RSC Advances

PAPER

View Article Online
View Journal | View Issue



Cite this: *RSC Adv.*, 2016, **6**, 10541

# Intramolecular hydroamination reactions catalyzed by zirconium complexes bearing bridged bis(phenolato) ligands†

Yu Zhang, Qiu Sun, Yaorong Wang, Dan Yuan,* Yingming Yao* and Qi Shen

Received 5th November 2015
Accepted 15th January 2016

DOI: 10.1039/c5ra23270h

www.rsc.org/advances

Zirconium complexes stabilized by piperazidine- and imidazolidine-bridged bis(phenolato) ligands have been synthesized and characterized. Their activities in catalyzing intramolecular hydroamination reactions have been tested and compared, which reveals the significant role that the ancillary ligands play in influencing catalytic activities. Cationic species derived from zirconium dibenzyl complexes showed good activities in catalyzing intramolecular hydroamination reactions of both primary and secondary amines, and afforded the respective N-heterocycles in 85% to 99% yields. Moreover, this catalytic system also catalyzed sequential cyclization of primary aminodienes, and generated bicyclic tertiary amines in 94–99% yields.



## Introduction

Hydroamination reactions, which involve the direct addition of N–H bonds over carbon–carbon unsaturated bonds, represent one of the most atom-economic approaches to construct pharmaceutically and biologically important nitrogen-containing compounds.[1] Over the past decades, significant efforts have been devoted to develop efficient catalysts to promote such transformations, which involve early[1a] and late transition metal[1b,d,e] and main-group metal complexes.[1f] Group 4 metal complexes have drawn great interest due to their easy availability and high activity.[1a,g,2] Since the first zirconium catalysts for hydroamination reactions reported in the 1990s,[3] zirconium complexes of various structures and different activities have been developed. A major limitation of zirconium complexes in general is that they are only capable of catalyzing intramolecular hydroamination/cyclization of primary amines, while they show no activity towards reactions of secondary amines.[1a,g] On the other hand, cationic zirconium complexes in most instances showed great activities for secondary amines, while they are inactive for primary amines.[4] To date, zirconium complexes that are active for intramolecular hydroamination reactions of both primary and secondary amines are still relatively rare.[5,6]

Bis(phenolato) ligands are derived from readily available bis(phenol)s and can be conveniently tuned in terms of both electronic and steric properties. Recently, our group have reported a series of group 4 metal complexes stabilized by bridged bis(phenolato) ligands, which showed good activities in catalyzing intermolecular hydroamination reactions of both primary and secondary amines.[7] Ancillary ligands with different backbones and substituents are found to play significant roles in influencing catalytic activities of zirconium complexes.[7c] As a continuation of our study, a series of bis(phenolato) ligand stabilized zirconium complexes with different coordination environment were synthesized, and their activities for intramolecular hydroamination were tested and compared.

## Results and discussion

### Synthesis and characterization of zirconium complexes

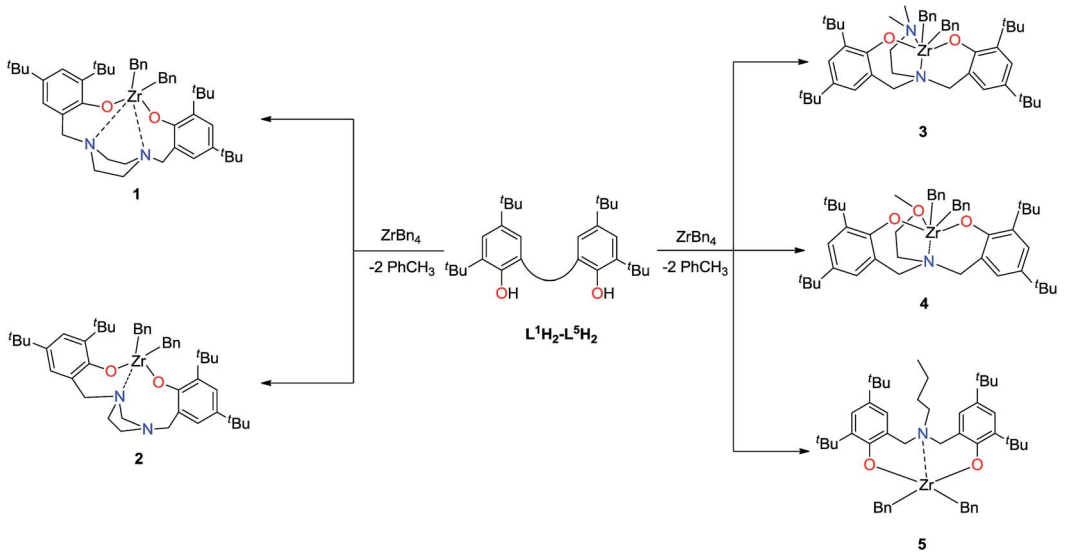
Ligand precursors $\mathbf{L^1H_2}$ and $\mathbf{L^2H_2}$ bearing piperazidine and imidazolidine bridges were treated with $ZrBn_4$, which generated zirconium dibenzyl complexes **1** and **2** in good yields of 80%, respectively (Scheme 1). Complexes **3–5** were synthesized according to literature methods for comparative study.[7,8]

The identity of complexes **1** and **2** were confirmed by $^1$H, $^{13}$C NMR and X-ray diffraction analysis, respectively. The $^1$H NMR spectrum of complex **1** suggests a $C_2$-symmetric molecule, and four signals at 2.90, 2.70, 2.60 and 1.04 ppm are assigned to eight methylene groups. In contrast, more signals are observed in the $^1$H NMR spectrum of complex **2**, revealing a non-symmetric structure, and seven methylene groups are found to resonate in the range of 4.32–2.17 ppm.

