ChemComm

COMMUNICATION

Check for updates

Cite this: Chem. Commun., 2019, 55, 12324

Received 13th August 2019, Accepted 18th September 2019

DOI: 10.1039/c9cc06282c

rsc.li/chemcomm

A sterically demanding silaamidine (ArN = Si(L)NHAr) ligand was synthesized and employed for the preparation of a yttrium dialkyl complex, which catalytically enabled the cyclotrimerization of isocyanate with high activity and excellent functional group tolerance.

Rare-earth metal (RE) dialkyl complexes have attracted considerable attention in a variety of chemical transformations such as hydroelementation, olefin polymerization and cyclic ester ring-opening polymerization because of the highly reactive RE–C bond.^{1,2} It is well-known that low-coordinate metal complexes feature unique reactivity and catalytic transformations.^{3,4} However, low-coordinate rare-earth metal dialkyl complexes are still relatively undeveloped.⁵ Thus, significant efforts have been made on the development of bulky ancillary ligands for the support of low-coordinate complexes.

Silaimines ($R_2Si=NR'$), compared to analogous imines ($R_2C=NR'$), possess highly polarized silicon-nitrogen double bonds because of the electropositive silicon atom.⁶ The related silaamidinates (Chart 1) are isoelectronic with widely used amidinate ligands that have played important roles in the stabilization of transition metals and main group and rare-earth complexes.^{7,8} It is envisioned that silaamidinate with sterically demanding substituents could support highly Lewis acidic metal ions because of the two highly negative nitrogen donors. However, silaamidinates have been rarely studied as ligands because they are not easily accessible regarding the poor π -bonding ability of the silicon atom. Recent advances in silylene and silicon multiple bonding chemistry have shown that a silaimine moiety could be effectively stabilized with a suitable Lewis base, leading to facile entries to varieties of silicon

Yttrium dialkyl supported by a silaamidinate ligand: synthesis, structure and catalysis on cyclotrimerization of isocyanates †‡

Deshuai Liu, 跑 a Dahai Zhou, 跑 a Hao Yang, 跑 a Jianfeng Li 跑 * and Chunming Cui ២ * ab



Chart 1 Amidinate vs. silaamidinate ligands.

multiple bonds.⁹ Herein, we report the successful and facile synthesis of silaamidine and its preliminary application as a ligand in rare-earth chemistry (Chart 1). The low-coordinate yttrium dialkyl complex supported by the silaamidinate ligand $[PhC(NtBu)_2Si(NAT)_2]Y(CH_2SiMe_3)_2$ (4, Ar = 2,6-iPr₂C₆H₃) exhibited high activity and excellent functional group tolerance for the catalytic cyclotrimerization of isocyanates, demonstrating the potential of this class of ligand in coordination chemistry and catalysis.

Preparation of the target silaamidine 3 was achieved in high yield over two steps from chlorosilylene (1) as outlined in Scheme 1.¹⁰ Treatment of 1 with 2,6-diisopropylphenyl azide resulted in chlorosilaimine (2) in 80% yield.⁹ The salt metathesis reaction between 2 and the lithium salt of 2,6-diisopropylaniline afforded silaamidine 3 in 67% yield. 3 has been characterized by elemental analysis as well as ¹H, ¹³C, and ²⁹Si NMR and IR spectroscopic methods. The ¹H and ¹³C NMR spectra of 3 corroborate the expected ligand connectivity. The ²⁹Si NMR spectrum shows a resonance at -85.7 ppm, which is consistent with the structure of silaimine.^{9b}

The yttrium dialkyl [PhC(NtBu)₂Si(NAr)₂]Y(CH₂SiMe₃)₂ **4** was obtained in 60% yield *via* an alkane elimination reaction of **3** with Y(CH₂SiMe₃)₃(THF)₂. The ¹H and ¹³C NMR spectra disclose that **4** is solvent free with C_2 symmetry in solution. This is a notable feature considering that four-coordinate and solvent-free rare-earth metal dialkyl complexes were relatively rare.^{1b} The two methylene protons of each $-CH_2$ SiMe₃ group in **4** are magnetically inequivalent in the ¹H NMR spectrum (C₆D₆, 23 °C), indicating the rotation of the Y–C bonds prohibited by a sterically demanding silaamidinate ligand.



