs and TOFs of 100,000 and 6,600 h^{-1}, respectively, at 0.001 mol% catalyst loadings. Mechanistic studies permitted the isolation of a phenylrhodium intermediate.

The ability to manipulate and assemble C–C bonds is paramount in organic chemistry. One such transformation is the conjugate addition of organometallic compounds to activated alkenes. In 1997, a practical method for rhodium-catalyzed addition of organoboron reagents to α,β-unsaturated carbonyls was disclosed by Miyaura.[1] Since then, efforts have focused on tailoring rhodium complexes to improve both activity and selectivity in this transformation, with particular attention paid to ancillary ligands.[2]

The generally accepted trend regarding ancillary ligand effects in Rh-catalyzed 1,4-addition is that activity increases with electron-poor ligands,[3] such as chiral dienes,[2d,2g,2i,4] diphosphines,[3] phosphoramidites[2f,2h,5] and BINAP-type ligands.[6] Recently, the activity of the electron-poor chiral diphosphine, MeO-F$_{12}$–BIPHEP on [RhCl(C$_2$H$_4$)$_2$]$_2$ was reported by Sakai,[3b] showing very high activity (TON and TOF of 320,000 and 53,000 h^{-1}, respectively at catalyst loading of 2.5×10^{-4} mol%), attributed to the superior π-accepting capability of the ligand, thereby inducing favourable conditions for transmetalation between boron and rhodium.[3a]

Mechanistic investigations by Hayashi,[6b] using [Rh(acac)((*S*)-binap)], identified a rhodium hydroxide species (formed *in situ* in an aqueous medium) as the active catalyst. Well-defined rhodium hydroxide complexes generally show improved efficiency compared to those prepared *in situ*.[6b]

Our recent success with well-defined gold[7] and copper[8] hydroxide complexes prompted us to examine whether the general synthetic methodology developed could be extended to rhodium. Reports of stable, well-defined monomeric Rh(I)–OH complexes are rare.[9] As Rh–OH bearing electron-poor ancillary ligands are highly unstable,[3a] the active species is usually prepared *in situ*, either by reaction of [Rh(cod)(μ-OH)]$_2$ with the desired ligand, or by transformation of the precatalyst in the presence of a base in aqueous media. Herein, we report that a number of strongly electron-donating *N*-heterocyclic carbenes (NHCs),

namely IPr (**2a**), ICy (**2b**) and IDD (**2c**) (Scheme 1), can stabilize the Rh–OH moiety and lead to the isolation of well-defined monomeric rhodium(I) hydroxide complexes (**3a–c**, Scheme 1).[10] Complexes **3a–c** were synthesized in a one-pot process by reacting [Rh(cod)Cl]$_2$ (**1**) with the free NHCs **2a–c** in the presence of CsOH (Scheme 1).
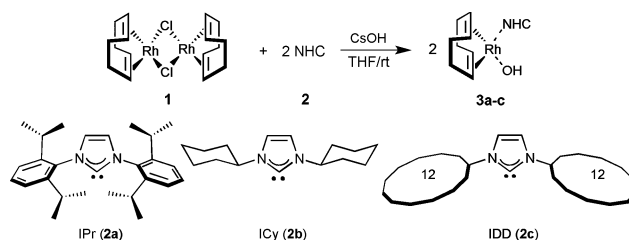
Scheme 1 Preparation of [Rh(cod)(NHC)(OH)] complexes **3a–c**.

Complexes **3a–c** are stable under inert conditions and were fully characterized. Single crystal X-ray analysis of **3a** and **3b** unambiguously confirmed the monomeric square planar geometry of the complexes.[10] Fig. 1 presents ORTEPs of **3a** and **3b**. Of note, the Rh–OH bonds were found to be 2.030(4) Å (**3a**) and 2.036(2) Å (**3b**), which is typical of M–OH bond lengths.[7b,11]
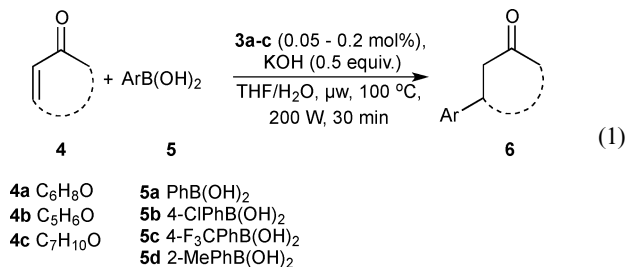

Fig. 1 ORTEPs of [Rh(cod)(IPr)(OH)] **3a** and [Rh(cod)(ICy)(OH)] **3b**, showing 50% thermal ellipsoid probability. Selected distances (Å) for **3a**: Rh1–NHC = 2.046(6), Rh1–O1 = 2.030(4) and **3b**: Rh1–NHC = 2.022(3), Rh1–O1 = 2.036(2).

EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, U.K.. E-mail: snolan@st-andrews.ac.uk

† Electronic supplementary information (ESI) available: Synthetic and structural data. See DOI: 10.1039/c1ob06112g
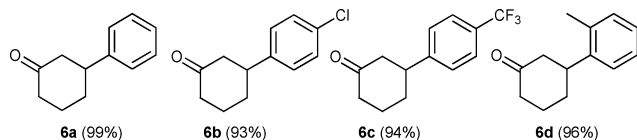
With complexes **3a–c** in hand, we turned our attention to the conjugate addition of arylboronic acids to α,β-unsaturated carbonyls. The addition of phenylboronic acid **5a** to cyclohexenone **4a** (eqn (1)) was selected as benchmark reaction. In a reaction conducted at room temperature, the desired product was obtained in 54% yield after 1 h with a catalyst loading of 0.2 mol% using [Rh(cod)(ICy)(OH)] **3b**.

$$\text{(1)}$$

4a C$_6$H$_8$O   **5a** PhB(OH)$_2$
4b C$_5$H$_6$O   **5b** 4-ClPhB(OH)$_2$
4c C$_7$H$_{10}$O   **5c** 4-F$_3$CPhB(OH)$_2$
       5d 2-MePhB(OH)$_2$

To rapidly afford optimized conditions and simultaneously test the thermal stability of our complexes under catalytic conditions, transformations were examined under microwave irradiation. Testing the well-defined **3a–c** at 0.05 mol% under conditions illustrated in eqn (1), the desired product (**6a**) was obtained in 59 (using **3a**), 86 (using **3b**) and 74% (using **3c**) isolated yield. The stronger σ-donating cycloalkyl-substituted NHC complexes **3b** and **3c** were found to outperform the aryl-substituted analogue **3a**. Among the cycloalkyl-NHCs, the complex containing the smaller[12] ICy ligand **2b** resulted in the highest yields. Under these reaction conditions, the catalysts appear very tolerant of elevated reaction temperatures.

Having identified [Rh(cod)(ICy)(OH)] **3b** as an active promoter for the 1,4-addition, it was tested at homeopathic quantities, achieving full conversion after 12 h under conventional heating (100 °C) at 0.001 mol%, with a TON of 100,000 and TOF of 6,600 h^{-1}. Gratifyingly, catalyst **3b** proved to be exceedingly stable, as gauged by ^{1}H NMR even after 16 h in C$_6$D$_6$ solution open to air.

A scope for the transformation was next examined to demonstrate the versatility of **3b**, we examined the coupling of arylboronic acids **5a–d**, substituted with activating and deactivating groups to three cyclic enones **4a–c** of differing ring size under optimized conditions (eqn (1)). Fig. 2 shows the products **6a–d**, with isolated yields, as representatives of the full scope, which can be found in the SI. Cyclopentenone **4b** and cycloheptenone **4c** proved more difficult substrates than cyclohexenone **4a**, particularly when reacted with the deactivated 4-chlorophenylboronic acid **5b** and 4-(trifluoromethyl)phenylboronic acid **5c**. The sterically demanding, 2-methylphenylbonic acid **5d** was found to give high yields with all enones examined. Phenylboronic acid pinacol ester and potassium phenyltrifluoroborate were also successfully used as an aryl transfer source. Yields of 89% and 87% respectively were

obtained using these two reagents,[13] further proving the versatility of the catalyst and the method employed.

