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## Planar three-coordinate iron(II) complexes supported by sterically demanding –Si(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub><sup>t</sup>Bu) ligands†

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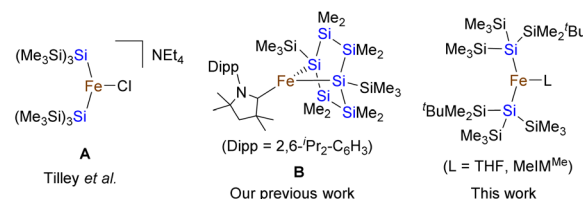
**Sterically demanding organosilyl ligands support the formation of coordinatively unsaturated complexes. In this study, we found that using the ligand –Si(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub><sup>t</sup>Bu) affords exclusively planar three-coordinate iron bis(silyl) complexes that show good catalytic performance in the hydrosilylation of acetophenone.**

The development of low-coordinated transition-metal complexes is generally driven by their excellent chemical reactivity. The introduction of organosilyl ligands is known to promote the formation of low-coordinated metal complexes due to their strong electron-donating properties and *trans*-influence.<sup>1</sup> It is therefore not surprising that a considerable number of metal complexes supported by organosilyl ligands has already been synthesized and applied as catalysts in a variety of transformations.<sup>1</sup> Reflecting the recently increased interest in the development of environmentally benign catalysts, substantial effort has been devoted to synthesizing coordinatively unsaturated iron complexes, and their catalytic performance has been showcased.<sup>2</sup> However well-characterized coordinatively highly unsaturated three-coordinate iron-silyl complexes have been limited to two previous examples (Fig. 1),<sup>†</sup> *i.e.*, anionic bis(silyl) iron complex **A** reported by Tilley *et al.*<sup>3</sup> and our bis(silyl) complex **B** supported by the <sup>Me</sup>CAAC ligand (<sup>Me</sup>CAAC = 1-(2,6-di-isopropylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene).<sup>4</sup> Complex **B** is the only example of a neutral complex, and the introduction of auxiliary ligands other than the <sup>Me</sup>CAAC ligand, such as *e.g.*, THF, pyridine, or an N-heterocyclic carbenes (NHC) on “Fe[Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub>” and its analogous fragment exclusively afford four-coordinate complexes.<sup>4,5</sup> Therefore, rational synthetic strategies for the

construction of coordinatively unsaturated three-coordinate iron-silyl complexes remain elusive so far.<sup>§</sup>

We have recently focused on the development of highly reactive Fe(II) and Mn(II) complexes, and found that the use of sterically demanding organosilyl ligands such as –Si(SiMe<sub>3</sub>)<sub>3</sub> effectively facilitates the synthesis of four-coordinate Fe(II) and Mn(II) complexes.<sup>5,6</sup> For instance, Fe[Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(THF)<sub>2</sub> (**1**) was produced in one step *via* the reaction of FeBr<sub>2</sub> with 2 equiv. of KSi(SiMe<sub>3</sub>)<sub>3</sub> in THF at room temperature.<sup>5</sup> Furthermore, the obtained compounds are good catalysts for reduction reactions such as the hydrosilylation of carbonyl compounds and the hydrogenation of alkenes.<sup>5,6</sup> As a continuation of this line of chemistry, we hypothesized that if the structure of the –Si(SiMe<sub>3</sub>)<sub>3</sub> ligand were appropriately modified, it might be possible to construct metal complexes with lower coordination numbers. Here, we report that the sterically demanding organosilyl ligand –Si(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub><sup>t</sup>Bu), in which one of the three –SiMe<sub>3</sub> moieties on the central silicon center is replaced with a SiMe<sub>2</sub><sup>t</sup>Bu group, exclusively produces planar three-coordinate Fe(II)-disilyl complexes when treated with FeBr<sub>2</sub>. The thus obtained complexes exhibit superior catalytic performance compared to four-coordinate complex **1** in the hydrosilylation of acetophenone.