View Article Online

^a State Key Laboratory of Elemento-organic Chemistry and College of Chemistry, Nankai University, Tianjin 300071, China. E-mail: lijf@nankai.edu.cn, cmcui@nankai.edu.cn

cmcui@nunkui.euu.en

^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

[†] Dedicated to 100th anniversary of Nankai University.

[‡] Electronic supplementary information (ESI) available: Experimental procedures, crystallographic data and NMR spectra. CCDC 1906987. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c9cc06282c



Scheme 1 Synthesis of ligand 3 and yttrium dialkyl complex 4.

The diagnostic methylene protons exhibit two doublets of doublet $(\delta - 0.12 \text{ and } -0.26 \text{ ppm})$, due to the characteristic coupling to ¹H and ⁸⁹Y nuclei (dd, ${}^{2}J_{HH}$ = 11.3 Hz, ${}^{2}J_{YH}$ = 1.7 Hz; dd, ${}^{2}J_{HH}$ = 11.4 Hz, $^{2}J_{\rm YH}$ = 2.3 Hz). In the 13 C NMR spectrum, the methylene carbons give rise to a doublet at 32.5 ppm (${}^{1}J_{YC}$ = 39.8 Hz). In comparison with the 13C NMR resonances of methylene carbons in the yttrium dialkyls with amidinate $[PhC(NAr)_2]Y(CH_2SiMe_3)_2(THF)$ (δ 39.5 ppm), guanidinate [Me2NC(NAr)2]Y(CH2SiMe3)2(THF) (& 37.6 ppm) and diimidosulfonate $[PhS(NAr)_2]Y(CH_2SiMe_3)_2(THF)_2$ (δ 36.0 ppm) ligands, the equivalent resonance in 4 is upfield-shifted, suggesting that the silaamidinate ligand is more electron-donating than these ligands.^{8a,c,g} The low ² J_{YH} coupling constants in 4, compared to those in $[PhC(NAr)_2]Y(CH_2SiMe_3)_2(THF)$ (² $J_{YH} = 3.0$ Hz) and $[Me_2NC(NAr)_2]$ - $Y(CH_2SiMe_3)_2(THF)$ (² J_{YH} = 2.9 Hz), may be attributed to the increased electronegativity of the yttrium ion in 4. Both the ¹H and ¹³C NMR spectra of 4 show two singlets (δ 0.32 and 4.65 ppm, respectively) for the methyl protons and carbons of the -CH₂SiMe₃ groups. The ²⁹Si NMR spectrum of 4 shows two resonances (δ -62.82 and -2.78 ppm), attributed to the silicon atom in PhC(NtBu)₂Si(NAr)₂ and silicon atoms in -CH₂SiMe₃ groups, respectively. The IR spectrum of 4 shows a stretching vibration band of Si=N at 1421 cm⁻¹, which is red shifted compared to that of the free ligand 3 (1493 cm^{-1}).

The molecular structure of 4 was determined by X-ray singlecrystal analysis (Fig. 1). In the solid state, 4 is essentially C_2 symmetric. The structure of 4 indicates that the yttrium atom is four-coordinate and solvent-free, being bonded to the silaamidinate ligand in η^2 fashion and two -CH₂SiMe₃ groups with a distorted tetrahedral geometry. In contrast, the known yttrium dialkyl complexes with similar bulky amidinate, guanidinate, diimidosulfonate and imidophosphonamide ligands are not solvent-free with at least one coordinated THF molecule.8 The Y-C bond lengths (2.449(5) and 2.426(5) Å) in 4 are elongated relative to those in [PhC(NAr)₂]Y(CH₂SiMe₃)₂(THF) (2.374(4) and 2.384(4) Å) and $[Me_2NC(NAr)_2]Y(CH_2SiMe_3)_2(THF)$ (2.388(2) and 2.407(2) Å). In contrast, the Y-N bond lengths (2.338(4) and 2.339(3) Å) in 4 are only marginally shorter than those in $[PhC(NAr)_2]Y(CH_2SiMe_3)_2(THF)$ (2.339(3) and 2.369(2) Å) and $[Me_2NC(NAr)_2]Y(CH_2SiMe_3)_2(THF)$ (2.345(2) and 2.338(2) Å). The bulkiness of the silicon substituents and the large ionic radius of silicon in 4 result in small Y–N–C angles (av. 131.3(2)°) but a large N-Y-N angle (67.89(12)°) compared to the corresponding



