ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: K. Huang, H. Li, T. P. Goncalves, Q. Zhao, D. Gong, Z. Lai, Z. Wang and J. Zheng, *Chem. Commun.*, 2018, DOI: 10.1039/C8CC05948A.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Journal Name

COMMUNICATION

Diverse catalytic reactivity of a dearomatized PN^3P^* -nickel hydride pincer complex towards CO_2 reduction

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

Huafeng Li,^a Théo P. Gonçalves,^a Qianyi Zhao,^a Dirong Gong,^a Zhiping Lai,^b Zhixiang Wang,^c
Junrong Zheng,^d and Kuo-Wei Huang^{*a}

DOI: 10.1039/x0xx00000x

www.rsc.org/

A dearomatized PN^3P^* -nickel hydride complex has been prepared by oxidative addition process. The first nickel-catalyzed hydrosilylation of CO_2 to methanol has been achieved, with unprecedented turnover numbers. Selective methylation and formylation of amines with CO_2 were demonstrated by such PN^3P^* -nickel hydride complex, highlighting its versatile functions in CO_2 reduction.

CO_2 is a renewable, nontoxic and abundant feedstock, and thus it is an attractive C1 building block for the synthesis of organic molecules.¹ However, the transformation and activation of CO_2 is highly challenging due to its inherent thermodynamic and kinetic stability.^{1f} Considerable efforts have been devoted to developing efficient catalysts or catalytic systems to overcome these challenges for the CO_2 utilization to produce various value-added chemicals.² In particular, the reduction of CO_2 to methanol under mild conditions is a challenging goal.³ While some homogeneous catalytic systems have been reported for the hydrogenation⁴ and the hydroboration of CO_2 to methanol,⁵ examples of hydrosilylation of CO_2 to methanol are still rare. $\text{Ir}(\text{CN})(\text{CO})\text{dppe}$ (dppe = 1,2-bis(diphenylphosphino)ethane) was the first reported catalyst for the hydrosilylation of CO_2 to silylated methanol from which methanol could be generated upon hydrolysis in 1989 by Eisenberg and Eisenschmid,⁶ but the catalytic efficiency was very low as the transformation required weeks to complete. In 2009, Zhang and Ying group reported the reduction of CO_2 to silylated methanol with silanes catalyzed by

N-heterocyclic carbenes with the highest turnover number (TON) of 1840.⁷ These reports remain the only two homogeneously catalyzed systems to directly reduce CO_2 to silylated methanol in one-step. More recently, the groups of Fontaine,⁸ Oestreich⁹ and Abu-Omar¹⁰ developed the hydrosilylation of CO_2 to silylated formate or silylated formal compounds, rather than silylated methanol. These products could in turn be reduced to silylated methanol by addition of an additional reductant, at elevated reaction temperatures or over a longer reaction time. The selective one-step reduction to silylated methanol for the hydrosilylation of CO_2 to methanol remains challenging.

On the other hand, efficient hydrosilylation of CO_2 to valuable formamides, methylamines or aminals in the presence of amines has emerged as a promising methodology recently.¹¹ These novel catalytic strategies for CO_2 utilization feature the formation of the new carbon-nitrogen bond. Cantat and co-workers first described the catalytic reductive formylation of amines using CO_2 and silanes in 2012.¹² The catalytic reduction of CO_2 with hydrosilanes and amines to methylamines was unveiled independently by Cantat and co-workers and Beller and co-workers in 2013.¹³ After these initial reports, rapid progress in this area has led to the discovery of several amine formylation or methylation catalysts for the hydrosilylation of CO_2 .¹¹ However, among these systems, only a few cases have been reported where not only methylamines but also formamides could be selectively produced using the same catalyst.^{14, 15} These catalysts suffer from either the low reactivity or the poor selectivity, especially for the methylation reaction. Interestingly, both of formylation and methylation reactions could be achieved by using an inorganic salt (e.g. Cs_2CO_3)^{14b} or an organic inner salt (Betaine)¹⁵ as catalysts, but they only showed moderate reactivity towards the methylation reaction of primary amines along with the formation of mixtures of the monomethylated and dimethylated products. Clearly, the development of a general and highly active catalytic system for the selective formation of methylamines and formamides derived from CO_2 and amines is still highly desirable.