The synthetic strategy used in this study is similar to that previously used to obtain **1**. KSi(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub><sup>t</sup>Bu) was generated *in situ* according to the methods reported by Marschner<sup>7a,b</sup> and Li<sup>7c</sup> and subsequently treated with 0.5



**Fig. 1** Previously reported three-coordinate iron(II)-silyl complexes and the complexes reported in this study.

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equiv. of  $\text{FeBr}_2$  in THF at room temperature for 30 min; the resulting planar three-coordinate iron(II)-disilyl complex **2** was isolated in 83% yield in the form of green crystals (Scheme 1). Complex **2** is paramagnetic and its  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ; room temperature) exhibits broad signals attributable to  $\text{SiMe}_3$  and  $\text{SiMe}_2^t\text{Bu}$  at  $-47.08$ ,  $11.09$ , and  $23.99$  ppm, as well as broad resonances at  $0.28$  and  $1.01$  ppm derived from the coordinated THF molecule. The solution magnetic moment measured using the Evans method<sup>8</sup> ( $\mu_{\text{eff}} = 4.49$ ) is consistent with an open-shell  $S = 2$  ground state. The molecular structure of **2** in the solid state was unequivocally determined by a single-crystal X-ray diffraction (XRD) analysis.

The Fe, Si(1), Si(2) and O(1) atoms in **2** are aligned nearly coplanar, with deviations of  $0.002$ – $0.007$  Å, and the sum of the angles around the iron center is  $359.99^\circ$ . Thus, it can be concluded that the iron center in **2** adopts a planar three-coordinate structure with two  $-\text{Si}(\text{SiMe}_3)_2(\text{SiMe}_2^t\text{Bu})$  ligands and one THF ligand. The Fe–Si bonds (Fe–Si(1):  $2.4892(6)$  Å; Fe–Si(2):  $2.4751(6)$  Å) are significantly shorter than those in four-coordinate iron(II)-disilyl complex **1** (Fe–Si:  $2.5445(8)$  Å), whereas the Si(1)–Fe–Si(2) angle ( $139.27(2)^\circ$ ) is comparable to that seen in **1** ( $135.23(3)^\circ$ ).<sup>5</sup> It should also be noted here that the Fe–Si bonds in **2** are slightly shorter than those of recently reported three-coordinate iron(II) disilyl complex **B** (Fig. 1;  $2.4923(11)/2.5209(12)$  Å), presumably due to the steric repulsion induced by  $\text{Me}^{\text{CAAC}}$  in **B**.<sup>4</sup> Moreover, the Fe–Si bonds in **2** are comparable to those in Tilley's anionic iron(II) disilyl complex **A** (Fe–Si:  $2.488(6)/2.491(6)$  Å).<sup>3</sup>

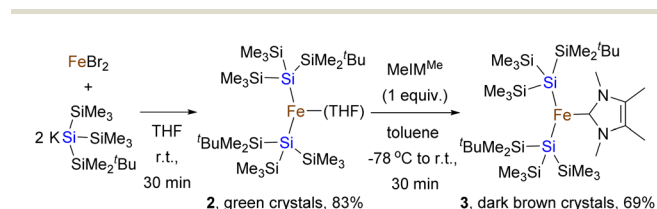
Recently, we have reported that the two THF ligands in **1** can be readily exchanged for two N-heterocyclic carbene (NHC) ligands such as 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene ( $\text{MeIM}^{\text{Me}}$ ). During this reaction, a change in the coordination geometry from tetrahedral to square planar occurred, to furnish  $\text{trans-Fe}[\text{Si}(\text{SiMe}_3)_3]_2(\text{MeIM}^{\text{Me}})_2$ , i.e., a planar four-coordinate iron(II) complex with a *trans* configuration.<sup>4</sup> To further investigate the coordination behavior of  $\text{MeIM}^{\text{Me}}$ , it was treated with **2** in toluene at  $-78^\circ\text{C}$  and allowed to warm to room temperature; the resulting planar three-coordinate complex  $\text{Fe}[\text{Si}(\text{SiMe}_3)_2(\text{SiMe}_2^t\text{Bu})]_2(\text{MeIM}^{\text{Me}})$  (**3**) was obtained in 69% yield as a sole product *via* a simple ligand-exchange reaction (Scheme 1). Complex **3** is paramagnetic, and in its  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$  at room temperature, the signals derived from the  $\text{SiMe}_3$  and  $\text{SiMe}_2^t\text{Bu}$  groups appear at  $-26.32$ ,  $9.99$ , and  $26.78$  ppm, while those of the coordinated  $\text{MeIM}^{\text{Me}}$  appear at  $0.28$  and  $73.13$  ppm. The estimated magnetic

moment of **3** based on the Evans method ( $\mu_{\text{eff}} = 5.32$ ) is comparable to that observed in **2**, suggesting that the spin state and coordination geometry around the iron center are maintained in the reaction. The molecular structure of **3** in the solid state was determined by single-crystal XRD analysis (Fig. 2).