Fig. 1 ORTEP representation of the X-ray structure of **4** with 30% ellipsoid probability. Hydrogen atoms are omitted for clarity.

angles determined for amidinate, guanidinate and diimidosulfonate yttrium dialkyls (ranging from 138.2 to 143.8° for Y–N–C angles and from 57.5 to 61.5° for N–Y–N angles). The average dihedral angle between the N–Y–N plane and the Ar rings is 43.4° , which is quite smaller than those (79.7 and 73.3°) in [PhC(NAr)₂]Y(CH₂SiMe₃)₂(THF) and [PhS(NAr)₂]Y(CH₂SiMe₃)₂(THF)₂, respectively. In the silaamidinate ligand of 4, the Si1–N1 and Si1–N2 bond lengths (1.662(4) and 1.670(3) Å) are noticeably longer than the silicon–nitrogen double bond length in 2 (1.545(2) Å) but shorter than the silicon–nitrogen single bond.

Isocyanurates, cyclotrimeric products of isocyanate, are commonly used as additives in polyurethane materials in order to enhance their physical properties.¹¹ Isocyanurates have also attracted considerable attention in microporous materials,¹² selective ion-bonding¹³ and drug delivery.¹⁴ Lewis bases,¹⁵ the main group complexes¹⁶ and transition metal complexes¹⁷ have been used as catalysts for isocyanate cyclotrimerization. However, many existing cyclotrimerization methodologies faced issues such as low activity, harsh reaction conditions, by-product formation and difficulty in product separation. Rare-earth metal catalysts have displayed mild reaction conditions and good selectivity in this transformation, but poor functional group tolerance is a serious constraint.¹⁸

The catalytic cyclotrimerization of 3-methylphenyl isocyanate using the yttrium dialkyl complex **4** as a catalyst has been examined (Table 1). It was observed that the catalytic reaction in THF displayed excellent activity and selectivity (entry 3, 98% isolated yield with 0.25 mol% catalyst loading) in contrast to those in toluene and Et_2O at 23 °C after 12 hours (entries 1 and 2). However, a decrease of the catalyst loading (0.1 mol%) and the reaction time (6 hours) led to the lowering of the isolated yields (71% in entry 4 and 76% in entry 5).

Table 1 Optimization of cyclotrimerization of 3-methylphenyl isocyanate catalysed by $\mathbf{4}^a$

Entry	Solvent	Cat. (mol%)	Time (h)	Isolated yield (%)
1	Toluene	0.25	12	27
2	Et_2O	0.25	12	31
3	THF	0.25	12	98
4	THF	0.1	12	71
5	THF	0.25	6	76

^a Reaction conditions: isocyanate (8 mmol), 5 mL solvent, 23 °C.

∬ 0 5d: 99%

OMe

5h: 98%



Under the optimized conditions, a range of functional isocyanates were examined with 0.25 mol% of 4 in THF at 23 °C. As shown in Table 2, 4 is one of the catalysts with the highest activity among the reported rare-earth metal catalysts for cyclotrimerization of isocyanates.¹⁸ Surprisingly, 4 exhibited excellent functional group tolerance, which is quite rare in the chemical transformation catalysed by rare-earth alkyl complexes. The substituted aromatic isocyanates can be catalysed to the corresponding cyclotrimeric products (5c cyano-, 5d chloro-, 5e bromo-, 5f nitro-, 5g trifluoromethyl- and 5h methoxy-) in excellent yields (88-99%). We reasoned that the excellent functional group tolerance of 4 could be attributed to the electron-donating feature of the silaamidinate ligand, which may increase the electron density and reduce the Lewis acidity of the yttrium ion. It was found that the steric effects of the substrates are also pronounced. The catalytic cyclotrimerization of 2-methylphenyl (5i) and 2-nitrophenyl (5j) isocyanates gave relatively low yields, and the reaction of 2,6-dimethylphenyl isocyanate cannot take place under the optimized conditions. The activities of aromatic and aliphatic isocyanates were different due to the electronic effects. Benzyl isocyanate afforded the cyclotrimeric product 5k in 56% yield, whereas isopropyl and cyclohexyl isocyanates were not able to undergo cyclotrimerization under the catalytic conditions. We also carried out catalytic cyclotrimerization of phenyl isothiocyanate with 4, but no cyclotrimeric product was observed.

