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Structure and small molecule activation reactivity of a metallasilsesquioxane of divalent ytterbium.

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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The first metallasilsesquioxane of a divalent lanthanide, [Yb{Cy₇Si₇O₁₁(OSiMe₃)}(THF)]₂, 1, was synthesized and structurally characterized. The Cy₇Si₇O₁₁(OSiMe₃)²⁻ ligands in 1 bind two Yb(II) ions in a bridging mode. The dinuclear complex effects the twoelectrons reduction of azobenzene yielding the Yb(III) complex [{Yb(Cy₇Si₇O₁₁(OSiMe₃))(THF)₂}₂(PhNNPh)], 2, and the CO₂ reduction to CO and carbonate.

Metallasilsesquioxanes¹ of f-elements are of interest in material science and catalysis because they provide attractive homogeneous analogues of silica-supported lanthanide catalysts² and precursors to rare earth silicates which find application in optoelectronics.³ However, the chemistry of metallasilsesquioxanes of f-elements remain limited to a few examples in part due to the difficulties encountered in the crystallization and characterization of these compounds. Moreover, the synthesis of silsesquioxane complexes of highly reducing low-valent f elements is anticipated to be particularly challenging because of the tendency of silsesquioxanes to promote metal oxidation (U(IV) to U(VI)⁴ and Ce(III) to Ce(IV)⁵). This chemistry differs from that of monoanionic siloxides which led to the isolation of U(III). U(IV)⁶. Ce(III)⁷ and Ln(II)⁸ complexes.

Metallasilsesquioxane complexes have been reported only recently for uranium in different oxidation states ranging from +IV to +VI.⁴ ⁹ In contrast, the first example of a Ce(IV) silsesquioxane, $[Ce(Cy_7Si_8O_{13})_2(py)_3]$, which is a molecular

analogue of silica-supported Ce(IV) oxidation catalyst was reported 20 years ago by Edelmann and coworkers.⁵ In the last 20 years a handful of silsesquioxane complexes of lanthanides in the +III oxidation have also been synthesized and characterized^{1b, 2d, 10} for Nd,¹¹ Yb,¹² Sm,¹³ Eu¹⁴ and Er¹⁵ providing attractive functional models for heterogenous Ln(III) silicate catalyst¹⁶ that find application in important organic transformations.

The catalytic activity of heterogeneous systems comprising divalent lanthanides is increasingly studied.¹⁷ Moreover, it has become evident that ligand design is particularly important for tuning the reactivity of complexes of divalent lanthanides in small molecule activation.¹⁸ However, despite the attractive redox reactivity and properties of the few isolated Ln(II) complexes of monoanionic siloxides,^{8, 19} ^{17b, 20} silsesquioxane complexes of lanthanides in the +2 oxidation state have not yet been reported.

Here we report the synthesis of the first example of a metallasilsesquioxane of a divalent lanthanide, and we show that silsesquioxanes can act as effective supporting ligands in Ln(II) chemistry.

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Scheme 1. Synthesis of complex 1.

The divalent ytterbium complex [Yb{Cy₇Si₇O₁₁(OSiMe₃)} (THF)]₂, **1**, was obtained in 73 % yield by reacting [Yb{N(SiMe₃)₂}₂(THF)₂] with one equivalent of the monosilylated silsesquioxane Cy₇Si₇O₉(OSiMe₃)(OH)₂ ²¹ (Cy = cyclohexyl) in THF at room temperature (Scheme 1). Crystals of **1** suitable for X-ray diffraction were obtained from a concentrated THF solution of complex **1** after one night at room temperature.

The complex **1** crystallizes in the triclinic space group $P2_1/c$. The molecular structure of 1 is presented in Figure 1 and shows the presence of a centrosymmetric dinuclear complex. Two divalent ytterbium centers are five-coordinate in a distorted square pyramidal geometry and bound by three siloxide oxygen atoms, one silyl ether oxygen and one THF molecule. Two siloxide oxygen atoms bridge both Yb(II) ions in a symmetric fashion. The Yb-Yb distance in 1 (3.625 (2) Å) is slightly bigger than in the dinuclear Yb(II) siloxide complex $[Yb_2L_4]$ (L = (O^tBu)₃SiO⁻) (3.2303(3) Å)^{19b} due to the presence of the bulkier silsesquioxane ligand. The values of the Yb–O_{siloxide} distances 1 (2.193(13) - 2.397(13) Å) are larger than those found in the mononuclear Yb(III) silsesquioxane complex [Li₂Yb{Cy₇Si₇O₁₂} {Cy₇Si₇O₁₁(OSiMe₃)}(THF)₂(MeCN)] (2.115(12) – 2.236(11) Å).^{12b} This is in agreement with the presence of the larger ytterbium(II) (difference in ionic radius = 0.15 Å) in complex **1**.