A series of stoichiometric reactions were then conducted to shed light on the mechanism at play in this transformation. [Rh(cod)(ICy)Ph] **7** was prepared from [Rh(cod)(ICy)(OH)] **3b** and phenylboronic acid **5a** in C$_6$H$_6$ in a very rapid transformation as shown in eqn (2). ^{1}H NMR analysis confirmed complete conversion of **3b** into **7** after only 15 min at room temperature.

$$\text{(2)}$$
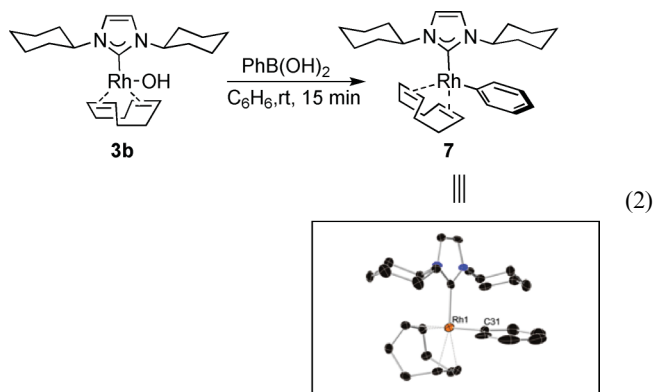
When the reaction was repeated with [Rh(cod)(IPr)(OH)] **3a** only 50% conversion as evaluated by ^{1}H NMR was noted after 16 h.

This difference in the rate of transmetalation between **3a** and **3b** may very well account for the lower activity of **3a** observed during catalyst screening, the ligand principal effect being steric. The phenylrhodium **7** was fully characterized and single crystal X-ray analysis (eqn (2)) unambiguously confirmed the square planar arrangement about the Rh center.[10] Bond lengths and angles were found to agree with similar Rh-aryl complexes found in the literature.[14]

Hartwig[15] has shown that transmetalation of an aryl moiety from boron to rhodium occurs *via* formation of a rhodium aryl-boronate (RhOB(OH)Ar) species, followed by β-aryl elimination to give the arylrhodium complex. The reaction with **3b** is too rapid to observe this intermediate but might be observable using a Rh-species with a slower transmetalation rate. The phenylrhodium complex **7** was used to catalyze the conjugate addition of phenyl-boronic acid **5a** and cyclohexenone **4a** under microwave conditions and resulted in nearly identical activity to that of **3a** (98%). Additionally, the reaction of **7** with 2 equivalents of cyclohexenone **4a** in THF/H$_2$O resulted in the formation of **6a** in a yield of 72% under catalytic conditions. These experiments strongly suggest that the phenylrhodium **7** is an important intermediate along the catalytic pathway. Reaction between **7** and cyclohexenone **4a** in various solvents was very slow, even at elevated temperatures, indicating the allyl formation as the possible rate-determining step. This is in contrast to previous studies reporting transmetalation as the rate-determining step.[16]

The role played by the base in the reaction is still somewhat unclear. Several reports have indicated that base is essential for the *in situ* preparation of the hydroxorhodium species,[2e,3a,17] where precatalysts such as [RhCl(cod)]$_2$ or [Rh(acac)(C$_2$H$_4$)$_2$] are used. Inorganic bases have been shown to accelerate transmetalation between organoboron reagents and metal complexes,[2c] *via* attack upon the boronic acid to form an anionic organoboronate,

Fig. 2 Conjugated products from the addition of arylboronic acids (**5a–d**) to cyclohexenone **4a**. Reaction conditions: **3b** (0.2 mol%), KOH (0.5 equiv.), THF/H$_2$O, μw, 100 °C, 200 W, 30 min. Isolated yields are average of two runs, after flash chromatography. See ESI for details of full scope.†

which subsequently coordinates the metal centre, promoting transmetalation. This concept has been explored by Suzuki[18] in Pd-catalyzed cross-coupling and supported by DFT studies.[19] The theory has been extended to Rh-systems[2c] but is not yet supported experimentally. Miyaura and co-workers[2e] suggested that the base might play a further role in facilitating hydrolysis of the enolate intermediate. To examine the role of the base, our present systems, by already bearing the base, may facilitate analysis of stoichiometric reactions and shed light on its role under catalytic conditions. Using a [Rh(cod)(NHC)(OH)] catalyst eliminates the need for *in situ* preparation of a Rh-(OH) and the swift transformation from Rh–OH **3b** to Rh–Ph **7** (eqn (2)) suggests that base might not be required up to that point. However, catalysis in the absence of a base produces the conjugated product in less than 10% yield. Reactions performed with D_2O resulted in deuterium incorporation into the conjugated product **6a**, α- to the carbonyl (confirmed by NMR studies, see ESI†). These data support hydrolytic cleavage of **6a** by H_2O from the rhodium center.

