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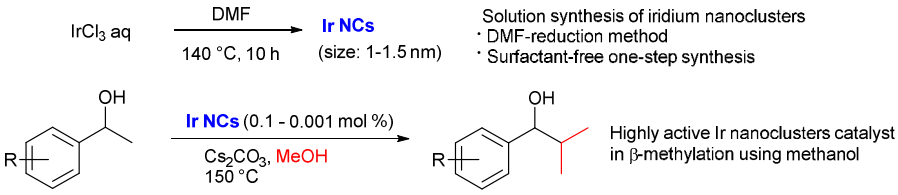
Graphical Abstract

DMF-stabilized Ir nanoclusters showed an efficient catalytic activity in the β-methylation of alcohols using methanol as the C1 source



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COMMUNICATION

Preparation and use of DMF-stabilized iridium nanoclusters as methylation catalysts using methanol as the C1 source

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We report methylations of alcohols and anilines catalyzed by DMF-stabilized Ir nanoclusters using methanol as the C1 source. The DMF-stabilized Ir nanoclusters were prepared in one step and have diameters of 1–1.5 nm. They react in a borrowing-hydrogen reaction and are efficient methylation catalysts (TON up to 310,000).

Transition-metal-catalyzed C–C bond formation through borrowing-hydrogen (or hydrogen-autotransfer) reactions has attracted much attention for the manufacture of bulk and fine chemicals.[1] In particular, methylation is vital for the synthesis of biologically active molecules[2] Conventional methylation uses iodomethane, diazomethane, dimethyl sulfate and dimethyl carbonate as the common methylating reagent.[3] However, some reagents are dangerous as they have explosive or corrosion properties. The development of a green and sustainable methylation process that uses methanol, an abundant and renewable C1 source, is therefore desired by the chemical industry.[4]

It is well known that Ir, Ru, and Rh complexes are efficient catalysts for the dehydrogenation of alcohols, and these complexes have been utilized in α- or β-alkylations involving borrowing-hydrogen reactions.[5] Our group has developed Ir-catalyzed borrowing-hydrogen reactions for various substrates using alcohols as the alkylation reagents.[6] However, it has been difficult to apply methanol as the alkylation reagent owing to its high dehydrogenation energy compared with that of other alcohols, such as ethanol and higher alcohols.[7]

Recently, the transition-metal-catalyzed dehydrogenation of methanol and its use in C1 alkylation has been developed.[8] Donohoe,[8a,b] Andersson,[8c] and our group[8e] have reported the α-methylation of ketones using methanol. Among the previously reported studies, Beller has reported the methylation of alcohols to give alcohol products.[8d] However, the methylation of secondary alcohol starting materials has not yet been reported. To achieve this, the development of a highly reactive catalyst is required.

Metal nanoclusters (M NCs) are proposed to be highly active catalysts owing to their large surface areas and corner/edges sites compared with those of bulk metals.[9] To avoid aggregation of the M NCs to bulk metal, external stabilizers (e.g., functionalized polymers, dendrimers, and metal oxides) and reductants (e.g., $NaBH_4$) are generally considered essential in a typical M NC synthesis.[10]

As an alternative methodology, the solution synthesis of *N*,*N*-dimethylformamide (DMF)-stabilized metal NCs (<2 nm) and nanoparticles (NPs, >2 nm) of Au, Pt, Pd, and Cu have been reported as surfactant-free stable M NCs.[11] Other than DMF, this protocol does not require any external additives; DMF serves as a solvent, reductant, and stabilizer in the metal NP synthesis. The obtained Pd NCs and Cu NPs showed high catalytic activity in cross-coupling reactions, including Suzuki–Miyaura, Mizoroki–Heck, and Ullmann couplings.[11]

Herein, we present the solution synthesis of DMF-stabilized Ir NCs and their use as a catalyst in the β-methylation of alcohols using methanol as the C1 source.