Complex **1** is the first example of a divalent lanthanide complex supported by incompletely condensed polyhedral oligomeric silsesquioxane cages.



Figure 1. Solid-state molecular structure of **1** (50% probability ellipsoids). Hydrogen atoms, cyclohexyl groups, residual solvent molecules and a second molecule of **1** present in the unit cell are omitted for clarity. Selected bond lengths (Å): Yb1–Yb1¹ = 3.6253(19); Yb–O_{siloxide} range= 2.193(13) – 2.397(13);

 $\label{eq:mean Yb-O_{slloxide} = 2.29(8); Yb-O_{sllylether} = 2.621(13) - 2.651(14); Yb-O_{THF} = 2.423(13) - 2.445(14).$ Symmetry transformation used to generate equivalent atoms: 1 1-x, 2-y, 1-z.

The ¹H NMR spectrum of **1** in THF-d₈ shows the presence of broad overlapping signals assigned to the protons of the ligand's cyclohexyl groups along with a narrow signal at δ = 0.3 ppm assigned to the CH₃ protons of the OSiMe₃ moiety. The ¹H NMR spectrum of **1** in Tol-d₈ is better defined with seven sets of signals identified for the cyclohexyl's protons and the signal corresponding to the CH₃ protons of the OSiMe₃ moiety at δ = 0.6 ppm. In both solvents the ¹H NMR signals are all found in the diamagnetic region in agreement with the presence of the f¹⁴ Yb(II) ions in **1**.

Complex **1** is stable in solid state and in solution at -40 °C, however, slight signs of decomposition can be detected by ¹H NMR studies after 24 h at room temperature in THF-d₈, and complete decomposition is observed in Tol-d₈ after one week resulting in the formation of paramagnetic Yb(III) species (see Supporting Information). Decomposition is likely to arise from solvent reduction which is often observed in low valent lanthanide chemistry²² but alternative decomposition pathways involving Ln(II) disproportionation to Ln(III) and Ln(0)²³ cannot be ruled out.



Scheme 2. Reductive disproportionation of carbon dioxide by 1.

Preliminary reactivity studies were carried out with azobenzene and CO_2 in order to assess the ability of silsesquioxanes to act as effective supporting ligands in Ln(II) chemistry.

When a THF-d₈ solution of 1 was exposed to ¹³CO₂ (~5 equivalents) an immediate colour change was observed from orange to yellow. ¹H NMR studies of the reaction mixture in THF-d₈ shows the immediate disappearance of the signal assigned to 1. The ¹³C NMR spectrum of the reaction mixture in THF-d₈ shows two signals corresponding to free ¹³CO and excess ¹³CO₂. The formation of CO suggests that the complex **1** effects the reductive disproportionation of CO₂ to afford CO and carbonate (Scheme 2). The signal corresponding to ¹³CO₃²⁻ was, however, not observed in the ¹³C NMR spectrum in THF-d₈, suggesting that it is bound to the paramagnetic Yb(III) metal center in solution. The formation of Yb(III)-carbonate species is likely to proceed via a concerted mechanism as previously found for the reductive disproportionation of CO₂ promoted by mononuclear and dinuclear Ln(II) complexes supported by bulky ligands^{19c, 24} rather than involve oxo formation.

The quantitative ¹³C NMR spectrum of the residue (after removal of the solvent and of excess ¹³CO₂) in basic D₂O (pD = 13), confirmed the presence of carbonate (δ = 168.3 ppm) as the product of carbon dioxide reduction in 100% yield with respect

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to the value expected from the conversion of 2 CO₂ molecules into ¹³CO₃²⁻ and CO (measured using ¹³C labelled sodium acetate). The formation of carbonate in 100% yield was also obtained when the reaction of **1** with CO₂ was carried out in a non-polar solvent (toluene). The high selectivity towards carbonate formation from the reductive disproportionation of CO₂ observed for the Yb(II) silsesquioxane complex contrasts with the lower selectivity reported in apolar solvents for the reaction of the Yb(II) siloxide complex [Yb₂L₄K₂]⁸ (CO₃²⁻:C₂O₄²⁻ =2.2:1). A slightly lower selectivity was also reported for [Yb₂L₄]^{19c} (CO₃²⁻:C₂O₄²⁻ =50:1). These results suggest that the bulky silsesquioxane ligand provide a better control of the Yb(II) redox reactivity.