A proposed mechanism is presented in Scheme 2 which is consistent with the one proposed by Hayashi.[6b] Activation of the arylboronic acid by the Rh–OH **3b** forms the Rh-aryl complex **7**, followed by enone insertion to most likely give the unobserved transient oxa-π-allyl Rh intermediate **8**. Hydrolysis of **8** completes the cycle with release of the 1,4-addition product **6a** and reformation of the Rh–OH complex.
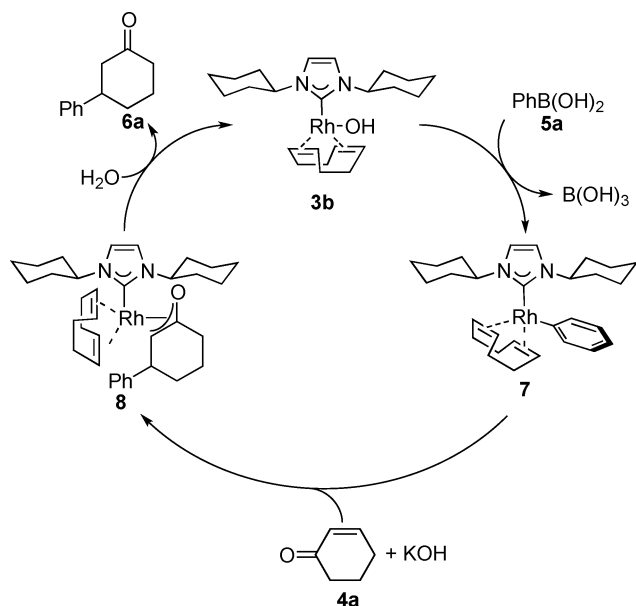
Scheme 2 Proposed catalytic cycle for Rh-catalyzed 1,4-addition.

In conclusion, three well-defined monomeric rhodium(I) hydroxide complexes **3a–c** bearing NHC ligands **1a–c** have been prepared and exhibit high stability. The [Rh(cod)(ICy)(OH)] **3b** complex is a very efficient catalyst in the conjugate addition of arylboronic acids to cyclic enones, promoting full conversion at 0.001 mol%, with TON and TOF 100,000 and 6,600 h⁻¹, respectively. This high activity/productivity is in contrast with previous reports where ancillary ligands with weaker electron donating properties were found to lead to optimal catalytic conversions.[3] Furthermore, potassium aryltrifluoroborates and aryl boronic esters were also found to serve as viable reaction partners in the conjugate addition, leading to high conversions. Mechanistic studies were performed, enabling isolation of the phenylrhodium intermediate **7**. Further catalytic potential of this novel well-defined Rh-hydroxide is currently under investigation.

Experimental section

General considerations

Synthesis of Rh-complexes was performed inside an MBraun Glovebox under inert conditions. All reagents were supplied by Aldrich and used without further purification and solvents were distilled and dried as required. NMR data was obtained using either a Bruker 400 MHz or 300 MHz spectrometer at 303 K in the specified deuterated solvent. All chemical shifts are given in ppm and coupling constants in Hz. Spectra were referenced to residual protonated solvent signals (C_6D_6:1H δ 7.16 ppm, ¹³C δ 128.06 ppm). Reactions under microwave irradiation were performed in a CEM Discover single-mode microwave apparatus, producing controlled irradiation at 2450 MHz. Reaction times refer to hold times at the indicated temperature and not total irradiation times with constant cooling *via* propelled air flow at a set power of 200 W. Elemental analyses were performed at the London Metropolitan University.

Representative synthesis of [Rh(cod)(ICy)(OH)] 3a–c

[Rh(cod)Cl]₂ **1** (100 mg, 0.2 mmol), free carbene **2a–c** (0.4 mmol) and CsOH (0.8 mmol) were stirred in THF (5 mL) overnight. The suspension was filtered and the eluent concentrated *in vacuo*. The resultant solid was washed with hexane (3 × 10 mL) and dried *in vacuo* to give [Rh(NHC)(ICy)(OH)] **3a–c**.