The difference in solution behaviors between complexes **1** and **2** is also observed in their solid state structures. As depicted in Fig. 1, the zirconium center in complex **1** is hexa-coordinated

*Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China. E-mail: yuandan@suda.edu.cn; yaoym@suda.edu.cn*

† Electronic supplementary information (ESI) available: $^1$H and $^{13}$C NMR spectra of complexes **1** and **2**, and hydroamination products. X-ray crystallographic data of **1** and **2**. CCDC 1433490 and 1433491. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra23270h




Scheme 1 Synthesis of zirconium complexes stabilized by bis(phenolato) ligands.

by two N and two O atoms of the ligand $L^1$ and two benzyl groups. Complex **1** adopts an octahedral geometry. Bond distances of Zr–N bonds amount to 2.389(5) Å, while bond lengths of Zr–O bonds are 2.048(4) Å. In contrast, ligand $L^2$ in complex **2** coordinates through one N and two O atoms (Fig. 2), while the distance between Zr1 and N2 (3.907 Å) is not within that of a reasonable bond. Both nitrogen atoms are reported to bind to the same metal centers in mononuclear lanthanide and yttrium complexes bearing the same ligand $L^2$, probably as a result of their larger ionic radii.[9] Benzyl groups in complexes **1** and **2** are located *cis* to each other, as evidenced by the C–Zr–C angles of 107.95° (for complex **1**) and 120.04° (for complex **2**), while two O atoms of phenolate groups are arranged in a *trans* configuration. This observation is in consistent with that of Zr complexes stabilized by various bridged bis(phenolato) ligands.[8]

## Catalytic intramolecular hydroamination reactions of aminoalkenes

Intramolecular hydroamination reaction of 2,2-diphenylpent-4-enyl-amine (**6a**) was first studied to compare catalytic activities of complexes **1–5** (Table 1). In general, 5 mol% of these complexes catalyzed this reaction, and afforded the cyclized product **7a** in 70–97% yields (entry 1, 2, 4, 5), with the exception of complex **3** (entry 3). Clearly subtle modifications in ligands result in profound changes in catalytic activities. Steric congestions around metal centers in complexes **2**, **3** and **4** may account for their lower activity. Moreover, with the addition of the cationic reagent $[Ph_3C][B(C_6F_5)_4]$ (TB), the yields of **7a** were largely improved to 91–99%. *In situ* generated cationic complexes are believed to possess increased Lewis acidity and reduced steric hindrance, which facilitates the catalytic cyclization process. Similar trends have been observed for intermolecular hydroamination reactions catalyzed by cationic Zr complexes[7] and group 3 metal complexes.[10] It is noteworthy the mixture of complex **1** and TB showed overall the best activity, as the model reaction resulted in >99% yield within 4 h (entry 6).

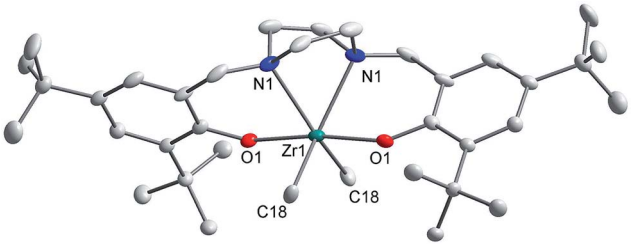



Fig. 1 Molecular structure of **1** showing 30% probability ellipsoids. Two phenyl groups of benzyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zr1–O1 2.048(4), Zr1–N1 2.389(5), Zr1–C1 2.273(6), O1–Zr1–N1 73.02(17), O1–Zr1–N2 113.93(18), O1–Zr1–C1 89.9(2), O1–Zr1–C2 85.7(2), N1–Zr1–N2 61.7(3), N1–Zr1–C1 102.4(2), N1–Zr1–C2 142.6(2), C1–Zr1–C2 108.0(4).

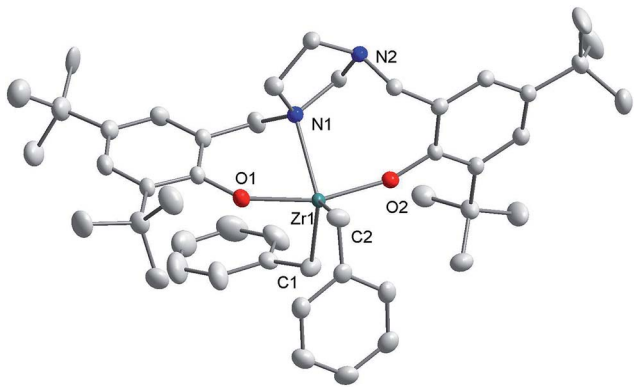



Fig. 2 Molecular structure of **2** showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zr1–O1 2.001(3), Zr1–O2 1.999(3), Zr1–N1 2.356(3), Zr1–C1 2.294(4), Zr1–C2 2.287(4), O1–Zr1–N1 75.81(12), O1–Zr1–C1 91.22(14), O1–Zr1–C2 95.75(15), N1–Zr1–O2 85.39(11), N1–Zr1–C1 121.49(14), N1–Zr1–C2 118.05(14), O2–Zr1–C1 95.48(14), O2–Zr1–C2 96.41(14), C1–Zr1–C2 119.92(16).

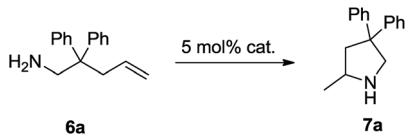
No cyclization reaction was detected in the presence of $[Ph_3C][B(C_6F_5)_4]$ only (entry 11).[11]

Under optimal conditions, a range of primary aminoalkenes with different functional groups were studied, and the results are summarized in Table 2. Both aliphatic and aromatic primary amines underwent hydroamination/cyclization reactions to generate six- and five-membered N-heterocycles in 88–97% yields (Table 2, entry 1–4). The transformation of more challenging internal alkene **6c** worked less efficiently, and afforded cyclized product **7c** in 88% yield at an elevated temperature of 135 °C after prolonged reaction time of 48 h (entry 2). The reaction with the *ortho*-allylaniline **6e** afforded 2-methylindoline, which required higher temperature and longer reaction time than that of aliphatic analogue **6a** (entry 4).

To probe the activity of Zr bis(phenolato) complexes in catalyzing intramolecular hydroamination of secondary aminoalkenes, a comparative study between neutral complex **1** and its cationic derivative was conducted. No yield was detected in the presence of neutral complex **1** (Table 3, entry 1), while a dramatic increase to >99% yield was observed with *in situ* generated cationic species (entry 2). Comparing to complexes **2–5** under identical conditions, the mixture of **1** and TB showed the highest catalytic activity, which is consistent with the result obtained from primary aminoalkene cyclization (*vide supra*) (entry 2–6).