As part of our ongoing interest in the PN^3 -pincer complexes for their unique kinetic and thermodynamic properties,¹⁶ we report

^a Division of Physical Sciences and Engineering, KAUST Catalysis Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia. E-mail: hkw@kaust.edu.sa

^b Division of Physical Sciences and Engineering, Advanced Membranes & Porous Materials Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

^c College of Chemistry and Chemical Engineering, Graduate University of the Chinese Academy of Sciences, Beijing 100049, China.

^d College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

[†] Electronic Supplementary Information (ESI) available: Experimental details, NMR spectra of products. CCDC 1505721, 1530059 and 1571043. For crystallographic data in CIF or other electronic format see DOI:

Fig. 1 ORTEP diagram of PN³P*-Ni hydride complexes **Ni1**, **Ni2** and **Ni3** at 30% ellipsoid probability. Hydrogen atoms (except for pincer arms and Ni-H) are omitted for clarity.

Scheme 1 Synthesis of the dearomatized Ni-H pincer complexes via oxidative addition.

herein the preparation of well-defined dearomatized PN³P*-nickel hydride complexes and their applications on hydrosilylation of CO₂. To the best of our knowledge, this catalytic system represents the first nickel-catalyzed hydrosilylation of CO₂ to methanol, with the highest TON reported to date. To further extend the diverse range of products accessible from CO₂ and silanes, this dearomatized PN³P*-nickel hydride catalytic system is employed to the reductive functionalization of CO₂ with amines as well to offer a methodology for the selective formation of formamides and methylamines.

The dearomatized PN³P*-nickel hydride complexes **Ni1**, **Ni2**, and **Ni3** were synthesized by oxidative addition of the corresponding pincer ligands (**L1-L3**) to bis(1,5-cyclooctadiene)nickel(0) in toluene in one step (Scheme 1).¹⁷ In ¹H NMR spectra, the characteristic Ni-H resonance appears at -15.87, -15.62, and -16.44 ppm for complexes **Ni1**, **Ni2**, and **Ni3**, respectively. The ³¹P NMR spectra show two doublets, corresponding to the two magnetically different phosphorus atoms of the dearomatized pincer ligands. All **Ni1**, **Ni2** and **Ni3** were characterized by single crystal X-ray diffraction, exhibiting a similar coplanar geometry with shorter C-N bond distance for the imine arm of the dearomatized pyridine ring (Fig. 1).

The catalytic studies of the PN³P*-Ni hydride complexes commenced with the reduction of 1 atm of CO₂ in DMF using Ph₂SiH₂ as a reductant under various conditions (Table 1). The hydrosilane was fully consumed in 12 hours as monitored by GC-MS when using complex **Ni1** as the catalyst (Table 1, entry 1). Gratifyingly, after the CO₂-reduction product was subjected to hydrolysis, methanol was obtained in 91% yield. Either in the absence of catalyst or using **L1** alone, only trace amounts of methanol was observed, although Ph₂SiH₂ was completely consumed (Table 1, entries 2 and 3).⁸ Relatively lower yields of methanol were observed when complexes **Ni2** and **Ni3** were tested (Table 1, entries 4 and 5; Table S3, entries 2 and 3). Further optimization revealed that DMF was a better solvent. The reaction could also work well in polar solvents such as THF,

and CH₃CN, albeit with slower reaction rates. No methanol was formed when the solvent was changed to the nonpolar solvents, **Table 1** Hydrosilylation of CO₂ with diphenylsilane catalyzed by PN³P*-Ni hydride complexes.^a

$$\text{CO}_2 + \text{Ph}_2\text{SiH}_2 \xrightarrow[\text{DMF, RT to 60 } ^\circ\text{C}]{[\text{Ni-H}] \text{ catalyst}} \xrightarrow[\text{rt, 24 h}]{\text{NaOH/H}_2\text{O}} \text{CH}_3\text{OH}$$