[Rh(cod)(IPr)(OH)] 3a. (190.0 mg, 75.8%) As a yellow solid; ¹H NMR (300 MHz, C_6D_6): δ 7.27–7.35 (2H, m, ArH), 7.20–7.26 (4H, m, ArH), 6.59 (2H, s, NCH), 4.29–4.42 (2H, m, cod-CH), 3.35 (4H, m, cod-CH₂), 2.99 (2H, d, J = 2.5, cod-CH), 1.83–2.02 (4H, m, cod-CH₂), 1.59–1.72 (2H, m, CH), 1.49 (12H, d, J = 6.6, CH₃), 1.46–1.54 (2H, m, CH), 1.06 (12H, d, J = 6.9, CH₃); ¹³C NMR (75 MHz, C_6D_6): δ 191.8 (d, $^1J_{RhC}$ = 56.3), 147.0, 137.3, 129.9, 123.9, 92.5 (d, $^1J_{RhC}$ = 9.0), 63.5 (d, $^1J_{RhC}$ = 12.0), 33.7, 29.0, 28.9, 26.5, 23.2; Anal. Calcd for $C_{35}H_{49}N_2ORh$ (MW 621.08): C, 68.17, H, 8.01, N, 4.54. Found: C, 68.26; H, 7.87; N, 4.38.

[Rh(cod)(ICy)(OH)] 3b. (163 mg, 84.4%) As a yellow solid; ¹H NMR (300 MHz, C_6D_6) δ 6.42 (2H, s, NCH), 5.73 (2H, tt, J = 12.1, 3.9, cod-CH), 5.13–5.30 (2H, m, cod-CH), 3.08 (2H, dd, J = 5.2, 2.2, NCH), 2.47–2.63 (4H, m, cod-CH₂), 2.30 (2H, d, J = 12.2, CH₂), 2.12 (2H, quint, J = 6.9, CH₂), 1.84–2.00 (4H, m, cod-CH₂), 1.34–1.73 (10H, m, CH₂), 1.27 (2H, qd, J = 12.5, 3.6, CH₂), 1.10 (2H, qd, J = 12.5, 3.8, CH₂), 0.94 (2H, qt, J = 12.8, 3.7, CH₂); ¹³C NMR (75 MHz, C_6D_6) δ 186.3 (d, $^1J_{RhC}$ = 57.0), 117.2, 97.4 (d, $^1J_{RhC}$ = 8.3), 66.7 (d, $^1J_{RhC}$ = 12.8), 60.5, 34.9, 34.5, 34.4, 29.5, 26.4, 26.0, 25.7. Anal. Calcd for $C_{23}H_{37}N_2ORh$ (MW 460.46): C, 59.99; H, 8.10; N, 6.08. Found: C, 59.90, H, 8.02; N, 5.97.

[Rh(cod)(IDD)(OH)] 3c. (180.0 mg, 70.9%) As a yellow solid; ¹H NMR (300 MHz, C_6D_6) δ 6.45 (2H, s, NCH), 5.83–5.98 (2H, m, cod-CH), 5.20 (2H, m, cod-CH), 3.04–3.15 (2H, m, NCH), 2.53–2.72 (4H, m, cod-CH₂), 2.01–2.13 (4 H, m, CH₂), 1.87–1.97 (4H, m, cod-CH₂), 1.68–1.84 (10H, m, CH₂), 1.15–1.54 (30H, m,

This journal is © The Royal Society of Chemistry 2011

CH_2); ^{13}C NMR (75 MHz, C_6D_6): δ 187.1(d, [1]J_{RhC} = 57.0), 117.2, 96.0 (d, [1]J_{RhC} = 8.3), 62.4 (d, [1]J_{RhC} = 12.8), 57.4, 34.4, 32.2, 31.7, 29.4, 25.0, 24.7, 24.3, 24.1, 24.0, 23.7, 23.2, 22.7, 22.5; Anal. Calcd for $C_{35}H_{61}N_2ORh$ (MW 628.78): C, 66.86; H, 9.78; 4.46. Found: C, 66.88; H, 9.65; N, 4.46.