Reactions with other secondary amines also worked straightforwardly in the presence of **1** and TB, and generated a series of tertiary amines in good to excellent yields (Table 4). The reaction with secondary amine **6g** proceeded smoothly under room temperature, and furnished the desired product **7g** in 95% yield within 6 h (entry 1). The piperidine derivative **7h** formed in an almost quantitative yield of 97% (entry 2). Secondary amines with different *N*-substituents were also tested, and 85–97% yields of desired products **7i–7k** were isolated (entry 3–5), showing a good group tolerance of the cationic system. Bicyclic tertiary amines **7l** and **7m** formed in good yields of 94 and 99%, respectively, from sequential cyclization of aminodienes **6l** and **6m** (entry 7 and 8). The reaction of

Table 1 Intramolecular hydroamination of 2,2-diphenylpent-4-enyl-amine (**6a**) catalyzed by complexes **1–5**[a]

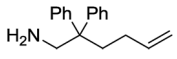
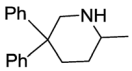
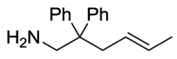
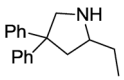
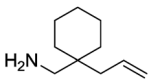
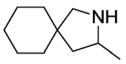
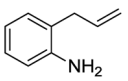
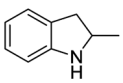



**6a** **7a**

| Entry | Cat. | Time | Yield[b] (%) |
|---|---|---|---|
| 1 | **1** | 8 | 94 |
| 2 | **2** | 12 | 70 |
| 3 | **3** | 12 | Trace |
| 4 | **4** | 12 | 82 |
| 5 | **5** | 12 | 97 |
| 6 | **1** + TB | 4 | >99 |
| 7 | **2** + TB | 12 | 94 |
| 8 | **3** + TB | 12 | 94 |
| 9 | **4** + TB | 12 | 96 |
| 10 | **5** + TB | 12 | 99 |
| 11 | TB | 12 | Trace |

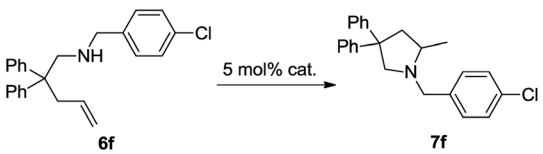
[a] Conditions: 2,2-diphenylpent-4-enyl-amine **6a** (118 mg, 0.5 mmol), precatalyst **1–5** (0.025 mmol, 5 mol%), $[Ph_3C][B(C_6F_5)_4]$ (TB) (23 mg, 0.025 mmol) if necessary, PhCl (2 mL), 100 °C. [b] Isolated yield based on the mass of purified products after column chromatography.

Table 2 Intramolecular hydroamination reactions of primary amines catalyzed by complex **1** and TB[a]

| Entry | Aminoalkene | Conditions | Product | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  **6b** | 110 °C 18 h |  **7b** | 97 |
| 2 |  **6c** | 135 °C 48 h |  **7c** | 88 |
| 3 |  **6d** | 140 °C 8 h |  **7d** | 95[c] |
| 4 |  **6e** | 140 °C 48 h |  **7e** | 94[c,d] |

[a] Conditions: **6** (0.5 mmol), **1** (20 mg, 0.025 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB) (23 mg, 0.025 mmol), PhCl (2 mL). [b] Isolated yield based on the mass of purified products after column chromatography. [c] PhBr-$d_5$ (0.7 mL), determined by $^1$H NMR spectroscopy. [d] 10 mol% catalyst loading.

Table 3 Intramolecular hydroamination of *N*-(4-chlorobenzyl)-2,2-diphenylpent-4-enyl-amine (**6f**) catalyzed by complexes **1–5**[a]

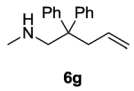
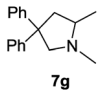
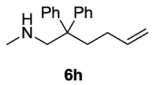
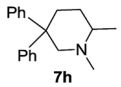
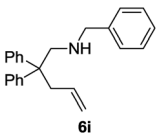
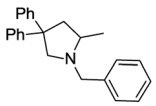
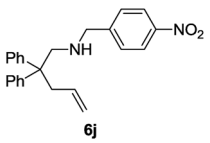
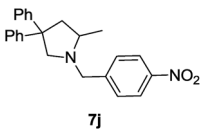
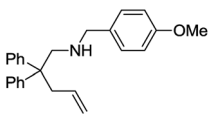
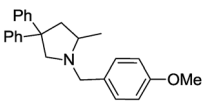
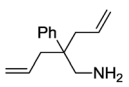
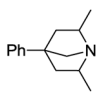
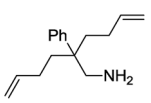
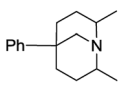



**6f** **7f**

| Entry | Cat. | Time (h) | Yield[b] (%) |
|---|---|---|---|
| 1 | **1** | 20 | Trace |
| 2 | **1** + TB | 20 | >99 (87)[c] |
| 3 | **2** + TB | 20 | 79 |
| 4 | **3** + TB | 20 | 90 |
| 5 | **4** + TB | 20 | 58 |
| 6 | **5** + TB | 20 | 94 |

[a] Conditions: *N*-(4-chlorobenzyl)-2,2-diphenylpent-4-enyl-amine **6f** (181 mg, 0.5 mmol), precatalyst **1–5** (0.025 mmol, 5 mol%), $[Ph_3C][B(C_6F_5)_4]$ (TB) (23 mg, 0.025 mmol) if necessary, PhCl (2 mL), 140 °C. [b] PhBr-$d_5$ (0.7 mL), determined by $^1$H NMR spectroscopy. [c] Isolated yield based on the mass of purified products after column chromatography.

Table 4 Intramolecular hydroamination reactions of secondary amines catalyzed by complex **1** and TB[a]

| Entry | Aminoalkene | Conditions | Product | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  **6g** | 25 °C 6 h |  **7g** | 95 |
| 2 |  **6h** | 60 °C 48 h |  **7h** | 97 |
| 3 |  **6i** | 140 °C 50 h |  **7i** | 85 |
| 4 |  **6j** | 140 °C 48 h |  **7j** | 97 |
| 5 |  **6k** | 140 °C 60 h |  **7k** | 88 |
| 6 |  **6l** | 140 °C 70 h |  **7l** | 94[c] |
| 7 |  **6m** | 140 °C 96 h |  **7m** | 99[c,d] |

[a] Conditions: **6** (0.5 mmol), **1** (20 mg, 0.025 mmol), $[Ph_3C][B(C_6F_5)_4]$(TB) (23 mg, 0.025 mmol), PhCl (2 mL). [b] Isolated yield based on the mass of purified products after column chromatography. [c] PhCl-$d_5$ (0.7 mL), determined by $^1$H NMR spectroscopy. [d] 10 mol% catalyst loading.