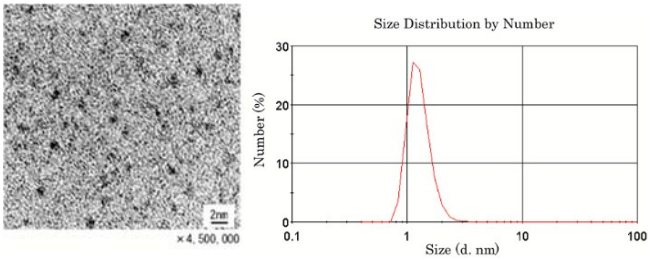

Fig. 1 Left: Transmission electron microscopy image of DMF-stabilized Ir nanoclusters (NCs). Bar length: 2 nm. Right: Dynamic light scattering spectrum of Ir NCs.

The DMF-stabilized Ir NCs are simply prepared according to the following one-step procedure. A solution of 0.5 mL of 0.1 M

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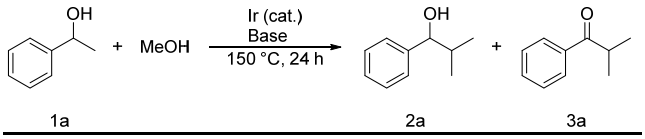
[b] *†Electronic Supplementary Information (ESI) available: Experimental procedures and compound characterization data. See DOI:*

aqueous $IrCl_3$ was added to 50 mL of DMF at 140 °C, and the DMF solution was heated at 140 °C in a flask fitted with a reflux condenser for 10 h.

The resulting orange solution of Ir NCs in DMF was photoluminescent, as observed for another M NCs.[11] The maximum emission wavelength was around 450 nm with UV excitation at 350 nm (Fig. S1-2, ESI†).

High resolution transmission electron microscopy (HR-TEM) and showed that the diameters of the NCs were about 1–1.5 nm (Fig. 1 and Fig S3 (ESI†)). To identify the binding layers surrounding the Ir NCs, ^{1}H NMR and FT-IR analyses of the NCs were performed (Figures in the ESI†). In the ^{1}H NMR spectrum, the signal at 8.15 ppm, assigned to the formyl proton of DMF binding to the Ir NCs, was shifted to lower field compared with that in free DMF (7.92 ppm) (Fig. S4, ESI†). The IR spectrum contains a peak at around 1670 cm^{-1}, which corresponds to the ν(C=O) vibration of DMF and suggests that the DMF molecules interact with the Ir NCs (Fig. S7, ESI†).

Table 1. Screening of reaction conditions[a]



1a 2a 3a

Entry	[Ir]	Base	Conv. (**1a**) [%]	Total yield [%][b,c] Selectivity (**2a** : **3a**)[d]
1	Ir NCs	Cs_2CO_3	>99	68 (85 : 15)
2	$IrCl_3$	Cs_2CO_3	48	16 (46 : 54)
3[e]	$IrCl_3$	Cs_2CO_3	49	16 (33 : 67)
4[e]	$[IrCl(cod)]_2$	Cs_2CO_3	48	21 (28 : 72)
5[e,f]	$[IrCl(cod)]_2/PPh_3$	Cs_2CO_3	44	18 (- : >99)
6[e]	$[Cp^*IrCl_2]_2$	Cs_2CO_3	44	25 (25 : 75)
7	Ir NCs	KOH	>99	53 (87 : 13)
8	Ir NCs	KO^{t}Bu	>99	52 (87 : 13)
9	Ir NCs	K_2CO_3	59	31 (75 : 25)
10	Ir NCs	none	26	n.d.
11	none	Cs_2CO_3	30	n.d.
12	none	KOH	60	9 (>99 : -)
13[g]	Ir NCs	Cs_2CO_3	11	3 (48 :52)
14[h]	Ir NCs	Cs_2CO_3	>99	quant [87][c] (94 :6)
15[h,i]	Ir NCs	Cs_2CO_3	57	24 (94 : 6)

[a]Reaction conditions: **1a** (1 mmol) was allowed to react with methanol (2 mL), redissolved Ir NCs (0.1 mol%) and Cs_2CO_3 (1 mmol) at 150 °C for 24 h. [b]GC yield based on **1a** used. [c]The numbers in the square bracket show isolated yields. [d]The numbers in parentheses show the selectivity for the alcohol and ketone products. [e]Ir catalyst (5 mol%) was used. [f]PPh_3 (10 mol%) was used. [g]At 100 °C. [h]Cs_2CO_3 (3 mmol) was used. [i]Ir NCs (0.001 mol%) for 48 h.