In order to gain insight into the mechanism of isocyanate cyclotrimerization, the stoichiometric reaction of 4 with 3-methylphenyl isocyanate was investigated. The insertion of isocyanates into the two Y-C bonds led to the formation of





 $[PhC(NtBu)_{2}Si(NAr)_{2}]Y[OC(CH_{2}SiMe_{3})N(3-MeC_{6}H_{4})]_{2}$ (6) in 59% yield (Scheme 2). The reactions of rare-earth alkyl complexes with isocyanate have been previously investigated.¹⁹ The molecular structure of 6 was confirmed by ¹H, ¹³C and ²⁹Si NMR, IR and X-ray single-crystal analysis (Fig. S1 in ESI‡). Significant downfield shifts were observed for -CH2SiMe3 group resonances in the ¹H NMR (δ –0.12 and –0.26 ppm in 4 and 1.85 ppm in 6) and ²⁹Si NMR spectra of 6 (δ –2.78 ppm in 4 and 0.86 ppm in 6) compared to those of 4, owing to the insertion reactions. In the IR spectrum of 6, a new strong band was observed at 1521 cm⁻¹, which is assigned to the absorption of the delocalized O-C-N moieties.

The double insertion product 6 was the major product even when one equivalent of isocyanate was used. When the amount of isocyanate was increased (more than two equivalents), a cyclotrimerization product can be observed. The catalytic behaviours of the insertion product 6 (97% isolated yield of 5a) were comparable to those of 4, indicating that 6 is the key intermediate in the catalytic cycle. The proposed mechanism is depicted in Fig. 2.²⁰ The insertion of isocyanates into the two Y-C bonds of 4 resulted in the formation of the intermediate 6, which further underwent insertion reactions with the isocyanate to give intermediates A and B. Finally, the intermediate B underwent intramolecular cyclotrimerization to give the product 5 and regenerated the intermediate 6.

In conclusion, a sterically demanding silaamidinate ligand has been prepared and successfully employed for the synthesis of well-defined rare-earth complexes for the first time. The unique electronic structure of the ligand renders the lowcoordinate and solvent-free yttrium complex less Lewis acidic and tolerant to some functional groups. Preliminary reactivity studies demonstrated that this complex enabled the catalytic cyclotrimerization of a series of isocyanates with a wide range



Fig. 2 Proposed mechanism of isocyanate cyclotrimerization.

of substrate scope. Further studies on silaamidinate rare-earth metal complexes and their reactions are currently in progress.