In view of these results we also set out to explore the reactivity of **1** with azobenzene.

The addition of 1 equivalent of azobenzene to an orange THF solution of 1, at -40 °C, resulted in the immediate darkening of the solution (Scheme 3). ¹H NMR spectroscopy studies showed the complete disappearance of the signal assigned to 1 in THF-d₈ and the appearance of new sets of signals in the paramagnetic region. The two-electrons reduced azobenzene product [{Yb(Cy₇Si₇O₁₁(OSiMe₃))(THF)₂}₂(μ - η ₂: η ₁PhNNPh)], 2, could be isolated from the reaction mixture in 72 % yield. Crystals of 2 suitable for X-ray diffraction were obtained by storage of a concentrated THF solution of complex 1 at room temperature for 2 days.



Scheme 3. Two electron reduction of azobenzene by 1 affording complex 2.

The complex **2** crystallizes in the triclinic space group $P\overline{1}$ (Figure 2). The solid-state structure shows the presence of an asymmetric dinuclear complex displaying a two-electron reduced azobenzene moiety bridging the two trivalent ytterbium metal centers. One ytterbium center is six-coordinate and bound by three siloxide oxygen atoms, two oxygen atoms from two THF molecules, and one hydrazido nitrogen from the reduced PhNNPh2-. The second ytterbium ion is sevencoordinate and bound by two siloxide oxygen atoms, two oxygen atoms from two THF molecules, one silyl ether O atom from a silsesquioxane ligand and two nitrogen atoms from the reduced PhNNPh²⁻ moiety. The two ytterbium centers are bridged by a reduced PhNNPh²⁻ moiety in a η_2 : η_1 fashion and by a siloxide oxygen. The azobenzene moiety in 2 is oriented in a cis-fashion as found in the previously reported Sm(III) $[(C_5Me_5)Sm{\mu-OSi(OtBu)_3}_2(N_2Ph_2)SmOSi(OtBu)_3]^{25}$ and Yb(III) $[Me_2Si(C_5Me_4)(NPh)Yb(thf)(N_2Ph_2)Yb(NPh)(C_5Me_4)SiMe_2]^{26}$

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complexes. The Yb–Yb distance in 2 (3.7038(6) Å) is slightly bigger than in 1 (3.6253(19) Å) which is consistent with the incorporation of the bridging PhNNPh²⁻ ligand. The mean Yb(III)–O_{siloxide} distance in **2** (2.19(9) Å) is reasonably close to the mean distance (2.20(4) Å)^{12b} found in the mononuclear Yb(III)silsesquioxane complex reported by H.C. Aspinall et al. The N1-N2 bond length in 2 (1.433(7) Å) is longer compared to free azobenzene (1.25 Å)^{27} and the radical anion KPhNNPh (1.331(17) Å)⁸ which is consistent with the presence of a dianionic reduced azobenzene. Furthermore, the value of the N1-N2 bond length in 2 is similar to those found in other ytterbium-PhNNPh²⁻ complexes (1.470(6) and 1.47(2) Å). ^{18b, 28} The Yb–N distances in 2 (2.148(5) – 2.576(5) Å) are comparable with those reported for the ytterbium complexes [Me⁵Cp(THF)(N₂Ph₂)Yb^{III}]₂ ^{18b} (2.188(5) – 2.572(5) Å) and [Yb₄(µ- $\eta_2: \eta_2 N_2 Ph_2)_4(\mu_3 - NPh)_2(THF)_4]^{28} (2.20(2) - 2.57(1) Å).$