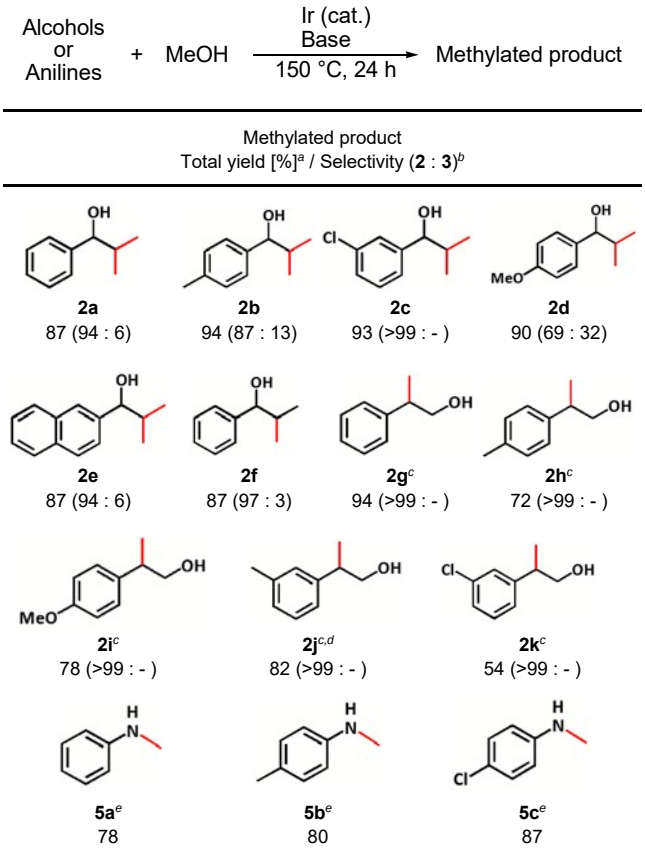
Thermogravimetric analysis–differential thermal analysis (TG-DTA) was measured to confirm the thermal stability of the Ir NCs (Fig. S8, ESI†).

The results showed that the DMF properly protected the Ir metal and weight loss began at around 100 °C.

On heating the solution, a portion of the protective DMF is expected to be liberated from the Ir metal, generating Ir NCs with partially open sites that could act as active catalysts in the methylation reaction.

Initially, we examined the Ir-NC-catalyzed β-methylation of 1-phenyl-1-ethanol (**1a**) with methanol (Table 1). The reaction of **1a** (1 mmol) with methanol (2 mL) was performed in the presence of Ir NCs (0.1 mol%) and Cs_2CO_3 (1 mmol) as the base at 150 °C for 24 h under Ar. Ir NCs were more effective than other Ir complexes for the β-methylation, and gave the desired product in 68% total yield with high alcohol selectivity (entry 1). Under these conditions, we did not observe any metal aggregation or precipitation from the Ir NCs solution after the reaction. Use of $IrCl_3$ (0.1 and 5 mol %), which was the starting complex for the synthesis of the DMF-stabilized Ir NCs, resulted in lower yields, and the ketone product (**3a**) was preferentially obtained (entries 2-3).

Table 2. Ir NC-catalyzed β-methylation of alcohols and *N*-methylation of aniline derivatives with methanol[a]



[a]Conditions: same as Table 1 in entry 12 unless otherwise noted. All yields are isolated yields. [b]The numbers in parentheses show the selectivity for the alcohol (**2**) and ketone (**3**) products. [c]For 48 h. [d]Cs_2CO_3 (1 mmol). [e]Anilines (**4**) (1 mmol), methanol (2 mL), Ir NCs (0.1 mol%) and Cs_2CO_3 (0.5 mmol) at 150 °C for 24 h.

$[Cp^*IrCl_2]_2$ and $[IrCl(cod)]_2$, known to be a good catalyst for hydrogen-transfer reactions, including α-methylation,[8d] also

resulted in lower yields and preferentially gave the ketone product (**3a**) (entries 4-6).

The poisoning test in the presence of mercury (5 equiv) with **1a** was carried out under the conditions using the Ir NCs (entry 1), which gave the methylated products in 33% yield (**2a**:**3a** = 72:28) with 81% conversion, whereas only trace amount of **2a**/**3a** with low conversion occurred with $IrCl_3$ catalyst (under the conditions of entry 2).