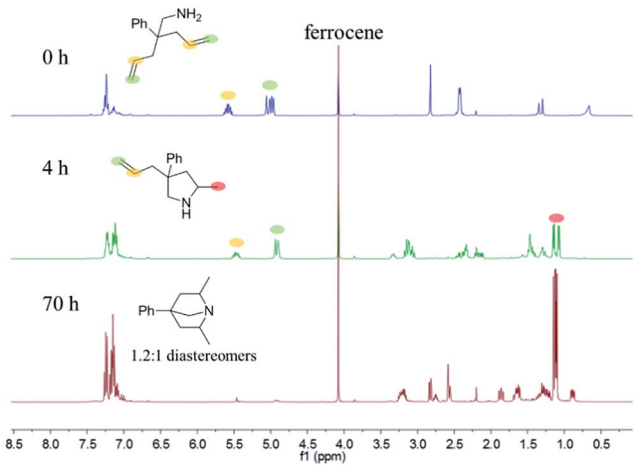


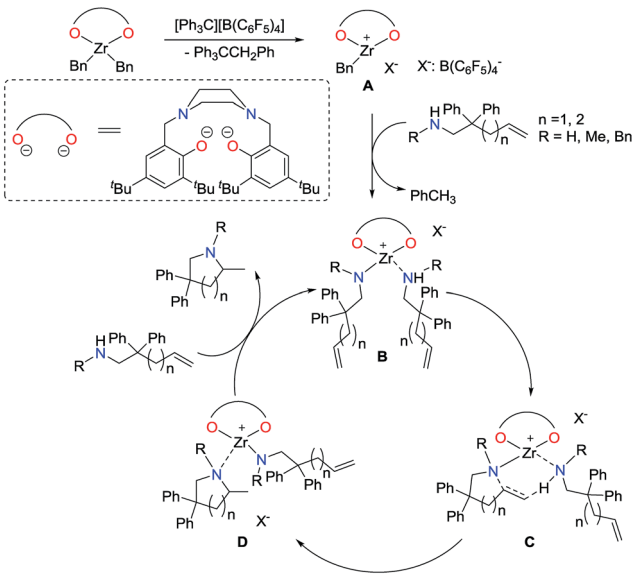

Fig. 3 $^1$H NMR monitoring of sequential cyclization of **6l**.

aminodiene **6l** (entry 7) was monitored by $^1$H NMR spectroscopy (Fig. 3), which revealed that the first-step cyclization was complete within the first four hours, while the cyclization of secondary amine took much longer time of 66 hours.

To ascertain the formation of cationic complex from **1** and TB, $^1$H NMR monitoring of the reaction was performed. After reaction, all methylene protons of ligand $L^1$ become diastereotopic, and give rise to eight doublets/multiplets in the range of 5.44–1.00 ppm (ESI†). Moreover, a characteristic signal corresponding to $Ph_3CCH_2Ph$ that formed as a by-product is detected at 3.83 ppm, which provides some indirect evidence on cationic complex formation. However, all attempts to isolate the cationic species failed.

Based on the afore-discussed results, it is thus conclusive that the cationic species generated from complex **1** and TB represents one of the most active group 4 metal systems for cyclization of both primary and secondary amine.[4] On the basis of previous studies on an oxazolinylborate-supported Zr catalyst,[12] a tethered bis(ureate) Zr complex,[5f] and an amino acid derived [ONO]-type ligated Zr complex[2b] which provide solid evidence on a proton-assisted C–N bond formation mechanism, a plausible mechanism involving concerted C–H and C–N bond formation is proposed in Scheme 2. Reaction of neutral complex **1** and TB generates cationic complex **A**, which undergoes aminolysis with excess amine to form Zr–amide complex **B**. Based




Scheme 2 Plausible mechanism.

on the finding that **A** is an active precatalyst for both primary and secondary amine transformation, Zr–imido intermediates are excluded in this system. Intramolecular hydroamination reaction takes place *via* concerted C–H and C–N bonds formation (intermediate **C**),[2b,5f,12] followed by the disassociation of the cyclized product. However, the possibility of alkene insertion into Zr–amido bond cannot be unambiguously ruled out, which requires further mechanistic investigations.

## Conclusion

In summary, zirconium complexes stabilized by bridged bis(phenolato) ligands have been prepared, which showed good activities in catalyzing intramolecular hydroamination reactions. Ancillary ligands are found to play significant roles in influencing activities of complexes through tuning the steric and electronic environment around the metal center. Various aminoalkenes including primary and secondary amine-tethered terminal and internal alkenes with different functional groups were transformed into respective N-heterocycles in 85% to 99% yields. Sequential cyclization of primary aminodienes was also studied, which generated bicyclic tertiary amines in 94–99% yields. Further studies on development of application of group 4 metal complexes are ongoing in our laboratory.

## Experimental section

### General considerations

All manipulations of air- or moisture sensitive compounds were performed under an inert atmosphere of argon or nitrogen using flame-dried Schlenk glassware or glovebox techniques. Toluene and hexane were distilled over Na wire prior to use under argon. PhCl, PhBr-$d_5$ and PhCl-$d_5$ were dried over $CaH_2$. $ZrBn_4$ were prepared using $ZrCl_4$ and BnMgCl.[13] Ligand precursors $\mathbf{L^1H_2}$ (ref. 14) and $\mathbf{L^2H_2}$ (ref. 9*b*) and complexes **3–5** (ref. 7 and 8) were prepared according to literature methods. $CHCl_3$ was distilled under argon from $P_2O_5$. NMR spectra were recorded on a 400 MHz spectrometer. X-ray crystallographic data were obtained with an AXS D8 X-ray diffractometer.

### Preparation of $Zr(CH_2Ph_2)_2L^1$ (1)

To a solution of $ZrBn_4$ (0.91 g, 2 mmol) in toluene (10 mL), a solution of $\mathbf{L^1H_2}$ (1.05 g, 2 mmol) in toluene was added at room temperature, during which the colour of the solution changed from orange to yellow. After the solution was stirred overnight, it was filtered and concentrated to 4 mL. Crystals suitable for X-ray diffraction analyses were obtained at room temperature after a few days upon standing (1.27 g, 1.6 mmol, 80%). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.60 (s, 2H, ArH), 6.97 (d, 8H, $J$ = 23.33 Hz, ArH), 6.77 (s, 2H, ArH), 6.69 (s, 2H, ArH), 2.90 (s, 4H, $ArCH_2$), 2.71 (s, 4H, $NCH_2CH_2N$), 2.61 (s, 4H, $NCH_2CH_2N$), 1.89 (s, 18H, *o*-$C(CH_3)_3$), 1.41 (s, 18H, *p*-$C(CH_3)_3$), 1.05 (s, 4H, $CCH_2N$). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$): 158.2, 148.7, 140.8, 138.3, 126.9, 124.0, 123.1, 121.2 (Ar–C), 70.5 (Ar–$CH_2N$), 59.5 ($NCH_2CH_2N$), 48.6 ($NCH_2CH_2N$), 36.1 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 32.4 ($C(CH_3)_3$), 30.9 ($C(CH_3)_3$). Anal. calcd for $C_{48}H_{66}N_2O_2Zr$: C, 72.58; H, 8.38; N, 3.53. Found: C, 72.55; H, 8.40; N, 3.51.