Entry	Catalyst	Catalyst loading [% Si-H]	Time [h] ^b	Yield [%] ^c	TON
1	Ni1	1.25	12	91	73
2 ^d	—	—	72	Trace	—
3	L1	1.25	72	Trace	—
4	Ni2	1.25	24	87	70
5	Ni3	1.25	17	82	66
6	Ni1	5.00	6	91	18
7	Ni1	2.50	10	91	36
8	Ni1	0.50	14	92	184
9	Ni1	0.25	24	90	360
10 ^e	Ni1	0.02	54	98	4900

^a CO₂ balloon, catalyst, 1.0 mmol of Ph₂SiH₂, 2.0 mL of DMF. ^b Time required for the full consumption of Ph₂SiH₂ monitored by GC/MS. ^c Yields of CH₃OH determined by GC based on Si-H. ^d Without catalyst. ^e 2.0 mmol of Ph₂SiH₂ was used.

such as CH₂Cl₂ and toluene (Table S1). Other hydrosilanes were also investigated when using the same equivalent of Si-H groups. Reactions with PhSiH₃ resulted in a good yield of methanol, yet a prolonged reaction time was needed. The bulkier trisubstituted hydrosilanes did not give methanol as the final product (Table S2). The influence of the catalyst loadings was then examined. Catalyst **Ni1** showed high activity even with a catalyst loading as low as 0.02% with the TON up to 4900 (Table 1, entry 10). To the best of our knowledge, this is the highest TON reported for the reduction of CO₂ with silane to methanol.

We next further explored the reductive functionalization of CO₂ with amines. The reaction of dibenzylamine **1a** was chosen as a model substrate when employing Ph₂SiH₂ as the reducing agent and CO₂ as a C1 source (Table S4). To our delight, the notable reactivity afforded methylamine **2a** in 85% and formamide **3a** in 11% yield, observed when using 3 mol% **Ni1**, 5 equiv. of Ph₂SiH₂ and 2.7 atm of CO₂ at 100 °C for 24 h (Table S3, entry 1). Only small amounts of **3a** was detected in the absence of the catalyst (Table S3, entry 2). We found that the higher reaction temperature was favorable for the formation of methylation product (**2a**). Finally, the highest activity towards the formation of **2a** was provided at 120 °C under 2.7 atm of CO₂ (Table S3, entry 3). Interestingly, with the increasing of the CO₂ pressure or decreasing of the reaction temperatures, the improved yields of **3a** were achieved (Table S3, entries 4 and 5).

Meanwhile, the decreased amount of the reducing agent and solvent has a positive influence on the selectivity for the

Table 2 Methylation of various amines using CO₂ and Ph₂SiH₂ catalyzed by **Ni1**.^a

$\begin{array}{c} \text{R}^1 \\ \\ \text{NH} \\ \\ \text{R}^2 \end{array} + \text{CO}_2 + \text{Ph}_2\text{SiH}_2 \xrightarrow[120^\circ\text{C, CH}_3\text{CN}]{\text{Ni1 (3 mol\%)}} \begin{array}{c} \text{R}^1 \\ \\ \text{N}-\text{CH}_3 \\ \\ \text{R}^2 \end{array} \text{ or } \begin{array}{c} \text{R}^1 \\ \\ \text{N}-\text{CH}_3 \\ \\ \text{R}^2 \end{array} \quad (\text{R}^2=\text{H})$				
Entry	Substrate	Product	Yield [%] ^b	
1	1a R ¹ =Bn, R ² =Bn	2a	84	
2	1b R ¹ =Bn, R ² =Me	2b	91	
3	1c R ¹ =Cy, R ² =Cy	2c	82	
4	1d R ¹ =R ² =CH ₃ (CH ₂) ₁₁	2d	88	
5 ^c	1e R ¹ = <i>t</i> Bu, R ² =Me	2e	85	
6	1f	2f	84	
7	1g Ar=Ph, R=Me	2g	86	
8	1h Ar=Ph, R=Et	2h	88	
9	1i Ar=4-CH ₃ OC ₆ H ₄ , R=Me	2i	90	
10	1j Ar=4-ClC ₆ H ₄ , R=Me	2j	91	
11	1k Ar=4-BrC ₆ H ₄ , R=Me	2k	87	
12	1l Ar=4-MeOC ₆ H ₄	2l	86	
13 ^c	1m	2m	92	
14	1n	2n	86	
15	1o	2o	84	
16	1p R=Bn	2p	77	
17 ^c	1q R= <i>t</i> Bu	2q	90	
18	1r R=4-ClC ₆ H ₄ CH ₂	2r	81	
19	1s R=4-MeOC ₆ H ₄ CH ₂	2s	85	
20	1t R=Me	2t	89	
21	1u R=Ph	2u	84	
22	1v Ar=4-MeC ₆ H ₄	2v	86	
23	1w Ar=2-MeC ₆ H ₄	2w	83	
24	1x Ar=4-MeOC ₆ H ₄	2x	90	
25	1y Ar=2-MeOC ₆ H ₄	2y	85	
26	1z Ar=4-BrC ₆ H ₄	2z	87	
27	1aa Ar=4-FC ₆ H ₄	2aa	78	
28	1ab Ar=3,5-Me ₂ C ₆ H ₃	2ab	81	
29	1ac Ar=2,6-Me ₂ C ₆ H ₃	2ac	84	
30	1ad Ar=2,6- <i>i</i> PrC ₆ H ₃	2ad	79	
31	1ae Ar=2,4,6-Me ₃ C ₆ H ₂	2ae	78	
32	1af Ar=4-EtO ₂ CC ₆ H ₄	2af	76	