We thank the National Natural Science Foundation of China (21890722 and 21632006) for financial support.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) P. W. Roesky, Molecular Catalysis of Rare-Earth Elements, Springer, Berlin, 2010, vol. 137, p. 1; (b) A. A. Trifonov and D. M. Lyubov, Coord. Chem. Rev., 2017, 340, 10; (c) D. Liu, B. Liu, Z. Pan, J. Li and C. Cui, Sci. China: Chem., 2019, 62, 571; (d) S. Hong and T. J. Marks, Acc. Chem. Res., 2004, 37, 673; (e) M. Nishiura, F. Guo and Z. Hou, Acc. Chem. Res., 2015, 48, 2209; (f) J. Gromada, J.-F. Carpentier and A. Mortreux, Coord. Chem. Rev., 2004, 248, 397.
- 2 R. Anwander, *Principles in Organolanthanide Chemistry*, Springer, Berlin Heidelberg, 1999, p. 3.
- 3 (a) P. P. Power, Chem. Rev., 2012, **112**, 3482; (b) D. L. Kays, Dalton Trans., 2011, **40**, 769.
- 4 Representative examples: (a) M. I. Lipschutz, T. Chantarojsiri, Y. Dong and T. D. Tilley, J. Am. Chem. Soc., 2015, **137**, 6366; (b) G. Ung and J. C. Peters, Angew. Chem., Int. Ed., 2015, **54**, 532; (c) C. Chen, T. R. Dugan, W. W. Brennessel, D. J. Weix and P. L. Holland, J. Am. Chem. Soc., 2014, **136**, 945.
- 5 (a) P. G. Hayes, W. E. Piers, L. W. M. Lee, L. K. Knight, M. Parvez, M. R. J. Elsegood and W. Clegg, Organometallics, 2001, 20, 2533; (b) S. Hong, S. Tian, M. V. Metz and T. J. Marks, J. Am. Chem. Soc., 2003, 125, 14768; (c) D. Wang, S. Li, X. Liu, W. Gao and D. Cui, Organometallics, 2008, 27, 6531; (d) K. D. Conroy, W. E. Piers and M. Parvez, J. Organomet. Chem., 2008, 693, 834; (e) A. L. Kenward, J. A. Ross, W. E. Piers and M. Parvez, Organometallics, 2009, 28, 3625; (f) A. L. Kenward, W. E. Piers and M. Parvez, Organometallics, 2009, 28, 3012; (g) K. R. D. Johnson, A. P. Côté and P. G. Hayes, J. Organomet. Chem., 2010, 695, 2747; (h) D. Li, S. Li, D. Cui, X. Zhang and A. A. Trifonov, Dalton Trans., 2011, 40, 2151.
- 6 (a) J. Niesmann, U. Klingebiel, M. Schäfer and R. Boese, Organometallics, 1998, 17, 947; (b) N. Kocher, J. Henn, B. Gostevskii, D. Kost, I. Kalikhman, B. Engels and D. Stalke, J. Am. Chem. Soc., 2004, 126, 5563; (c) L. Kong and C. Cui, Organometallics, 2010, 29, 5738.
- 7 (a) J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, 133, 219;
 (b) A. Kissounko, M. V. Zabalov, G. P. Brusova and D. A. Lemenovskii, *Russ. Chem. Rev.*, 2006, 75, 351; (c) F. T. Edelmann, *Chem. Soc. Rev.*, 2012, 41, 7657.
- 8 Representative examples of rare-earth metal: (a) S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2003, 522; (b) S. Bambirra, M. W. Bouwkamp, A. Meetsma and B. Hessen, *J. Am. Chem. Soc.*, 2004, **126**, 9182; (c) S. Ge, A. Meetsma and B. Hessen, *Organometallics*, 2008, **27**, 3131; (d) L. Zhang, M. Nishiura, M. Yuki, Y. Luo and Z. Hou, *Angew. Chem., Int. Ed.*, 2008, **47**, 2642; (e) J. Hong, H. Tian, L. Zhang, X. Zhou, I. Del Rosal, L. Weng and L. Maron, *Angew. Chem., Int. Ed.*, 2018, **57**, 1062; (f) B. Liu, L. Li, G. Sun, D. Liu, S. Li and D. Cui, *Chem. Commun.*,

2015, **51**, 1039; (g) B. Liu, L. Li, G. Sun, J. Liu, M. Wang, S. Li and D. Cui, *Macromolecules*, 2014, **47**, 4971.