### Preparation of $Zr(CH_2Ph_2)_2$ $L^2$ (2)

Complex **2** was prepared in analogous to that of complex **1** from $ZrBn_4$ (0.91 g, 2 mmol) and $\mathbf{L^2H_2}$ (1.02 g, 2 mmol). Yield: 1.25 g, 1.6 mmol, 80%. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.62 (d, 2H, $J$ = 2.66 Hz, ArH), 7.21 (d, 2H, $J$ = 8.22 Hz, ArH), 7.08 (d, 2H, $J$ = 9.05 Hz, ArH), 7.02–6.95 (m, 4H, ArH), 6.85–6.76 (m, 3H, ArH), 6.67–6.66 (m, 1H, ArH), 4.31 (d, 1H, $J$ = 9.51 Hz, $ArCH_2$), 2.93 (s, 2H, $CCH_2N$), 2.76–2.66 (m, 6H, $NCH_2CH_2CH_2N$), 2.54–2.48 (m, 3H, $ArCH_2$), 2.19–2.17 (m, 2H, $NCH_2C$), 1.88 (s, 18H, *o*-$C(CH_3)_3$), 1.37 (s, 18H, *p*-$C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$): 158.5, 146.2, 142.9, 142.2, 137.7, 129.7, 129.0, 127.9, 126.0, 124.5, 123.5, 122.5 (Ar–C), 79.1 (Ar–$CH_2N$), 66.4 (Ar–$CH_2N$), 65.2 ($NCH_2N$), 57.4 ($NCH_2CH_2N$), 49.6 ($NCH_2CH_2N$), 36.0 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$). Anal. calcd for $C_{47}H_{64}N_2O_2Zr$: C, 72.35; H, 8.27; N, 3.59. Found: C, 72.33; H, 8.29; N, 3.60.

### General procedure for hydroamination reactions

The reactions were carried out in a glovebox filled with nitrogen. Complex **1** (20 mg, 0.025 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (23 mg, 0.025 mmol) were mixed in PhCl (2 mL). The solution was stirred for five minutes, and **6** was added subsequently. The resulting solution was stirred at the desired temperature for the desired time. After reaction, the solvent was removed under reduced pressure and the products were isolated by column chromatography (petroleum ether/ethyl acetate 100/1, silica gel) and characterized by $^1$H and $^{13}$C NMR spectroscopy.

### 2-Methyl-4,4-diphenyl-pyrrolidine (7a)

**7a** was prepared from **6a** (119 mg, 0.5 mmol) as a colourless oil in 99% yield (117 mg). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.21–7.12 (m, 8H, ArH), 7.05 (t, 2H, ArH), 3.56 (d, 2H, $J$ = 11.72 Hz, $NCH_2C$), 3.35 (d, 2H, $J$ = 11.78 Hz, $NCH_2C$), 3.31–3.22 (m, 1H,

NCH), 2.66–2.51 (m, 1H, $CCH_2C$), 2.35 (s, 1H, NH), 1.94 (t, 1H, $CCH_2C$), 1.09 (d, 3H, $J = 7.64$ Hz, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 147.8, 147.1, 128.4, 128.8, 127.1, 127.1, 126.1 (Ar–C), 57.9 ($NCH_2$), 57.2 ($CPh_2$), 53.2 (NCH), 47.1 ($CH_2$), 22.5 ($CH_3$).

### 2-Methyl-5,5-diphenylpiperidine (7b)

**7b** was prepared from **6b** (126 mg, 0.5 mmol) as a colourless oil in 97% yield (122 mg). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.40 (d, 2H, $J = 7.28$ Hz, ArH), 7.33 (t, 2H, ArH), 7.08–7.23 (m, 6H, ArH), 3.89 (dd, $J = 3.19$ Hz, $J = 3.15$ Hz, 1H), 3.09 (d, 1H, $J = 13.53$ Hz, $NCH_2C$), 2.80–2.72 (m, 1H, NCH), 2.67–2.73 (m, 1H, $CCH_2C$), 2.24–2.16 (m, 1H, $CCH_2C$), 1.65–1.61 (m, 1H, $CCH_2C$), 1.48 (s, 1H, NH), 1.20–1.10 (m, 1H, $CCH_2C$) 0.99 (d, 3H, $J = 6.33$ Hz, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 149.0, 144.9, 128.4, 128.8, 128.4, 126.6, 126.0 (Ar–C), 56.0 ($NCH_2$), 52.5 ($CPh_2$), 45.4 (NCH), 35.6 ($CH_2$), 31.6 ($CH_2$), 22.6 ($CH_3$).

### 2-Ethyl-4,4-diphenylpyrrolidine (7c)

**7c** was prepared from **6c** (132 mg, 0.5 mmol) as a colourless oil in 88% yield (117 mg). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.28–7.10 (m, 10H, ArH), 3.64 (d, 1H, $J = 13.39$ Hz, $NCH_2C$), 3.35 (d, 1H, $J = 10.08$ Hz, $NCH_2C$), 3.13–3.08 (m, 1H, NCH), 2.74–2.70 (m, 1H, $CCH_2C$), 1.98–1.96 (m, 1H, $CCH_2C$), 1.46–1.21 (m, 2H, $CCH_2C$), 1.20 (s, 1H, NH), 0.89 (t, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 147.9, 147.1, 130.0, 128.5, 128.4, 127.2, 127.1, 126.2 (Ar–C), 59.6 ($NCH_2$), 57.8 (NCH), 56.9 ($CPh_2$), 45.1 ($CH_2$), 30.5 ($CH_2$), 11.8 ($CH_3$).

### 3-Methyl-2-azaspiro[4.5]decane (7d)

**7d** was prepared from **6d** (46 mg, 0.3 mmol) in 95% yield. $^1H$ NMR (400 MHz, PhBr-$d_5$): $\delta$ 2.85–2.76 (m, 1H, NCH), 2.48 (d, 1H, $J = 10.32$ Hz, $NCH_2$), 2.28 (d, 1H, $J = 11.16$ Hz, $NCH_2$), 1.42–1.35 (m, 1H, $CCH_2C$), 1.12–1.06 (m, 1H, $CCH_2C$), 1.28 (s, 1H, NH), 1.12–1.06 (m, 10H, $CCH_2CH_2CH_2CH_2CH_2C$), 0.83 (d, 3H, $J = 7.64$ Hz, $CH_3$), 0.69–0.64 (m, 1H, $CCH_2C$).

### 2-Methylindoline (7e)

**7e** was prepared from **6e** (40 mg, 0.3 mmol) in 94% yield. $^1H$ NMR (400 MHz, PhBr-$d_5$): $\delta$ 7.19–6.44 (m, 4H, ArH), 3.39 (s, 2H, $CH_2$), 1.95 (s, 1H, NH), 1.65 (s, 1H, CH), 0.81 (s, 3H, $CH_3$).