Preparation of [Rh(cod)(ICy)Ph] 7. [Rh(cod)(ICy)(OH)] **3b** (500 mg, 1.08 mmol) and phenylboronic acid **5a** (130.0 mg, 1.08 mmol) were stirred in C_6H_6 (5 mL) for 1 h. The solution was filtered and reduced *in vacuo* to a yellow solid. The solid was dissolved in hexane (20 mL) and filtered before being dried *in vacuo* to give [Rh(cod)(ICy)Ph] **7** (488.3 mg, 87.4%) as an orange solid; ^{1}H NMR (400 MHz, C_6D_6): δ 7.81 (2H, d, J = 7.7, ArH), 7.23 (2H, t, J = 7.4, ArH), 6.99 (1H, t, J = 7.3, ArH), 6.21 (2H, s, NCH), 5.47 (2H, tt, J = 12.1, 3.5, cod-CH), 4.74 (2H, d, J = 2.7, cod-CH), 4.08 (2H, br.s., NCH), 2.45 (4H, m, cod-CH_2), 2.15 (4H, d, J = 8.9, CH_2), 1.99 (2H, d, J = 12.4, CH_2), 1.92 (2H, d, J = 12.1, CH_2),1.66 (4H, t, J = 12.7, CH_2), 1.55 (2H, d, J = 13.5, CH_2), 1.41–1.52 (4H, m, CH_2), 1.22 (2H, qd, J = 12.5, 3.6, CH_2), 1.06 (2H, qd, J = 12.5, 3.6, CH_2), 0.90–0.99 (2H, m, CH_2); ^{13}C NMR (75 MHz, C_6D_6): δ 189.9 (d, [1]J_{RhC} = 60.2), 177.4 (d, [1]J_{RhC} = 36.0), 138.2, 126.2, 121.0, 116.5, 87.5 (d, [1]J_{RhC} = 9.1), 81.7 (d, [1]J_{RhC} = 7.0), 60.4, 35.2, 34.7, 32.0, 31.9, 26.4, 25.9, 25.7; Anal. Calcd for $C_{29}H_{41}N_2Rh$ (MW 521.56): C, 66.91; H, 7.94; N, 5.38. Found: C, 66.81, H, 7.99 N, 5.31.

General procedure for catalysis. Arylboronic acid **5a–d** (0.6 mmol), [Rh(cod)(ICy)(OH)] **3b** (0.46 mg, 1.0 μmol, 0.20 mol%) and KOH (14 mg, 0.25 mmol) were charged to a 10 mL microwave vial with THF (1 mL) inside a glove box. The vial was sealed and removed to air, where it was charged with cyclic enone **4a–c** (0.50 mmol) and H_2O (100 μL) before being irradiated in the microwave at 100 °C, 200 W for 30 min. The resultant mixture was flash chromatographed (hexane-ethyl acetate) to afford the addition product **6a–l**.

References

1 M. Sakai, H. Hayashi and N. Miyaura, *Organometallics*, 1997, **16**, 4229.
2 (*a*) T. Hayashi and K. Yamasaki, *Chem. Rev.*, 2003, **103**, 2829; (*b*) T. Hayashi, *Pure Appl. Chem.*, 2004, **76**, 465; (*c*) K. Fagnou and M. Lautens, *Chem. Rev.*, 2003, **103**, 169; (*d*) R. Shintani and T. Hayashi, *Aldrichimica Acta*, 2009, **42**, 31; (*e*) R. Itooka, Y. Iguchi and N. Miyaura, *J. Org. Chem.*, 2003, **68**, 6000; (*f*) J. Boiteau, A. J. Minnaard and B. L. Feringa, *J. Org. Chem.*, 2003, **68**, 9481; (*g*) F. Chen, A. Kina and T. Hayashi, *Org. Lett.*, 2006, **8**, 341; (*h*) K. Kurihara, N. Sugishita, K.