Condition: ^a Complex **Ni1** (0.015 mmol), amine (0.50 mmol), Ph₂SiH₂ (2.5 mmol), CH₃CN (15.0 mL), 2.7 atm of CO₂, 120 °C. ^b Yield of isolated product. ^c Determined by ¹H NMR spectroscopy of the crude reaction mixture using CH₂Br₂ as the internal standard.

formylation reaction (Table S3, entry 6). By increasing the CO₂ pressure to 8.2 atm, the formylation reaction could be performed at room temperature with 96% yield of **3a** (Table S3, entry 7). On the basis of the reaction conditions of entry 3 and 7, the use of the other two PN³P*-Ni hydride complexes **Ni2** and **Ni3** showed lower selectivities or yields in comparison with **Ni1** (Table S3, entries 8-11).

With the optimized reaction conditions in hand, we began to examine the substrate scope for each transformation (Table 2 and 3). As shown in Table 2, sterically less sterically hindered aliphatic secondary amines (**1a**, **1b**, and **1d**) showed high reactivity to afford the corresponding methylamines. Moreover, the more hindered aliphatic secondary amines, such as *N,N*-dicyclohexylamine **1c**, *N*-*tert*-butylmethylamine **1e**, and 2,2,6,6-tetramethylpiperidine **1f**

afforded the corresponding methylamines in good yields. Meanwhile, secondary aromatic amines with both electron-donating

Table 3 Formylation of various amines using CO₂ and Ph₂SiH₂ catalyzed by **Ni1**.^a

$\begin{array}{c} \text{R}^1 \\ \\ \text{NH} \\ \\ \text{R}^2 \end{array} + \text{CO}_2 + \text{Ph}_2\text{SiH}_2 \xrightarrow[\text{RT, CH}_3\text{CN}]{\text{Ni1 (3 mol\%)}} \begin{array}{c} \text{R}^1 \\ \\ \text{N}-\text{CHO} \\ \\ \text{R}^2 \end{array}$				
Entry	Substrate	Product	Yield [%] ^b	
1	1a R ¹ =Bn, R ² =Bn	3a	89	
2	1d R ¹ =R ² =CH ₃ (CH ₂) ₁₁	3d	88	
3 ^c	1e R ¹ = <i>t</i> Bu, R ² =Me	3e	96	
4	1m X=O	3m	87	
5	1ag X=NCOPh	3ag	78	
6 ^c	1ah	3ah	95	
7	1ai	3ai	89	
8	1n	3n	90	
9	1o R=Me	3o	75	
10	1aj R=H	3aj	81	
11	1g Ar=Ph, R=Me	3g	78	
12	1h Ar=Ph, R=Et	3h	87	
13	1i Ar=4-CH ₃ OC ₆ H ₄ , R=Me	3i	89	
14	1j Ar=4-ClC ₆ H ₄ , R=Me	3j	92	
15	1ak Ar=Ph, R=Bn	3k	89	
16	1p R=Bn	3p	87	
17 ^c	1q R= <i>t</i> Bu	3q	95	
18	1r R=4-ClC ₆ H ₄ CH ₂	3r	85	
19	1s R=4-MeOC ₆ H ₄ CH ₂	3s	91	
20	1al R=2-MeOC ₆ H ₄ CH ₂	3al	86	
21 ^c	1am R=Cy	3am	93	
22	1t R=Me	3t	84	
23	1u R=Ph	3u	93	
24	1v Ar=4-MeC ₆ H ₄	3v	88	
25	1w Ar=2-MeC ₆ H ₄	3w	87	
26	1x Ar=4-MeOC ₆ H ₄	3x	91	
27	1an Ar=4- <i>t</i> BuC ₆ H ₄	3an	85	
28	1y Ar=2-MeOC ₆ H ₄	3y	87	
29	1z Ar=4-BrC ₆ H ₄	3z	82	
30	1ab Ar=3,5-Me ₂ C ₆ H ₃	3ab	84	
31	1ac Ar=2,6-Me ₂ C ₆ H ₃	3ac	81	
32	1ad Ar=2,6- <i>i</i> PrC ₆ H ₃	3ad	85	
33	1af Ar=4-EtO ₂ CC ₆ H ₄	3af	78	