These results indicate that the DMF-stabilized Ir NCs serves as dominant active catalyst and the DMF molecules would remain bound to the iridium clusters during the catalytic cycle.

Other bases, for example KOH, KO^{t}Bu, and K_2CO_3, gave the desired product in lower yields than the reaction with Cs_2CO_3 (entries 7-9).

Recently, transition-metal-free alkylations have been reported.[12] We therefore examined the reaction without Ir NCs and confirmed that the reaction did not proceed (entries 11-12). Temperature was an important factor for this reaction, and the optimum temperature was 150 °C. These results agree with the TG-DTA data showing that the Ir NCs are stable up to 100 °C (entry 13).

A clear improvement in the yield was observed when an increased amount of Cs_2CO_3 (3 mmol) was used (entry 14).

The β-methylation reaction proceeded with low catalyst loading, and the dimethyl product was obtained in 24% yield when 0.001 mol% Ir NCs was used as the catalyst. Furthermore, we achieved a turnover number (TON) of 48,000 for this reaction, and thus concluded that Ir NCs have high catalytic activity (entry 15).

β-Methylations of various secondary alcohols were performed under the optimized conditions (Table 2). Reaction of 1-phenyl-1-ethanol derivatives **1b**, **1c**, and **1d** with methanol afforded the corresponding methylation products **2b**, **2c**, and **2d** in 94%, 93%, and 90% yield, respectively. Through these results, we found that the reaction could be adapted for compounds with electron-donating and -withdrawing groups on the phenyl ring. Reaction of 1-(2-naphthyl)ethanol **1e** gave product **2e** in excellent yield. When 1-phenylpropanol **1f**, which contains one reaction point, was used, monomethylation product **2f** was obtained in excellent yield.

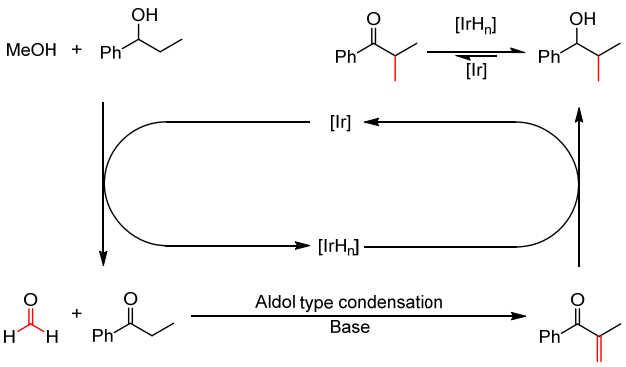
Next, β-methylations of primary alcohols were investigated. However, it was necessary to adjust the amount of base used because the acidity of the hydrogen atom was different.[13] 2-phenylethanol **1g** gave desired product **2g** in high yield and with good selectivity. Reactions of 2-arylethanols containing electron-donating or -withdrawing groups gave the corresponding products in high yields. Interestingly, all products from the primary alcohols were obtained with higher selectivity than those obtained from the secondary alcohols. This is probably a result of the different stabilities of the products due to conjugation. However, aliphatic alcohol such as *n*-decanol was not suitable under these conditions.

To expand the scope of this methylation reaction using methanol as the C1 source, we next performed *N*-methylations of primary anilines (Table S1; optimization results shown in the ESI†). Reactions of primary anilines with electron-donating and -withdrawing groups gave the corresponding products in excellent yields (Table 2, **5a**-**c**). To our delight, a high TON of 310,000 was achieved for the *N*-methylation of aniline (**4a**) to **5a** by lowering the catalyst loading (Table S2, ESI†).

Furthermore, to examine the mechanism for the generation of **3** as intermediate in this reaction, reaction of acetophenone with methanol was carried out under these conditions using Ir NCs catalyst. As a result, **2a** was obtained as major product along with the formation of **3a** (Scheme S1, ESI†). In addition, when the reaction of propiophenone with paraformaldehyde was performed, **2a** was obtained exclusively (Scheme S2 and Table S3 in ESI†). These results indicate that acetophenone (i.e. ketones **3**) and formaldehyde (from methanol) would pertain to this reaction as intermediates.