### 1-(4-Chlorobenzyl)-2-methyl-4,4-diphenylpyrrolidine (7f)

**7f** was prepared from **6f** (181 mg, 0.5 mmol) as a colourless oil in 87% yield (157 mg). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.21–7.05 (m, 14H, ArH), 3.96 (d, 1H, $J = 13.69$ Hz, $NCH_2C$), 3.54 (d, 1H, $J = 9.44$ Hz, $NCH_2C$), 3.16 (d, 1H, $J = 14.63$ Hz, $NCH_2C$), 289–2.84 (m, 1H, $NCH_2C$), 2.81–2.75 (m, 1H, $CCH_2C$), 2.71 (d, 1H, $J = 9.67$ Hz, $NCH_2C$), 2.20–2.14 (m, 1H, $CCH_2C$), 1.10 (d, 3H, $J = 6.00$ Hz, $CCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 150.6, 148.8, 138.9, 132.6, 130.1, 128.5, 128.1, 128.0, 127.6, 126.1, 128.0, 127.6, 125.7, 127.0, (Ar–C), 66.6 ($NCH_2Ph$), 59.8 ($NCH_2$), 57.5 (NCH), 52.7 ($CPh_2$), 48.1 ($CH_2$), 19.7 ($CH_3$).

### *N*-Methyl-2-methyl-5,5-diphenylpyrrolidine (7g)

**7g** was prepared from **6g** (126 mg, 0.5 mmol) as a colourless oil in 95% yield (119 mg). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.33–7.13 (m, 10H, ArH), 3.82 (d, 1H, $J = 8.96$ Hz, NCHC), 2.92–2.87 (m, 2H, $NCH_2C$), 2.56–2.48 (m, 1H, $CCH_2C$), 2.38 (s, 1H, $NCH_3$), 2.27–2.21 (m, 1H, $CCH_2C$), 1.16 (d, 3H, $J = 6.06$ Hz, $CCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 128.4, 128.3, 127.6, 127.3, 126.0, 125.7 (Ar–C), 70.5 ($NCH_3$), 62.1 ($NCH_2$), 52.8 ($CPh_2$), 48.7 (NCH), 40.7 ($CH_2$), 19.1 ($CCH_3$).

### *N*-Methyl-2-methyl-5,5-diphenylpiperidine (7h)

**7h** was prepared from **6h** (132 mg, 0.5 mmol) as a colourless oil in 97% yield (129 mg). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.41 (d, 2H, $J = 8.28$ Hz, ArH), 7.27–7.11 (m, 8H, ArH), 3.47 (d, 1H, $J = 11.8$ Hz, NCHC), 2.40–2.44 (m, 1H, $NCH_2C$), 2.28 (s, 1H, $NCH_3$), 2.19–2.11 (m, 1H, $NCH_2C$), 1.58–1.51 (m, 1H, $CCH_2C$), 1.31–1.21 (m, 1H, $CCH_2C$), 1.02 (d, 3H, $J = 6.06$ Hz, $CCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 149.1, 146.9, 128.9, 128.1, 127.8, 127.2, 126.8, 125.8, 125.3 (Ar–C), 66.0 ($NCH_3$), 59.0 ($NCH_2$), 46.8 ($CPh_2$), 43.2 (NCH), 35.2 ($CH_2$), 31.0 ($CH_2$), 19.7 ($CH_3$).

### 1-Benzyl-2-methyl-4,4-diphenylpyrrolidine (7i)

**7i** was prepared from **6i** (164 mg, 0.5 mmol) as a colourless oil in 85% yield (139 mg). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.37–7.08 (m, 15H, ArH), 4.06 (d, 1H, $J = 14.84$ Hz, $NCH_2C$), 3.61 (d, 1H, $J = 9.86$ Hz, $NCH_2C$), 3.22 (d, 1H, $J = 12.75$ Hz, $NCH_2C$), 2.93–2.88 (m, 1H, NCHC), 2.84–2.81 (m, 2H, $CCH_2C$), 2.76 (d, 1H, $J = 9.66$ Hz, $NCH_2C$), 2.22–2.17 (m, 1H, $CCH_2C$), 1.15 (d, 3H, $J = 6.08$ Hz, $CCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 150.8, 146.9, 148.9, 140.3, 128.8, 128.4, 128.3, 128.0, 127.6, 127.5, 127.0, 126.0, 125.6 (Ar–C), 66.7 ($NCH_2Ph$), 59.9 ($NCH_2$), 58.2 (NCH), 52.7 ($CPh_2$), 48.2 ($CH_2$), 19.7 ($CH_3$).

### 2-Methyl-1-(4-nitrobenzyl)-4,4-diphenylpyrrolidine (7j)

**7j** was prepared from **6j** (186 mg, 0.5 mmol) as a colourless oil in 97% yield (181 mg). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.06 (d, 2H, $J = 12.00$ Hz, ArH), 7.42 (d, 2H, $J = 7.63$ Hz, ArH), 7.15–7.02 (m, 10H, ArH), 3.99 (d, 1H, $J = 16.38$ Hz, $NCH_2C$), 3.49 (d, 1H, $J = 11.62$ Hz, $NCH_2C$), 3.30 (d, 1H, $J = 13.73$ Hz, $NCH_2C$), 2.85–2.78 (m, 2H, $CCH_2C$), 2.73 (d, 1H, $J = 9.79$ Hz, $NCH_2C$), 2.20–2.14 (m, 1H, NCHC), 1.07 (d, 3H, $J = 5.10$ Hz, $CCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 150.2, 148.5, 148.4, 147.2, 129.2, 128.4, 128.1, 127.5, 127.2, 126.1, 125.8, 123.7 (Ar–C), 66.6 ($NCH_2Ph$), 59.8 ($NCH_2$), 57.5 (NCH), 52.8 ($CPh_2$), 47.8 ($CH_2$), 19.9 ($CH_3$).

### 1-(4-Methoxybenzyl)-2-methyl-4,4-diphenylpyrrolidine (7k)

**7k** was prepared from **6k** (179 mg, 0.5 mmol) as a colourless oil in 88% yield (157 mg). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.30–7.09 (m, 12H, ArH), 6.86 (d, 2H, $J = 8.18$ Hz, ArH), 4.01 (d, 1H, $J = 14.37$ Hz, $NCH_2C$), 3.80 (s, 3H $OCH_3$), 3.62 (d, 1H, $J = 10.09$ Hz, $NCH_2C$), 3.18 (d, 1H, $J = 18.95$ Hz, $NCH_2C$), 2.95–2.89 (m, 1H, NCHC), 2.83–2.80 (m, 1H, $CCH_2C$), 2.75 (d, 1H, $J = 10.20$ Hz, $NCH_2C$), 2.23–2.18 (m, 1H, $CCH_2C$), 1.17 (d, 3H, $J = 5.36$ Hz, $CCH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 158.7, 150.87, 149.0, 132.3, 129.9, 128.3, 128.0, 127.6, 127.5, 126.0, 125.6, 113.8 (Ar–

C), 66.5 ($NCH_2Ph$), 59.8 ($NCH_2$), 57.5 (NCH), 55.5 ($OCH_3$), 52.6 ($CPh_2$), 48.2 ($CH_2$), 19.7 ($CH_3$).