Condition: ^a Complex **Ni1** (0.015 mmol), amine (0.50 mmol), Ph₂SiH₂ (1.25 mmol), CH₃CN (5.0 mL), 8.2 atm of CO₂, room temperature. ^b Yield of isolated product. ^c Determined by ¹H NMR spectroscopy of the crude reaction mixture using CH₂Br₂ as the internal standard.

and electron-withdrawing substituents at the para position (**1g-1k**) reacted smoothly and the corresponding products were obtained in good yields. Notably, the more challenging substrate diaryl secondary amine **1l** was found to be reactive as well.^{14b} Several cyclic aliphatic secondary amines (**1m-1o**) were employed and excellent yields of the cyclic methylamines were achieved. In addition, not only aliphatic primary amines (**1p-1u**) but also aromatic primary amines (**1v-1ae**) proceeded selectively to provide the dimethylated products. Remarkably, even the methylation of sterically hindered substrates (**1q**, and **1ac-1ae**) proceeded smoothly to give the corresponding dimethylated products. It is noteworthy that the methylation reaction could be performed in the presence of halides, such as F, Cl, or Br, and reductive dehalogenation was not observed. Furthermore, ester-substituted amine **1af** was well tolerated under our reducing conditions, providing the corresponding dimethylated amine **2af** in good yield.

Utilizing optimal formylation reaction conditions at room temperature, various aliphatic and aromatic, secondary and primary amines were successfully converted into the desired formamides with good to excellent yields (Table 3). Both of the acyclic (**1a**, **1d**, **1e**, **1g-1j**, and **1ak**) and cyclic (**1m-1o**, and **1ag-1aj**) secondary amines could be transformed to the corresponding formamides in excellent yields. Importantly, the hydrosilylation of CO₂ to formamides showed the potential chemoselectivity. The carbonyl and ester groups could be tolerated under these conditions, as exemplified by the substrate **1ag** and **1af**. Additionally, primary amines (**1p-1z**, **1ab-1ad**, and **1al-1an**) proceeded in a similar fashion to secondary amines, generating monoformylated products. The formylation protocol is also compatible with a variety of halides (**1i**, **1j**, **1r**, and **1z**). The sterically hindered amines (**1e**, **1q**, **1ac**, and **1ad**) were also suitable for this transformation, giving the desired formamides in good to excellent yields.

Mechanistic proposals on metal hydride complex catalyzed hydrosilylation of CO₂ usually involve the insertion of CO₂ into a metal-H bond and generate CH₄ as the final product.¹⁸ However, this pathway was ruled out since no reaction was observed between complex **Ni1** with CO₂ at 125 °C. This observation suggests that CO₂ insertion into the Ni-H bond of **Ni1** might not be a catalysis related event. Catalyst **Ni2** bearing a NMe arm showed some similar reactivity (Table 1, entry 4; Table S4, entries 8 and 10;), implying that the N-H group of **Ni1** was not necessary for the activation of CO₂. Although we have not identified the active catalyst in the above CO₂ reduction reactions, we speculate that an alternative pathway for CO₂ activation may involve the nucleophilic attack of CO₂ by the imine nitrogen of the ligand. The nucleophilicity of the imine arm could be enhanced while a strong σ -donating hydride ligand is introduced. Further mechanistic studies are ongoing.