Furthermore, reactions of benzophenone/styrene with methanol were performed by using the Ir NCs catalyst system, the corresponding hydrogenated products, benzhydrol/ethylbenzene were obtained in high yields (Scheme S3, ESI†). We thus concluded that the Ir NCs serves as efficient catalyst for hydrogen transfer reactions.

On the basis of these results, we propose a mechanism for the β-methylation of alcohols using methanol (Scheme 1). The transformation begins with the oxidation of the alcohol to the ketone/aldehyde and oxidation of methanol to formaldehyde with the generation of an Ir NCs-hydride species. Subsequently, an aldol-type reaction of the resulting ketone/aldehyde with formaldehyde gives the enone. Finally, the desired alcohol product is obtained through hydrogenation of the unsaturated bonds in the enone by the Ir NCs hydride species. To indicate characteristics of the Ir NCs, we examined the transformation of **2a** to **3a** under these conditions between the Ir NCs and $IrCl_3$ catalysts. As a result, conversion of **2a** to **3a** was found to be very low (10 %) with the Ir NCs, whereas 26% conversion to **3a** was observed with $IrCl_3$ (Scheme S3, ESI†). These results indicate that the Ir NCs possess advantage to the selective formation of **2a** (in preference to **3a**) in this types of reactions.



Scheme 1. A plausible β-methylation pathway

In summary, we have successfully synthesized DMF-stabilized Ir NCs and developed a methylation reaction using methanol as the C1 source. From TEM and DLS analyses, we found that the particle size of the DMF-stabilized Ir NCs was 1–1.5 nm. ^{1}H-NMR, TG-DTA, and FT-IR results indicated that the surface of the Ir NCs was protected by DMF molecules. In addition, the Ir NCs have high catalytic activity towards β- and *N*-methylations, and an extremely high TON of 310,000 was achieved for the *N*-methylation of primary amines by lowering the catalyst loading

to 0.0001 mol% (10^{-4} mol%). The reaction is widely applicable to the β-methylation of various primary and secondary alcohols. Further studies towards a detailed understanding of the overall scope and the reaction are currently underway in our laboratory.

Notes and references

1 a) K. Shimizu, *Catal. Sci. Technol.*, 2015, **5**, 1412–1427. b) C. Gunanathan and D. Milstein, *Science*, 2013, **341**, 1229712. c) M. H. S. A. Hamid, P. A. Slatford and J. M. J. Williams, *Adv, Synth. Catal.*, 2007, **349**, 1555-1575. d) T. D. Nixon, M. K. Whittlesey and J. M. J. Williams, *Dalton Trans.,* 2009, 753-762. e) G. Guillena, D. J. Ramón and M. Yus, *Chem. Rev.,* 2010, **110**, 1611-1641. f) F. Huang, Z. Liu and Z. Yu, *Angew. Chem. Int. Ed.,* 2016, **55**, 862-875. g) C. S. Cho, B. T. Kim, T.-j. Kim and S. C. Shim, *J. Org. Chem.,* 2001, **66**, 9020-9022. h) S. Pan and T. Shibata, *ACS Catal.,* 2013, **3**, 704-712. i) J. T. Kozlowski and R. J. Davis, *ACS Catal.*, 2013, **3**, 1588-1600. j) G. Guillena, D. J. Ramón and M. Yus, *Angew. Chem. Int. Ed.*, 2007, **46**, 2358-2364 and referenced therein.

2 a) E. J. Barreiro, A. E. Kümmerle and C. A. M. Fraga, *Chem. Rev.*, 2011, **111**, 5215–5246. b) H. Schönherr and T. Cernak, *Angew. Chem. Int. Ed.,* 2013, **52**, 12256-12267. c) G. Yan, A. J. Borah, L. Wang and M. Yang, *Adv. Synth. Catal.,* 2015, **357**, 1333-1350.

3 Y. Yokoyama and K. Mochida, *J. Organomet. Chem*., 1995, **499**, C4-C6. b) K. Maruoka, A. B. Concepcion and H. Yamamoto, *Synthesis*, 1994, 1283-1290.