#### 2,6-Dimethyl-4-phenyl-1-azabicyclo[2.2.1]hexane (7l)

**7l** was prepared from **6l** (60 mg, 0.3 mmol) in 94% yield. $^1$H NMR (400 MHz, PhCl-$d_5$) (**7lA** : **7lB** ≈ 1.2 : 1) (**7lA**): $\delta$ 7.27–6.98 (m, 5H, ArH), 3.16–3.27 (m, 2H, NCHNCH), 2.58 (d, 2H, $J$ = 11.70 Hz, $NCH_2C$), 1.69–1.60 (m, 2H, $CCH_2C$), 1.38–1.19 (m, 2H, $CCH_2C$), 1.13 (d, $J$ = 1.71 Hz, 3H $CH_3$), 1.11 (d, $J$ = 2.52 Hz, 3H, $CH_3$); (**7lB**) $\delta$ 7.27–6.98 (m, 5H, ArH), 2.84–2.71 (m, 2H, NCHNCH), 1.89–1.84 (m, 2H, $NCH_2C$), 1.38–1.19 (m, 2H, $CCH_2C$), 1.16 (s, 3H, $CH_3$), 1.10 (s, 3H, $CH_3$), 0.91–0.86 (m, 2H, $CCH_2C$).

#### 2,8-Dimethyl-5-phenyl-1-azabicyclo[3.3.1]nonane (7m)

**7m** was prepared from **6m** (69 mg, 0.3 mmol) in 99% yield. $^1$H NMR (400 MHz, PhCl-$d_5$): $\delta$ 7.42–7.07 (m, 5H, ArH), 3.40 (d, 1H, $J$ = 13.87 Hz, $NCH_2$), 3.03–2.96 (m, 1H, NCH), 2.86 (s, 1H, NCH), 2.63 (d, 1H, $J$ = 13.43 Hz, $NCH_2$), 1.87–1.62 (m, 6H, $CH_3$), 1.36–1.06 (m, 8H, $CH_2$).

#### X-ray crystallographic structure determination

Suitable single crystals of complexes **1** and **2** were sealed in a thin-walled glass capillary for determination the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in $\omega$ scan mode using Mo-K$\alpha$ radiation ($\lambda$ = 0.71070 Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. The hydrogen atoms in these complexes were generated geometrically, assigned appropriate isotropic thermal parameters, and were allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELEXL-97 programs.

## Acknowledgements

Financial support from the National Natural Science Foundation of China (Grants 21402135), the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (14KJB150021), the China Postdoctoral Science Foundation (2013M541712), PAPD, and the Qing Lan Project is gratefully acknowledged.

## Notes and references

1 For recent reviews: (*a*) A. L. Reznichenko and K. C. Hultzsch, *Top. Organomet. Chem.*, 2013, **43**, 51–114; (*b*) N. Nishina and Y. Yamamoto, *Top. Organomet. Chem.*, 2013, **43**, 115–144; (*c*) A. L. Reznichenko, A. J. Nawara-Hultzsch and K. C. Hultzsch, *Top. Curr. Chem.*, 2014, **343**, 191–260; (*d*) L. Huang, M. Arndt, K. Gooβen, H. Heydt and L. J. Gooβen, *Chem. Rev.*, 2015, **115**, 2596–2697; (*e*) E. Bernoud, C. Lepori, M. Mellah, E. Schulz and J. Hannedouche, *Catal. Sci. Technol.*, 2015, **5**, 2017–2037; (*f*) V. Rodriguez-Ruiz, R. Carlino, S. Bezzenine-Lafollée, R. Gil, D. Prim, E. Schulz and J. Hannedouche, *Dalton Trans.*, 2015, **44**, 12029–12059; (*g*) S. A. Ryken and L. L. Schafer, *Acc. Chem. Res.*, 2015, **48**, 2576–2586; (*h*) J. Hannedouche and E. Schulz, *Chem.–Eur. J.*, 2013, **19**, 4972–4985; (*i*) C.-V. T. Vo and J. W. Bode, *J. Org. Chem.*, 2014, **79**, 2809–2815; (*j*) S. M. Bronner and R. H. Grubbs, *Chem. Sci.*, 2014, **5**, 101–106; (*k*) X. Yang, Q. Wang, B. Zhao and Y. Yao, *Chin. J. Org. Chem.*, 2015, **35**, 1598–1614.

2 For recent reports: (*a*) K. Manna, N. Eedugurala and A. D. Sadow, *J. Am. Chem. Soc.*, 2015, **137**, 425–435; (*b*) X. Zhou, B. Wei, X.-L. Sun, Y. Tang and Z. Xie, *Chem. Commun.*, 2015, **51**, 5751–5753; (*c*) J. M. P. Lauzon and L. L. Schafer, *Z. Anorg. Allg. Chem.*, 2015, **641**, 128–135; (*d*) E. Chong, S. Qayyum, L. L. Schafer and R. Kempe, *Organometallics*, 2013, **32**, 1858–1865; (*e*) P. R. Payne, R. K. Thomson, D. M. Medeiros, G. Wan and L. L. Schafer, *Dalton Trans.*, 2013, **42**, 15670–15677; (*f*) A. T. Normand, A. Massard, P. Richard, C. Canovas, C. Balan, M. Picquet, A. Auffrant and P. L. Gendre, *Dalton Trans.*, 2014, **43**, 15098–15110; (*g*) I. A. Tonks, J. C. Meier and J. E. Bercaw, *Organometallics*, 2013, **32**, 3451–3457; (*h*) C. Brahms, P. Tholen, W. Saak and S. Doye, *Eur. J. Org. Chem.*, 2013, 7583–7592; (*i*) L. H. Lühning, C. Brahms, J. P. Nimoth, M. Schmidtmann and S. Doye, *Z. Anorg. Allg. Chem.*, 2015, **641**, 2071–2082; (*j*) L. Luconi, A. Rossin, A. Motta, G. Tuci and G. Giambastiani, *Chem.–Eur. J.*, 2013, **19**, 4906–4921; (*k*) W. D. Clark, J. Cho, H. U. Valle, T. K. Hollis and E. J. Valente, *J. Organomet. Chem.*, 2014, **751**, 534–540; (*l*) J. Liu, Y. Cao, L. Li, H. Pei, Y. Chen, J. Hu, Y. Qin, Y. Li, W. Li and W. Liu, *RSC Adv.*, 2015, **5**, 10318–10325; (*m*) J.-J. Zhao, H. Pei, Y.-M. Chen, N. Lu, J.-N. Liu, J.-F. Hu, W. Liu, W. Li and Y. Li, *Z. Anorg. Allg. Chem.*, 2015, **641**, 1322–1382; (*n*) S. Barroso, S. R. M. M. de Aguiar, R. F. Munhá and A. M. Martins, *J. Organomet. Chem.*, 2014, **760**, 60–66; (*o*) K. Manna, W. C. Everett, G. Schoendorff, A. Ellern, T. L. Windus and A. D. Sadow, *J. Am. Chem. Soc.*, 2013, **135**, 7235–7250; (*p*) N. Yonson, J. C.-H. Yim and L. L. Schafer, *Inorg. Chim. Acta*, 2014, **422**, 14–20; (*q*) J. C.-H. Yim, J. A. Bexrud, R. O. Ayinla, D. C. Leitch and L. L. Schafer, *J. Org. Chem.*, 2014, **79**, 2015–2028.