The two electron reduction of azobenzene by mononuclear divalent lanthanide complexes was reported previously for La, Sm, Yb and Tm with cyclopentadienyl derivatives, naphthalenide and amide as supporting ligands.^{18b, 25-26, 28-29} In most cases, the reaction is accompanied by ligand scrambling and/or by the formation of azobenzene four-electron reduction products.^{28, 29b, 29d, 30} Only one example of a two-electron azobenzene reduction by a binuclear Yb(II) complex was reported previously.²⁵ In contrast, the Eu(II) siloxide complex $[Eu^{II}(OSi(OtBu)_3)_4K_2]$ only effects the one electron reduction of azobenzene to yield the azobenzene radical anion mononuclear complex $[Eu(\eta^2-PhNNPh)(OSi(OtBu)_3)_4K_2]$.⁸ In the case of Yb(II) compounds, the [Yb(C₁₀H₈)(thf)] complex promoted both the two- and four-electron reduction of azobenzene affording the ligand redistribution product $[Yb_4(\mu-\eta_2:\eta_2-N_2Ph_2)_4(\mu_3-NPh)_2(THF)_4]$.²⁸ Ligand redistribution was also observed after the two-electron reduction of azobenzene by [Me5Cp2Yb(THF)] to yield [Me5Cp(THF)(N2Ph2)Yb^{III}]2.18b Here, the dinuclear complex **1** promotes the selective two-electron reduction of azobenzene. Moreover, the dianionic charge and the polydentate binding mode of the silsesquioxane prevent ligand redistribution during the reaction of **1** with azobenzene.



Figure 2. Solid-state molecular structure of 2 (50% probability ellipsoids). Hydrogen atoms, cyclohexyl groups and residual solvent molecules are omitted for clarity. Selected bond lengths (Å): Yb1–Yb2 = 3.7038(6); Yb– $O_{siloxide}$ range= 2.078(4) - 2.328(4); mean Yb– $O_{siloxide}$ = 2.19(9); Yb– $O_{silylether}$ = 2.921(4); Yb1–N1 = 2.335(5); Yb2–N1 = 2.576(5); Yb2–N2 = 2.148(5). N1–N2 = 1.433(7), Yb– O_{THF} = 2.323(5) - 2.418(5).

In summary we have synthesised and crystallographically characterized the first example of a metallasilsesquioxane of a divalent lanthanide. The dinuclear complex $[Yb{Cy_7Si_7O_{11}(OSiMe_3)}(THF)]_2$, **1**, was prepared in good yield from the protonolysis of $[Yb{N(SiMe_3)}_2]_2(THF)_2]$ with the mono-

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silylated silsesquioxane Cy₇Si₇O₉(OSiMe₃)(OH)₂. The dianionic Cy₇Si₇O₁₁(OSiMe₃)²⁻ ligand acts as a tridentate bridging ligand holding together the two Yb(II) ions. We also showed that silsesquioxane acts as an effective ligand for building dinuclear complexes of Ln(II) that can transfer two electrons to substrates such as azobenzene or CO₂, without undergoing ligand scrambling or ligand loss. Future studies will be directed to investigate the silsesquioxane chemistry with other Ln(II) ions and Sm(II) in particular.

We acknowledge support from the Swiss National Science Foundation grant number 200021_178793 and from the École Polytechnique Fédérale de Lausanne (EPFL).

Conflicts of interest

There are no conflicts to declare

Notes and references

- 1. (a)V. Lorenz and F. T. Edelmann, in *Advances in Organometallic Chemistry, Vol 53*, eds. R. West and A. F. Hill, 2005, vol. 53, pp. 101-153; (b)M. M. Levitsky and A. N. Bilyachenko, *Coord. Chem. Rev.*, 2016, **306**, 235-269; (c)H. C. L. Abbenhuis, *Chem. Eur. J.*, 2000, **6**, 25-32.
- (a)E. A. Quadrelli and J. M. Basset, *Coord. Chem. Rev.*, 2010,
 254, 707-728; (b)R. Murugavel, A. Voigt, M. G. Walawalkar and H. W. Roesky, *Chem. Rev.*, 1996, **96**, 2205-2236; (c)V. Lorenz, A. Fischer, S. Giessmann, J. W. Gilje, Y. Gun'ko, K. Jacob and F. T. Edelmann, *Coord. Chem. Rev.*, 2000, **206**, 321-368; (d)V. Lorenz, A. Edelmann, S. Giessmann, C. G. Hrib, S. Blaurock and F. T. Edelmann, *Z. Anorg. Allg. Chem.*, 2010, **636**, 2172-2191.
- 3. (a)G. L. Davies, J. O'Brien and Y. K. Gun'ko, *Sci. Rep.*, 2017, **7**, 45862; (b)N. Yuan, Y. C. Liang, E. S. Erichsen and R. Anwander, *RSC Adv.*, 2015, **5**, 83368-83376.
- 4. S. Giessmann, V. Lorenz, P. Liebing, L. Hilfert, A. Fischer and F. T. Edelmann, *J. Chem. Soc.-Dalton Trans.*, 2017, **46**, 2415-2419.
- 5. Y. K. Gun'ko, R. Reilly, F. T. Edelmann and H. G. Schmidt, *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 1279-1281.
- (a)V. Mougel, C. Camp, J. Pecaut, C. Coperet, L. Maron, C. E. Kefalidis and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 12280-12284; (b)O. Cooper, C. Camp, J. Pécaut, C. E. Kefalidis, L. Maron, S. Gambarelli and M. Mazzanti, *J. Am. Chem. Soc.*, 2014, **136**, 6716-6723.
- 7. R. P. Kelly, L. Maron, R. Scopelliti and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2017, **56**, 15663-15666.
- 8. J. Andrez, J. Pecaut, P.-A. Bayle and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2014, **53**, 10448-10452.
- 9. M. K. Assefa, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2020, **142**, 8738-8747.
- 10. V. Lorenz and F. T. Edelmann, *Adv. Organomet. Chem.*, 2005, **53**, 101-153.
- (a)G. M. Wu, Y. F. Chen, D. J. Xu, J. C. Liu, W. L. Sun and Z. Q. Shen, *J. Organomet. Chem.*, 2009, **694**, 1571-1574; (b)W. A. Herrmann, R. Anwander, V. Dufaud and W. Scherer, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 1285-1286.
- 12. (a)V. Lorenz, S. Giessmann, Y. K. Gun'ko, A. K. Fischer, J. W. Gilje and F. T. Edelmann, *Angew. Chem. Int. Ed. Engl.*, 2004,