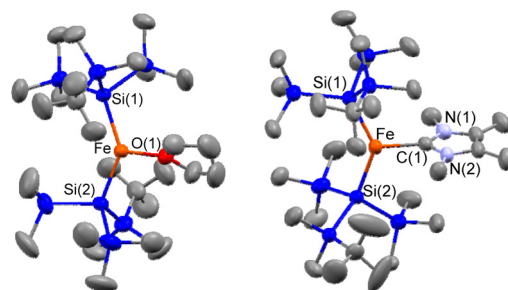
Similar to **2**, **3** adopts a three-coordinate planar structure in which the sum of the three angles around the iron center is  $359.67^\circ$ . The Si–Fe–Si angle ( $135.43(2)^\circ$ ) is comparable to that of **2**, and the Fe–Si bonds are slightly elongated ( $2.5020(7)/2.5096(6)$  Å) than **2**, presumably due to steric repulsion between the  $-\text{SiMe}_2^t\text{Bu}$  groups and the  $\text{MeIM}^{\text{Me}}$  ligand. The Fe–C(1) bond length is  $2.1150(14)$  Å in **3**. The Fe–Si and Fe–C bond distances in  $\text{trans-Fe}[\text{Si}(\text{SiMe}_3)_3]_2(\text{MeIM}^{\text{Me}})_2$  were reported to be  $2.5385(4)$  Å and  $1.9563(15)$  Å, respectively; the former is slightly longer than those in **3**, whereas the latter is significantly shorter than that in **3**. This elongation of the Fe–C(NHC) bond in **3** might be induced by the steric repulsion between the  $^t\text{Bu}$  group on the Si atom and the Me substituent on the nitrogen atom of the  $\text{MeIM}^{\text{Me}}$  ligand.

Thus, it can be concluded that the substitution of one of three  $\text{SiMe}_3$  groups on the central silicon atom of the  $-\text{Si}(\text{SiMe}_3)_3$  ligand for a  $-\text{SiMe}_2^t\text{Bu}$  moiety effectively promotes the formation of three-coordinate planar Fe(II)-disilyl complexes **2** and **3**. Given their high coordinative unsaturation, we expected that **2** and **3** would exhibit good reactivity. In our previous paper, we reported that tetrahedral four-coordinate complex **1** and the aforementioned four-coordinate planar complex  $\text{trans-Fe}[\text{Si}(\text{SiMe}_3)_3]_2(\text{MeIM}^{\text{Me}})_2$  show good catalytic performance in the hydrosilylation of acetophenone.<sup>4,5</sup> Thus, the catalytic performance of **2** and **3** was examined in the hydrosilylation of acetophenone using the hydrosilanes,  $\text{Ph}_2\text{SiH}_2$  and 1,1,3,3-tetramethyldisiloxane (TMDS).<sup>9</sup>

In the hydrosilylation of acetophenone with  $\text{Ph}_2\text{SiH}_2$  catalyzed by  $0.1$  mol% of **2**, complete conversion of acetophenone after 20 min was confirmed when the reaction was performed at room temperature (entry 2, Table 1). In stark contrast, when four-coordinate **1** was used, 1 h was required for the full conversion of acetophenone in the reaction with  $\text{Ph}_2\text{SiH}_2$  (entry 1).<sup>4,5</sup> Moreover, complete conversion of acetophenone was confirmed after 1 h by  $0.1$  mol% of **3** (entry 3). These reactions

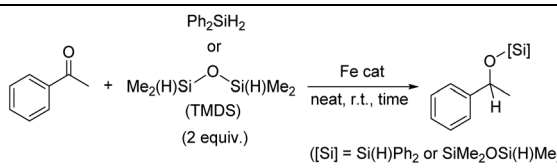


**Scheme 1** Synthesis of planar three-coordinate iron(II) complexes **2** and **3** supported by two  $-\text{Si}(\text{SiMe}_3)_2(\text{SiMe}_2^t\text{Bu})$  ligands.