3 (*a*) P. J. Walsh, A. M. Baranger and R. G. Bergman, *J. Am. Chem. Soc.*, 1992, **114**, 1708–1719; (*b*) P. L. McGrane, M. Jensen and T. Livinghouse, *J. Am. Chem. Soc.*, 1992, **114**, 5459–5460; (*c*) P. L. McGrane and T. Livinghouse, *J. Am. Chem. Soc.*, 1993, **115**, 11485–11489.

4 (*a*) D. V. Gribkov and K. C. Hultzsch, *Angew. Chem., Int. Ed.*, 2004, **43**, 5542–5546; (*b*) S. Tobisch, *Dalton Trans.*, 2006, 4277–4285; (*c*) A. Mukherjee, T. K. Sen, S. K. Mandal, B. Maity and D. Koley, *RSC Adv.*, 2013, **3**, 1255–1264; (*d*) P. D. Knight, I. Munslow, P. N. O'Shaughnessy and P. Scott, *Chem. Commun.*, 2004, 894–895.

5 (*a*) D. C. Leitch, P. R. Payne, C. R. Dunbar and L. L. Schafer, *J. Am. Chem. Soc.*, 2009, **131**, 18246–18247; (*b*) B. D. Stubbert and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 6149–6167; (*c*) S. Majumder and A. L. Odom, *Organometallics*, 2008, **27**,

1174–1177; (*d*) C. Müller, W. Saak and S. Doye, *Eur. J. Org. Chem.*, 2008, 2731–2739; (*e*) Y.-C. Hu, C.-F. Liang, J.-H. Tsai, G. P. A. Yap, Y.-T. Chang and T.-G. Ong, *Organometallics*, 2010, **29**, 3357–3361; (*f*) D. C. Leitch, R. H. Platel and L. L. Schafer, *J. Am. Chem. Soc.*, 2011, **133**, 15453–15463.

6 (*a*) X. Wang, Z. Chen, X.-L. Sun, Y. Tang and Z. Xie, *Org. Lett.*, 2011, **13**, 4758–4761; (*b*) L. Luconi, J. Klosin, A. J. Smith, S. Germain, E. Schulz, J. Hannedouche and G. Giambastiani, *Dalton Trans.*, 2013, **42**, 16056–16065; (*c*) L. Luconi, A. Rossin, G. Tuci, S. Germain, E. Schulz, J. Hannedouche and G. Giambastiani, *ChemCatChem*, 2013, **5**, 1142–1151.

7 (*a*) Q. Sun, Y. Wang, D. Yuan, Y. Yao and Q. Shen, *Organometallics*, 2014, **33**, 994–1001; (*b*) Q. Sun, Y. Wang, D. Yuan, Y. Yao and Q. Shen, *Chem. Commun.*, 2015, **51**, 7633–7636; (*c*) Q. Sun, Y. Wang, D. Yuan, Y. Yao and Q. Shen, *Dalton Trans.*, 2015, **44**, 20352.

8 (*a*) E. Y. Tshuva, I. Goldberg and M. Kol, *J. Am. Chem. Soc.*, 2000, **122**, 10706–10707; (*b*) E. Y. Tshuva, S. Groysman, I. Goldberg and M. Kol, *Organometallics*, 2002, **21**, 662–670; (*c*) E. Y. Tshuva, I. Goldberg, M. Kol, H. Weitman and Z. Goldschmidt, *Chem. Commun.*, 2000, 379–380; (*d*) E. Y. Tshuva, I. Goldberg, M. Kol and Z. Goldschmidt, *Organometallics*, 2001, **20**, 3017–3028.

9 (*a*) Z. Zhang, X. Xu, W. Li, Y. Yao, Y. Zhang, Q. Shen and Y. Luo, *Inorg. Chem.*, 2009, **48**, 5715–5724; (*b*) X. Xu, Y. Yao, Y. Zhang and Q. Shen, *Inorg. Chem.*, 2007, **46**, 3743–3751.

10 (*a*) F. Lauterwasser, P. G. Hayes, S. Bräse, W. E. Piers and L. L. Schafer, *Organometallics*, 2004, **23**, 2234–2237; (*b*) S. Bambirra, H. Tsurugi, D. van Leusen and B. Hessen, *Dalton Trans.*, 2006, 1157–1161.

11 T. Mahdi and D. W. Stephan, *Chem.–Eur. J.*, 2015, **21**, 11134–11142.

12 K. Manna, S. Xu and A. D. Sadow, *Angew. Chem., Int. Ed.*, 2011, **50**, 1865–1868.

13 (*a*) U. Zucchini, E. Albizzati and U. Giannini, *J. Organomet. Chem.*, 1971, **26**, 357–372; (*b*) Y. Rong, A. Al-Harbi and G. Parkin, *Organometallics*, 2012, **31**, 8208–8217; (*c*) M. R. Radlauer and T. Agapie, *Organometallics*, 2014, **33**, 3247–3250.

14 (*a*) S. Mohanty, D. Suresh, M. S. Balakrishna and J. T. Mague, *Tetrahedron*, 2008, **64**, 240–247; (*b*) J. D. Farwell, P. B. Hitchcock, M. F. Lappert, G. A. Luinstra, A. V. Protchenko and X.-H. Wei, *J. Organomet. Chem.*, 2008, **693**, 1861–1869.