In summary, we have successfully synthesized and fully characterized several readily accessible dearomatized PN³P*-nickel hydride pincer complexes via an oxidative addition process. The first example of nickel catalyzed hydrosilylation of CO₂ to methanol has been achieved, with an unprecedentedly high turnover number of 4900. Moreover, these PN³P*-nickel hydride pincer complexes are capable of selectively catalyzing reductive methylation and formylation of amines with CO₂ with a very broad substrate scope.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- For selected reviews of CO₂ transformation, see: (a) T. Sakakura, J.-C. Choi; H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365-2387; (b) S. N. Riduan; Y. Zhang, *Dalton Trans.*, 2010, **39**, 3347-3357; (c) M. Aresta, *Carbon dioxide as chemical feedstock*. Wiley-VCH: Weinheim, 2010; p xix, 394 p; (d) M. Aresta, A. Dibenedetto; A. Angelini, *Chem. Rev.*, 2014, **114**, 1709-1742; (e) C. Maeda, Y. Miyazaki; T. Ema, *Catal. Sci. Technol.*, 2014, **4**, 1482-1497; (f) Q. Liu, L. Wu, R. Jackstell; M. Beller, *Nat. Commun.*, 2015, **6**, 5933.
- For selected examples, see: (a) P. G. Jessop, F. Joo; C.-C. Tai, *Coord. Chem. Rev.*, 2004, **248**, 2425-2442; (b) R. Tanaka, M. Yamashita; K. Nozaki, *J. Am.*