**Fig. 2** Molecular structures of **2** (left) and **3** (right) in the solid state with thermal ellipsoids at 50% probability; all hydrogen atoms are omitted for clarity.



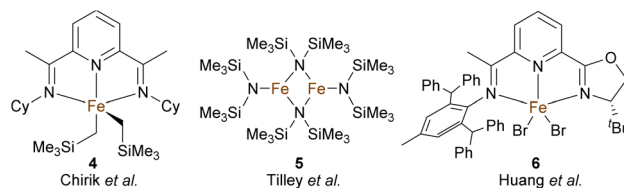
**Table 1** Hydrosilylation of acetophenone catalyzed by iron complexes **2** and **3**<sup>a</sup>


Entry	Cat.	Hydrosilane	Cat. loading (mol%)	Time (h)	Conv. <sup>b</sup> (%)
1 <sup>c</sup>	<b>1</b>	Ph <sub>2</sub> SiH <sub>2</sub>	0.1	1	>99
2 <sup>c</sup>	<b>2</b>	Ph <sub>2</sub> SiH <sub>2</sub>	0.1	0.33	>99
3 <sup>c</sup>	<b>3</b>	Ph <sub>2</sub> SiH <sub>2</sub>	0.1	1	>99
4 <sup>d</sup>	<b>4</b>	Ph <sub>2</sub> SiH <sub>2</sub>	0.1	3	>99
5 <sup>e</sup>	<b>5</b>	Ph <sub>2</sub> SiH <sub>2</sub>	0.55	0.5	>99
6 <sup>f</sup>	<b>6</b>	Ph <sub>2</sub> SiH <sub>2</sub>	1.0	3	>99
7 <sup>c</sup>	<b>1</b>	TMDS	0.5	24	30
8	<b>2</b>	TMDS	0.5	24	60
9	<b>3</b>	TMDS	0.5	24	81

<sup>a</sup> Reactions were performed using acetophenone (3 mmol) with Ph<sub>2</sub>SiH<sub>2</sub> (6.6 mmol) or acetophenone (1 mmol) with TMDS (2.2 mmol) in the presence of a catalytic amount of the iron catalyst under neat conditions at room temperature. <sup>b</sup> The conversion was determined using <sup>1</sup>H NMR spectroscopy in the presence of an internal standard (1,4-dioxane). <sup>c</sup> Reactions were performed using acetophenone (3 mmol) with Ph<sub>2</sub>SiH<sub>2</sub> (6.6 mmol) in benzene (3 mL) in the presence of 0.1 mol% of iron catalyst at room temperature. <sup>d</sup> For details, see ref. 10a. <sup>e</sup> For details, see ref. 10b. <sup>f</sup> For details, see ref. 10c.

were monitored by <sup>1</sup>H NMR spectrum, and the time course of these reaction was summarized in the ESI.† It was found that complex **2** apparently exhibited superior catalytic performance than four-coordinated catalyst **1**. Although full conversion of acetophenone was confirmed in the reaction catalyzed by both **1** and **3** after 1 h, induction period apparently observed in the reaction mediated by **1**, presumably due to the generation of active species from **1** by liberation of coordinated THF ligand (s). Subsequently, we performed the hydrosilylation of acetophenone with TMDS using 0.5 mol% of **2** at room temperature for 24 h, which resulted in 60% conversion of acetophenone (entry 8), whereas the conversion reached only 30% using **1** as the catalyst under otherwise identical reaction conditions.<sup>4,5</sup> A slight increase in conversion (81%) was observed when **3** was used as the catalyst under otherwise identical reaction conditions (entry 9). Thus, it can be concluded that substitution of one of the three SiMe<sub>3</sub> groups on the –Si(SiMe<sub>3</sub>)<sub>3</sub> ligand with a SiMe<sub>2</sub><sup>t</sup>Bu moiety leads to highly active iron catalysts.