4 a) A. Goeppert, M. Czaun, J.-P. Jones, G. K. S. Prakash and G. A. Olah, *Chem. Soc. Rev.,* 2014, **43**, 7995-8048.b) J. Moran, A. Preetz, R. A. Mesch and M. J. Krische, *Nat. Chem.*, 2011, **3**, 287-290. c) R. E. Rodríguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones and H. Grützmacher, *Nat. Chem.*, 2013, **5**, 342-347. d) R. Langer, I. Fuchs, M. Vogt, E. Balaraman, Y. Diskin-Posner, L. J. W. Shimon, Y. Ben-David and D. Milstein, *Chem. Eur. J.*, 2013, **19**, 3407-3414. e) A. Monney, E. Barsch, P. Sponholz, H. Junge, R. Ludwig and M. Beller, *Chem. Commun.*, 2014, **50**, 707-709. f) E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H. J. Drexler, W. Baumann, H. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 14162-14166. g) P. Hu, Y. Diskin-Posner, Y. Ben-David and D. Milstein, *ACS Catal.*, 2014, **4**, 2649-2652 and references therein.

5 a) K.-i. Fujita, C. Asai, T. Yamaguchi, F. Hanasaka and R. Yamaguchi, *Org. Lett.*, 2005, **7**, 4017-4019. b) R. Cano, M. Yus and D. J. Ramón, *Chem. Commun.*, 2012, **48**, 7628-7630. c) P. J. Black, G. Cami-kobeci, M. G. Edwards, P. A. Slatford, M. K. Whittlesey and J. M. J. Williams, *Org. Biomol. Chem.,* 2006, **4**, 116-125. d) G. E. Dobereiner and R. H. Crabtree, *Chem. Rev.,* 2010, **110**, 681-703. e) T. Suzuki, *Chem. Rev.,* 2011, **111**, 1825-1845. f) R. Kawahara, K. Fujita and R. Yamaguchi, *J. Am Chem. Soc.,* 2012, **134**, 3643-3646. g) M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali and M. Beller, *Nature*, 2013, **495**, 85-90. h) Q. Wang, K. Wu and Z. Yu, *Organometallics*, 2016, **35**, 1251-1256.

6 a) Y. Obora, *ACS Catal.*, 2014, **4**, 3972-3981. b) S. Hatanaka, Y. Obora and Y. Ishii, *Chem. Eur. J.*, 2010, **16**, 1883-1888. b) Y. Iuchi, Y. Obora and Y. Ishii, *J. Am. Chem. Soc.,* 2010, **132**, 2536-2537. c) Y. Obora, Y. Anno, R. Okamoto, T. Matsu-ura and Y. Ishii, *Angew. Chem. Int. Ed.,* 2011, ***50***, 8618-8622.

7 a) J. M. Mayer, D. A. Hrovat, J. L. Thomas and W. T. Borden, *J. Am. Chem. Soc*., 2002, **124**, 11142-11147. b) N. Yamamoto, Y. Obora and Y. Ishii, *J. Org. Chem*., 2011, **76**, 2937–2941.

8 a) L. K. M. Chan, D. L. Poole, D. Shen, M. P. Healy and T. J. Donohoe, *Angew. Chem. Int. Ed.*, 2014, **53**, 761–765. b) D. Shen, D. L. Poole, C. C. Shotton, A. F. Kornahrens, M. P. Healy and T. J. Donohoe, *Angew. Chem. Int. Ed.*, 2015, **54**, 1642–1645. c) X. Quan, S. Kerdphon and P. G. Andersson, *Chem. Eur. J.*, 2015, **21**, 3576-3579. d) Y. Li, H. Li, H. Junge and M. Beller, *Chem. Commun.*, 2014, **50**, 14991-14994. e) S. Ogawa and Y. Obora, *Chem. Commun.*, 2014, **50**, 2491-2493. f) C. Sun, X. Zou and F. Li, *Chem. Eur. J.*, 2013, **19**, 14030–14033. g) S.-J. Chen, G.-P. Lu and C. Cai, *RSC Adv.*, 2015, **5**, 70329–70332. h) F. Li, J. Xie, H. Shan, C. Sun and L. Chen, *RSC Adv*., 2012, **2**, 8645-8652. i) T. T. Dang, B. Ramalingam and A. M. Seayad, *ACS Catal*., 2015, **5**, 4082-4088.