- 9 (a) S. Khan, S. S. Sen, D. Kratzert, G. Tavčar, H. W. Roesky and D. Stalke, *Chem. – Eur. J.*, 2011, 17, 4283; (b) P. P. Samuel, R. Azhakar, R. S. Ghadwal, S. S. Sen, H. W. Roesky, M. Granitzka, J. Matussek, R. Herbst-Irmer and D. Stalke, *Inorg. Chem.*, 2012, 51, 11049.
- 10 C.-W. So, H. W. Roesky, J. Magull and R. B. Oswald, Angew. Chem., Int. Ed., 2006, 45, 3948.
- 11 (a) J. M. Kenny, L. Torre and L. M. Chiacchiarelli, *J. Appl. Polym. Sci.*, 2015, 132, 42750; (b) G. Wegener, M. Brandt, L. Duda, J. Hofmann, B. Klesczewski, D. Koch, R.-J. Kumpf, H. Orzesek, H.-G. Pirkl, C. Six, C. Steinlein and M. Weisbeck, *Appl. Catal.*, A, 2001, 221, 303.
- 12 (a) E. Preis, N. Schindler, S. Adrian and U. Scherf, *ACS Macro Lett.*, 2015, 4, 1268; (b) Y. Zhang, S. N. Riduan and J. Y. Ying, *Chem. Eur. J.*, 2009, **15**, 1077.
- 13 M. Mascal, I. Yakovlev, E. B. Nikitin and J. C. Fettinger, Angew. Chem., Int. Ed., 2007, 46, 8782.
- 14 (a) A. P. Murray and M. J. Miller, J. Org. Chem., 2003, 68, 191;
 (b) M. Ghosh and M. J. Miller, J. Org. Chem., 1994, 59, 1020.
- (a) Y. Taguchi, I. Shibuya, M. Yasumoto, T. Tsuchiya and K. Yonemoto, Bull. Chem. Soc. Jpn., 1990, 63, 3486; (b) D. Heift, Z. Benkő, H. Grützmacher, A. R. Jupp and J. M. Goicoechea, Chem. Sci., 2015, 6, 4017; (c) J. N. Gibb and J. M. Goodman, Org. Biomol. Chem., 2013, 11, 90; (d) S. M. Raders and J. G. Verkade, J. Org. Chem., 2010, 75, 5308; (e) Z. Pusztai, G. Vlad, A. Bodor, I. T. Horváth, H. J. Laas, R. Halpaap and F. U. Richter, Angew. Chem., Int. Ed., 2006, 45, 107; (f) J.-S. Tang and J. G. Verkade, Angew. Chem., Int. Ed. Engl., 1993, 32, 896; (g) H. A. Duong, M. J. Cross and J. Louie, Org. Lett., 2004, 6, 4679.
- 16 (a) M. K. Barman, A. Baishya, T. Peddarao and S. Nembenna, J. Organomet. Chem., 2014, 772–773, 265; (b) L. Orzechowski and S. Harder, Organometallics, 2007, 26, 2144; (c) S. R. Foley, Y. Zhou, G. P. A. Yap and D. S. Richeson, Inorg. Chem., 2000, 39, 924; (d) S. R. Foley, G. P. A. Yap and D. S. Richeson, Organometallics, 1999, 18, 4700.
- (a) S. G. Lee, K. Y. Choi, Y. J. Kim, S. Park and S. W. Lee, *Dalton Trans.*, 2015, 44, 6537; (b) F. Paul, S. Moulin, O. Piechaczyk, P. Le Floch and J. A. Osborn, *J. Am. Chem. Soc.*, 2007, 129, 7294; (c) H. R. Sharpe, A. M. Geer, H. E. L. Williams, T. J. Blundell, W. Lewis, A. J. Blake and D. L. Kays, *Chem. Commun.*, 2017, 53, 937.
- 18 (a) W. Yi, J. Zhang, L. Hong, Z. Chen and X. Zhou, Organometallics, 2011, 30, 5809; (b) X. Zhu, J. Fan, Y. Wu, S. Wang, L. Zhang, G. Yang, Y. Wei, C. Yin, H. Zhu, S. Wu and H. Zhang, Organometallics, 2009, 28, 3882; (c) W.-K. Wong, L. Zhang, W.-T. Wong, F. Xue and T. C. W. Mak, J. Chem. Soc., Dalton Trans., 1999, 615; (d) Y. Wu, S. Wang, X. Zhu, G. Yang, Y. Wei, L. Zhang and H.-b. Song, Inorg. Chem., 2008, 47, 5503; (e) H.-M. Wang, H.-X. Li, X.-Y. Yu, Z.-G. Ren and J.-P. Lang, Tetrahedron, 2011, 67, 1530.
- (a) J. Zhang, R. Ruan, Z. Shao, R. Cai, L. Weng and X. Zhou, Organometallics, 2002, 21, 1420; (b) X. Zhou, L. Zhang, M. Zhu, R. Cai, L. Weng, Z. Huang and Q. Wu, Organometallics, 2001, 20, 5700; (c) T. Li, M. Nishiura, J. Cheng, Y. Li and Z. Hou, Chem. – Eur. J., 2012, 18, 15079; (d) S. Li, M. Wang, B. Liu, L. Li, J. Cheng, C. Wu, D. Liu, J. Liu and D. Cui, Chem. – Eur. J., 2014, 20, 15493; (e) J. Hong, L. Zhang, K. Wang, Z. Chen, L. Wu and X. Zhou, Organometallics, 2013, 32, 7312; (f) J. Li, H. Huang, F. Wang and C. Cui, Organometallics, 2015, 34, 683.
- 20 (a) H. Wang, H.-W. Li and Z. Xie, *Organometallics*, 2003, 22, 4522;
 (b) Y. Wu, S. Wang, X. Zhu, G. Yang, Y. Wei, L. Zhang and H. Song, *Inorg. Chem.*, 2008, 47, 5503.