As described in Table 1, both complexes **2** and **3** showed good catalytic performance in the hydrosilylation of acetophenone with Ph<sub>2</sub>SiH<sub>2</sub>. It is known that hydrosilylation of acetophenone with Ph<sub>2</sub>SiH<sub>2</sub> is often used to evaluate the catalytic performance of newly synthesized iron complexes.<sup>10</sup> As the representative, Chirik's iron complex **4** shown in Fig. 3 was revealed to catalyze the hydrosilylation of acetophenone with Ph<sub>2</sub>SiH<sub>2</sub> effectively with 0.1 mol% of catalyst loading at room temperature, but complex **4** required 3 h to complete the reaction (entry 4).<sup>10a</sup> Tilley have reported that a dinuclear complex **5** also showed good catalytic performance for the same cataly-

**Fig. 3** Previously reported iron(II) catalysts that exhibited high catalytic performance for the hydrosilylation of acetophenone with Ph<sub>2</sub>SiH<sub>2</sub>.

sis at room temperature, but higher catalyst loading (0.55 mol%) is required (entry 5).<sup>10b</sup> In addition, Huang *et al.* have described that the same hydrosilylation proceeded at room temperature to quantitatively afford the desired product with 1 mol% of **5** in 3 h (entry 6).<sup>10c</sup> By comparison of the catalytic performance of **2** and **3** with aforementioned iron catalysts, it could be concluded that **2** and **3** could be categorized as one of the most active catalyst for the hydrosilylation of acetophenone among the iron catalyst. In conclusion, appropriate modification of the steric environment of the organosilyl ligand –Si(SiMe<sub>3</sub>)<sub>3</sub> to –Si(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub><sup>t</sup>Bu) led directly to the construction of highly coordinatively unsaturated planar three-coordinate Fe(II) complexes when KSi(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub><sup>t</sup>Bu) was treated with FeBr<sub>2</sub> in THF. The relatively labile THF ligand can subsequently be readily replaced by N-heterocyclic carbene (NHC) ligands such as 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene (MeIm<sup>Me</sup>). These Fe(II) complexes showed high catalytic activity in the hydrosilylation of acetophenone using the hydrosilanes, Ph<sub>2</sub>SiH<sub>2</sub> and 1,1,3,3-tetramethyldisiloxane (TMDS). In modern organosilicon chemistry, the design and application of sterically demanding substituents of the type –Si(SiR<sub>3</sub>)<sub>3</sub> to kinetically stabilize highly reactive compounds is currently a hot topic.<sup>11</sup> Using these precedents as a strategy for ligand design, we will continue working on a series of coordinatively unsaturated, highly reactive base-metal complexes and investigate their applications as catalysts in our laboratories.

## Author contributions

Y. Sunada designed the project. R. Ishii carried out all of the experiments. R. Ishii and Y. Sunada analyzed the data and wrote the paper. All authors discussed the results and made comments and edits to the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

‡ The synthesis and structural characterization of a three-coordinate iron complex supported by a silylene ligand have recently been reported; for details, see ref. 12.

§ Tilley *et al.* have obtained  $\text{Fe}[\text{Si}(\text{SiMe}_3)_3]_2(\text{L})$  ( $\text{L} = \text{Et}_2\text{O}$ , THF) from the reaction of anionic  $\{\text{Fe}(\text{Cl})[\text{Si}(\text{SiMe}_3)_3]_2\}^-$  with  $\text{Me}_3\text{SiOSO}_2\text{CF}_3$  in  $\text{Et}_2\text{O}$  or THF; however, a crystallographic analysis has not yet been reported for these complexes; for details, see ref. 3.