43, 4603-4606; (b)J. Annand, H. C. Aspinall and A. Steiner, *Inorg. Chem.*, 1999, **38**, 3941-3943.

- 13. (a)V. Lorenz, A. Fischer and F. T. Edelmann, *J. Organomet. Chem.*, 2002, **647**, 245-249; (b)P. L. Arnold, A. J. Blake, S. N. Hall, B. D. Ward and C. Wilson, *J. Chem. Soc., Dalton Trans.*, 2001, 488-491.
- 14. S. Marchesi, F. Carniato and E. Boccaleri, *New J. Chem.*, 2014, **38**, 2480-2485.
- 15. V. Lorenz, S. Blaurock, C. G. Hrib and F. T. Edelmann, *Eur. J. Inorg. Chem.*, 2010, 2605-2608.
- 16. (a)C. Coperet, A. Comas-Vives, M. P. Conley, D. P. Estes, A. Fedorov, V. Mougel, H. Nagae, F. Nunez-Zarur and P. A. Zhizhko, *Chem. Rev.*, 2016, **116**, 323-421; (b)G. Gerstberger, C. Palm and R. Anwander, *Chem. Eur. J.*, 1999, **5**, 997-1005; (c)R. Anwander, H. W. Gorlitzer, G. Gerstberger, C. Palm, O. Runte and M. Spiegler, *J. Chem. Soc. Dalton Trans.*, 1999, 3611-3615; (d)E. Le Roux, Y. C. Liang and R. Anwander, *Chemcatchem*, 2018, **10**, 1905-1911.
- (a)E. Le Roux, O. Michel, H. M. Sommerfeldt, Y. C. Liang, C. Maichle-Mossmer, K. W. Tornroos and R. Anwander, *J. Chem. Soc.-Dalton Trans.*, 2010, **39**, 8552-8559; (b)F. Allouche, K. W. Chan, A. Fedorov, R. A. Andersen and C. Coperet, *Angew. Chem. Int. Ed. Engl.*, 2018, **57**, 3431-3434.
- 18. (a)W. J. Evans, T. A. Ulibarri and J. W. Ziller, J. Am. Chem. Soc., 1988, 110, 6877-6879; (b)W. J. Evans, D. K. Drummond, L. R. Chamberlain, R. J. Doedens, S. G. Bott, H. M. Zhang and J. L. Atwood, J. Am. Chem. Soc., 1988, 110, 4983-4994; (c)M. G. Gardiner and D. N. Stringer, *Materials*, 2010, 3, 841-862; (d)N. W. Davies, A. S. P. Frey, M. G. Gardiner and J. Wang, Chem. Commun., 2006, 4853-4855; (e)M. Xemard, M. Cordier, E. Louyriac, L. Maron, C. Clavaguera and G. Nocton, J. Chem. Soc.-Dalton Trans., 2018, 47, 9226-9230; (f)W. J. Evans, Coord. Chem. Rev., 2000, 206, 263-283; (g)R. Yadav, T. Simler, M. T. Gamer, R. Koppe and P. W. Roesky, Chem. Commun., 2019, 55, 5765-5768; (h)T. Simler, T. J. Feuerstein, R. Yadav, M. T. Gamer and P. W. Roesky, Chem. Commun., 2019, 55, 222-225; (i)C. Schoo, S. Bestgen, R. Koppe, S. N. Konchenko and P. W. Roesky, Chem. Commun., 2018, 54, 4770-4773; (j)D. P. Halter, C. T. Palumbo, J. W. Ziller, M. Gembicky, A. L. Rheingold, W. J. Evans and K. Meyer, J. Am. Chem. Soc., 2018, 140, 2587-2594; (k)G. B. Deacon, Z. F. Guo, P. C. Junk and J. Wang, Angew. Chem. Int. Ed. Engl., 2017, 56, 8486-8489; (I)J. Jubb and S. Gambarotta, J. Am. Chem. Soc., 1994, 116, 4477-4478; (m)N. F. M. Mukthar, N. D. Schley and G. Ung, J. Chem. Soc.-Dalton Trans., 2020.
- (a)M. Nishiura, Z. M. Hou and Y. Wakatsuki, *Organometallics*, 2004, 23, 1359-1368; (b)D. Toniolo, A. Willauer, R. Scopelliti, J. Andrez, Y. Yang and L. Maron, *Chem. Eur. J.*, 2019; (c)A. Willauer, D. Toniolo, F. Fadaei-Tirani, Y. Yang, S. Laurent and M. Mazzanti, *J. Chem. Soc.-Dalton Trans.*, 2019, 48, 6100–6110.
- 20. D. J. Duncalf, P. B. Hitchcock and G. A. Lawless, J. Organomet. Chem., 1996, **506**, 347-349.
- 21. F. J. Feher, D. A. Newman and J. F. Walzer, *J. Am. Chem. Soc.*, 1989, **111**, 1741-1748.
- (a)R. P. Kelly, D. Toniolo, F. F. Tirani, L. Maron and M. Mazzanti, *Chem. Commun.*, 2018, **54**, 10268-10271; (b)C. Schoo, S. Bestgen, M. Schmidt, S. N. Konchenko, M. Scheer and P. W. Roesky, *Chem. Commun.*, 2016, **52**, 13217-13220; (c)T. Sanden, M. T. Gamer, A. A. Fagin, V. A. Chudakova, S. N. Konchenko, I. L. Fedushkin and P. W. Roesky, *Organometallics*, 2012, **31**, 4331-4339.