Oshita, D. Piao, Y. Yamamoto and N. Miyaura, *J. Organomet. Chem.*, 2007, **692**, 428; (*i*) K. Okamoto, T. Hayashi and V. H. Rawal, *Org. Lett.*, 2008, **10**, 4387; (*j*) Y. Ma, C. Song, C. Ma, Z. Sun, Q. Chai and M. B. Andrus, *Angew. Chem., Int. Ed.*, 2003, **42**, 5871.
3 (*a*) T. Korenaga, R. Maenishi, K. Hayashi and T. Sakai, *Adv. Synth. Catal.*, 2010, **352**, 3247; (*b*) T. Korenaga, K. Osaki, R. Maenishi and T. Sakai, *Org. Lett.*, 2009, **11**, 2325; (*c*) F. Berhal, O. Esseiva, C. Martin, H. Tone, J. Genet, T. Ayad and V. V. Ratovelomanana-Vidal, *Org. Lett.*, 2011, **13**, 2806.
4 T. Hayashi, K. Ueyama, N. Tokunaga and K. Yoshida, *J. Am. Chem. Soc.*, 2003, **125**, 11508.
5 J. Boiteau, R. Imbos, A. J. Minnaard and B. L. Feringa, *Org. Lett.*, 2003, **5**, 681.
6 (*a*) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai and N. Miyaura, *J. Am. Chem. Soc.*, 1998, **120**, 5579; (*b*) T. Hayashi, M. Takahashi, Y. Takaya and M. Ogasawara, *J. Am. Chem. Soc.*, 2002, **124**, 5052; (*c*) K. Lukin, Q. Zhang and M. R. Leanna, *J. Org. Chem.*, 2009, **74**, 929; (*d*) A. Kina, H. Iwamura and T. Hayashi, *J. Am. Chem. Soc.*, 2006, **128**, 3904; (*e*) W. Yuan, L. Cun, A. Mi, Y. Jiang and L. Gong, *Tetrahedron*, 2009, **65**, 4130; (*f*) W. Yuan, L. Cun, L. Gong, A. Mi and Y. Jiang, *Tetrahedron Lett.*, 2005, **46**, 509.
7 (*a*) I. I. F. Boogaerts and S. P. Nolan, *J. Am. Chem. Soc.*, 2010, **132**, 8858; (*b*) S. Gaillard, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.*, 2010, **46**, 2742.
8 (*a*) I. I. F. Boogaerts, G. C. Fortman, M. R. L. Furst, C. S. J. Cazin and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2010, **49**, 8674; (*b*) G. C. Fortman, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2010, **29**, 3966.
9 For a review on Transition Metal-OH complexes, see: (*a*) H. Roesky, S. Singh, K. K. M. Yusuff, J. A. Maguire and N. S. Hosmane, *Chem. Rev.*, 2006, **106**, 3813; (*b*) S. M. Kloek, M. D. Heinekey and K. I. Goldberg, *Angew. Chem., Int. Ed.*, 2007, **46**, 4736.
10 CCDC-823666 (**3a**), CCDC-823667 (**3b**) and CCDC-823668 (**7**) contain the supplementary crystallographic data for this contribution. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.
11 R. S. Ramón, S. Gaillard, A. Poater, L. Cavallo, A. M. Z. Slawin and S. P. Nolan, *Chem.–Eur. J.*, 2011, **17**, 1238.
12 For a discussion of NHC steric parameters see: (*a*) H. Clavier and S. P. Nolan, *Chem. Commun.*, 2010, **46**, 841; (*b*) P. de Frémont, N. Marion and S. P. Nolan, *Coord. Chem. Rev.*, 2009, **253**, 862For a review on Late Transition Metal-NHC complexes in catalysis: (*c*) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612.
13 Yields determined by ^{1}H NMR and GC. Reaction conditions were not optimized. See SI for details.
14 (*a*) C. Krug and J. F. Hartwig, *J. Am. Chem. Soc.*, 2004, **126**, 2694; (*b*) S. E. Boyd, L. D. Field, T. W. Hambley and M. G. Partridge, *Organometallics*, 1993, **12**, 1720.
15 P. Zhao, C. D. Incarvito and J. F. Hartwig, *J. Am. Chem. Soc.*, 2007, **129**, 1876.
16 A. Kina, Y. Yasuhara, T. Nishimura, H. Iwamura and T. Hayashi, *Chem.–Asian J.*, 2006, **1**, 707.
17 S. Sakuma and N. Miyaura, *J. Org. Chem.*, 2001, **66**, 8944.
18 N. Miyaura, K. Yamada, H. Suginome and A. Suzuki, *J. Am. Chem. Soc.*, 1985, **107**, 972.
19 (*a*) A. A. C. Braga, N. H. Morgon, G. Ujaque and F. Maseras, *J. Am. Chem. Soc.*, 2005, **127**, 9298; (*b*) A. A. C. Braga, G. Ujaque and F. Maseras, *Organometallics*, 2006, **25**, 3647; (*c*) A. A. C. Braga, N. H. Morgon, G. Ujaque, A. Lledos and F. Maseras, *J. Organomet. Chem.*, 2006, **691**, 4459.