- (a) J. Y. Corey, *Chem. Rev.*, 2016, **116**, 11291–11435; (b) J. Y. Corey, *Chem. Rev.*, 2011, **111**, 863–1071; (c) J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, 1999, **99**, 175–292.
- (a) Y. Sunada and H. Nagashima, *Dalton Trans.*, 2017, **46**, 7644–7655; (b) Y. Sunada, H. Ogushi, T. Yamamoto, S. Uto, M. Sawano, A. Tahara, H. Tanaka, Y. Shiota, K. Yoshizawa and H. Nagashima, *J. Am. Chem. Soc.*, 2018, **140**, 4119–4134; (c) Y. Sunada, H. Tsutsumi, K. Shigeta, R. Yoshida, T. Hashimoto and H. Nagashima, *Dalton Trans.*, 2013, **42**, 16687–16692; (d) Y. Sunada, H. Soejima and H. Nagashima, *Organometallics*, 2014, **33**, 5936–5939; (e) C. V. Thompson, H. D. Arman and Z. J. Tonzetich, *Organometallics*, 2022, **41**, 430–440; (f) H. Nakazawa, M. Itazaki, K. Kamata and K. Ueda, *Chem. – Asian J.*, 2007, **2**, 882–888; (g) L. J. Murphy, M. J. Ferguson, R. McDonald, M. D. Lumsden and L. Turculet, *Organometallics*, 2018, **37**, 4814–4826; (h) P. Zhang, X. Li, X. Qi, H. Sun, O. Fuhr and D. Fenske, *RSC Adv.*, 2018, **8**, 14092–14099; (i) G. Chang, P. Zhang, W. Yang, Y. Dong, S. Xie, H. Sun, X. Li, O. Fuhr and D. Fenske, *Dalton Trans.*, 2021, **50**, 17594–17602; (j) J. Ito, S. Hosokawa, H. B. Khalid and H. Nishiyama, *Organometallics*, 2015, **34**, 1377–1383.
- (a) D. M. Roddick, T. D. Tilley, A. L. Rheingold and S. J. Geib, *J. Am. Chem. Soc.*, 1987, **109**, 945–946; (b) R. H. Heyn and T. D. Tilley, *Inorg. Chim. Acta*, 2002, **341**, 91–98.
- R. Ishii, M. Nakagawa, Y. Wada and Y. Sunada, *Dalton Trans.*, 2023, **52**, 15124–15130.
- S. Arata and Y. Sunada, *Dalton Trans.*, 2019, **48**, 2891–2895.
- (a) Y. Kobayashi and Y. Sunada, *ACS Sustainable Chem. Eng.*, 2022, **10**, 1078–1082; (b) K. Saito, T. Ito, S. Arata and Y. Sunada, *ChemCatChem*, 2021, **13**, 1152–1156; (c) S. Arata, K. Suzuki, K. Yamaguchi and Y. Sunada, *Dalton Trans.*, 2020, **49**, 17537–17541.
- (a) C. Marschner, *Eur. J. Inorg. Chem.*, 1998, 221–226; (b) C. Kayser, R. Fischer, J. Baumgartner and C. Marschner, *Organometallics*, 2002, **21**, 1023–1030; (c) J. Luo, E.-H. Yan, H. Zhao, X.-Q. Xiao and Z. Li, *Polyhedron*, 2015, **102**, 233–238.
- (a) E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62; (b) C. Piguet, *J. Chem. Educ.*, 1997, **74**, 815–816; (c) G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532–536.
- J. Pesti and G. L. Larson, *Org. Process Res. Dev.*, 2016, **20**, 1164–1181.
- (a) A. M. Tondreau, E. Lobkovsky and P. J. Chirik, *Org. Lett.*, 2008, **10**, 2789–2792; (b) J. Yang and T. D. Tilley, *Angew. Chem., Int. Ed.*, 2010, **49**, 10186–10188; (c) Z. Zuo, L. Zhang, X. Leng and Z. Huang, *Chem. Commun.*, 2015, **51**, 5073–5076; (d) F. S. Wekesa, R. Arias-Ugarte, L. Kong, Z. Sumner, G. P. McGovern and M. Findlater, *Organometallics*, 2015, **34**, 5051–5056; (e) C. Grohmann, T. Hashimoto, R. Fröhlich, Y. Ohki, K. Tatsumi and F. Glorius, *Organometallics*, 2012, **31**, 8047–8050.
- (a) A. Sekiguchi and V. Ya. Lee, *Chem. Rev.*, 2003, **103**, 1429–1447; (b) K. Gour, M. K. Bisai and S. S. Sen, *Eur. J. Inorg. Chem.*, 2022, e202200071.
- (a) M. M. Hänninen, K. Pal, B. M. Day, T. Pugh and R. A. Layfield, *Dalton Trans.*, 2016, **45**, 11301–11305; (b) Y. Bai, J. Zhang and C. Cui, *Chem. Commun.*, 2018, **54**, 8124–8127; (c) Z. He, X. Xue, Y. Liu, N. Yu and J. P. Krogman, *Dalton Trans.*, 2020, **49**, 12586–12591.