- 23. (a)C. D. Berube, S. Gambarotta, G. P. A. Yap and P. G. Cozzi, *Organometallics*, 2003, **22**, 434-439; (b)M. L. Cole and P. C. Junk, *Chem. Commun.*, 2005, 2695-2697.
- 24. (a)M. Xemard, V. Goudy, A. Braun, M. Tricoire, M. Cordier, L. Ricard, L. Castro, E. Louyriac, C. E. Kefalidis, C. Clavaguera, L. Maron and G. Nocton, *Organometallics*, 2017, 36, 4660-4668;
 (b)L. Castro, S. Labouille, D. R. Kindra, J. W. Ziller, F. Nief, W. J. Evans and L. Maron, *Chem. Eur. J.*, 2012, 18, 7886-7895.
- 25. M. Nishiura, Z. M. Hou and Y. Wakatsuki, *Organometallics*, 2004, **23**, 1359-1368.
- 26. Z. M. Hou, T. Koizumi, M. Nishiura and Y. Wakatsuki, Organometallics, 2001, **20**, 3323-3328.
- 27. S. Patai, *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*, John Wiley, London, New York, 1975.
- 28. A. A. Trifonov, M. N. Bochkarev, H. Schumann and J. Loebel, Angew. Chem. Int. Ed. Engl., 1991, **30**, 1149-1151.
- 29. (a)W. J. Evans, D. S. Lee, J. W. Ziller and N. Kaltsoyannis, J. Am. Chem. Soc., 2006, 128, 14176-14184; (b)M. A. Katkova, G. K. Fukin, A. A. Fagin and M. N. Bochkarev, J. Organomet. Chem., 2003, 682, 218-223; (c)E. D. Brady, D. L. Clark, D. W. Keogh, B. L. Scott and J. G. Watkin, J. Am. Chem. Soc., 2002, 124, 7007-7015; (d)C. L. Pan, W. Chen and J. F. Song, Organometallics, 2011, 30, 2252-2260.
- 30. W. J. Evans and D. K. Drummond, J. Am. Chem. Soc., 1986, 108, 7440-7441.