9 a) M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.* 1987, **16**, 405. b) K. J. Klabunde, J. Stark, O. Koper, C. Mohs, D. G. Park, S. Decker, Y. Jiang, I. Lagadic and D. Zhang, *J. Phys. Chem.,* 1996, **100**, 12142-12153. c) J. Dupont and J. D. Scholten, *Chem. Soc. Rev.,* 2010, **39**, 1780-1804. d) K. An and G. A. Somorjai, *ChemCatChem,* 2012, **4**, 1512-1524. e) G. Li and R. Jin, *Acc. Chem. Res.,* 2013, **46**, 1749-1758. f) X. Liu, L. He, Y.-M. Liu and Y. Cao, *Acc. Chem. Res.,* 2014, **47**, 793-804.

10 a) J. C. Garcia-Martinez, R. Lezutekong and R. M. Crooks, *J. Am. Chem. Soc.*, 2005, **127**, 5097-5103. b) F. Lu and D. Astruc, *Eur. J. Inorg. Chem.,* 2015, 5595-5600. c) D. Astruc, *Tetrahedron Asymm.,* 2010, **21**, 1041-1054. d) G. L. Bezemer, J. H. Bitter, H. P. C. E. Kuipers, H. Oosterbeek, J. E. Holewijin, X. Xu, F. Kapteijn, A. J. V. Dillen and K. P. D. Jong, *J. Am. Chem. Soc.,* 2006, **128**, 3956-3964. e) C. He, J. Tao, G. He, P. K. Shen and Y. Qiu, *Catal. Sci. Technol*., 2016, **6**, 7316-7322. f) H. Zhang and H. Cui, *Langmuir,* 2009, **25**, 2604-2612. g) G. Zhang, H. Zhou, J. Hu, M. Liu and Y. Kuang, *Green Chem.,* 2009, **11**, 1428-1432.

11 a) X. Liu, C. Li, J. Xu, J. Lv, M. Zhu, Y. Guo, S. Cui, H. Liu, S. Wang, Y. Li, *J. Phys. Chem. C*, 2008, **112**, 10778-10783. b) H. Kawasaki, H. Yamamoto, H. Fujimori, R. Arakawa, Y. Iwasaki, M. Inada, *Langmuir*, 2010, **26**, 5926-5933. c) H. Kawasaki, H. Yamamoto, H. Fujimori, R. Arakawa, M. Inada, Y. Iwasaki, *Chem. Commun.,* 2010, **46**, 3759-3761. d) M. Hyotanishi, Y. Isomura, H. Yamamoto, H. Kawasaki and Y.Obora, *Chem. Commun.,* 2011, **47**, 5750. e) H. Yamamoto, H. Yano, H. Kouchi, Y. Obora, R. Arakawa and H. Kawasaki, *Nanoscale*, 2012, **4**, 4148-4154. f) Y. Isomura, T. Narushima, H. Kawasaki, T. Yonezawa and Y.Obora, *Chem. Commun.*, 2012, **48**, 3784-3786.

12 a) L. J. Allen and R. H. Crabtree, *Green Chem.*, 2010, **12**, 1362–1364. b) C. Guérin, V. Bellosta, G. Guillamot and J. Cossy, *Org. Lett.,* 2011, **13**, 3534-3537. c) Q. Xu, J. Chen, H. Tian, X. Yuan, S. Li, C. Zhou and J. Liu, *Angew. Chem. Int. Ed.*, 2014, **53**, 225–229. f) S. Das, F. D. Bobbink, G. Laurenczy and P. J. Dyson, *Angew. Chem. Int. Ed.,* 2014, **53**, 12876-12879. g) S. Li, X. Li, Q. Li, Q. Yuan, X. Shi and Q. Xu, *Green Chem.,* 2015, **17**, 3260-3265.

13 a) F. G. Bordwell and J. A. Harrelson Jr., *Can. J. Chem.,* 1990, **68**, 1714-1718.

14 a) J. Campos, L. S. Sharninghausen, M. G. Manas and R. H. Crabtree, *Inorg. Chem.* 2015, **54**, 5079-5084. b) T. T. Dang and A. M. Seayad, *Adv. Synth. Catal.,* 2016, **358**, 3373-3380.