- Chem. Soc.*, 2009, **131**, 14168-14169; (c) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem. Int. Ed.*, 2010, **49**, 9777-9780; (d) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg; M. Beller, *J. Am. Chem. Soc.*, 2012, **134**, 20701-20704; (e) S. Bontemps, L. Vendier; S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2014, **136**, 4419-4425.
- G. A. Olah, A. Goeppert; G. K. S. Prakash, In *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH: Weinheim, 2009.
- For CO₂ hydrogenation to methanol, see recent reviews: (a) Y.-N. Li, R. Ma, L.-N. He; Z.-F. Diao, *Catal. Sci. Technol.*, 2014, **4**, 1498-1512; (b) E. Alberico; M. Nielsen, *Chem. Commun.*, 2015, **51**, 6714; (c) J. Klankermayer, S. Wesselbaum, K. Beydoun; W. Leitner, *Angew. Chem. Int. Ed.*, 2016, **55**, 7296 and references therein.
- (a) C. Das Neves Gomes, E. Blondiaux, P. Thuéry; T. Cantat, *Chem. Eur. J.*, 2014, **20**, 7098 and references therein; (b) R. Pal, T. L. Groy; R. J. Trovitch, *Inorg. Chem.*, 2015, **54**, 7506-7515; (c) Y. Yang, M. Xu; D. Song, *Chem. Commun.*, 2015, **51**, 11293-11296; (d) A. Aloisi, J.-C. Berthet, C. Genre, P. Thuery; T. Cantat, *Dalton Trans.*, 2016, **45**, 14774-14788; (e) Q.-Q. Ma, T. Liu, S. Li, J. Zhang, X. Chen; H. Guan, *Chem. Commun.*, 2016, **52**, 14262-14265; (f) T. J. Hadlington, C. E. Kefalidis, L. Maron; C. Jones, *ACS Catal.*, 2017, **7**, 1853-1859; (g) T. Liu, W. Meng, Q.-Q. Ma, J. Zhang, H. Li, S. Li, Q. Zhao; X. Chen, *Dalton Trans.*, 2017, **46**, 4504-4509.
- T. C. Eisenschmid; R. Eisenberg, *Organometallics*, 1989, **8**, 1822-1824.
- S. N. Riduan, Y. Zhang; J. Y. Ying, *Angew. Chem. Int. Ed.*, 2009, **48**, 3322-3325, S3322/3321-S3322/3311.
- M.-A. Courtemanche, M.-A. Legare, E. Rochette; F.-G. Fontaine, *Chem. Commun.*, 2015, **51**, 6858-6861.
- T. T. Metsänen; M. Oestreich, *Organometallics*, 2015, **34**, 543-546.
- M. G. Mazzotta, M. Xiong; M. M. Abu-Omar, *Organometallics*, 2017, **36**, 1688-1691.
- (a) A. Tlili, E. Blondiaux, X. Frogneux; T. Cantat, *Green Chem.*, 2015, **17**, 157 and references therein; (b) Y. Li, X. Cui, K. Dong, K. Junge; M. Beller, *ACS Catal.*, 2017, **7**, 1077 and references therein.
- C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine; T. Cantat, *Angew. Chem. Int. Ed.*, 2012, **51**, 187-190.
- (a) Y. Li, X. Fang, K. Junge; M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 9568-9571; (b) O. Jacquet, X. Frogneux, C. Das Neves Gomes; T. Cantat, *Chem. Sci.*, 2013, **4**, 2127-2131.
- (a) X. Frogneux, O. Jacquet; T. Cantat, *Catal. Sci. Technol.*, 2014, **4**, 1529-1533; (b) C. Fang, C. Lu, M. Liu, Y. Zhu, Y. Fu; B.-L. Lin, *ACS Catal.*, 2016, 7876-7881; (c) S. Das, F. D. Bobbink, S. Bulut, M. Soudani; P. J. Dyson, *Chem. Commun.*, 2016, **52**, 2497-2500.
- X.-F. Liu, X.-Y. Li, C. Qiao, H.-C. Fu; L.-N. He, *Angew. Chem. Int. Ed.*, 2017, **56**, 7425-7429.
- (a) H. Li, B. Zheng; K.-W. Huang, *Coord. Chem. Rev.*, 2015, **293-294**, 116 and references therein-138; (b) Y. Pan, C.-L. Pan, Y. Zhang, H. Li, S. Min, X. Guo, B. Zheng, H. Chen, A. Anders, Z. Lai, J. Zheng; K.-W. Huang, *Chem. Asian J.*, 2016, **11**, 1357-1360; (c) D. Gong, X. Zhang; K.-W. Huang, *Dalton Trans.*, 2016, **45**, 19399-19407; (d) C. Guan, D.-D. Zhang, Y. Pan, M. Iguchi, M. J. Ajitha, J. Hu, H. Li, C. Yao, M.-H. Huang, S. Min, J. Zheng, Y. Himeda, H. Kawanami; K.-W. Huang, *Inorg. Chem.*, 2017, **56**, 438-445; (e) H. Li, Y. Wang, Z. Lai; K.-W. Huang, *ACS Catal.*, 2017, **7**, 4446-4450; (f) T. P. Gonçalves; K.-W. Huang, *J. Am. Chem. Soc.*, 2017, **139**, 13442-13449.
- (a) N. A. Eberhardt; H. Guan, *Chem. Rev.*, 2016, **116**, 8373-8426; (b) During the submission of this manuscript, a similar work was disclosed. see: D. Oren, Y. Diskin-Posner, L. Avram, M. Feller, D. Milstein, *Organometallics* 2018.
- (a) S. Chakraborty, J. A. Krause; H. Guan, *Organometallics*, 2009, **28**, 582-586; (b) S. Chakraborty, Y. J. Patel, J. A. Krause; H. Guan, *Polyhedron*, 2012, **32**, 30-34; (c) L. Gonzalez-Sebastian, M. Flores-Alamo; J. J. Garcia, *Organometallics*, 2013, **32**, 7186-7194; (d) K. Motokura, N. Takahashi, A. Miyaji, Y. Sakamoto, S. Yamaguchi; T. Baba, *Tetrahedron*, 2014, **70**, 6951-6956; (e) S. Chakraborty, P. Bhattacharya, H. Dai; H. Guan, *Acc. Chem. Res.*, 2015, **48**, 1995-2003; (f) O. Santoro, F. Lazreg, Y. Minenkov, L. Cavallo; C. S. J. Cazin, *Dalton Trans.*, 2015, **44**, 18138-18144.