**Showcasing research from Professor Kuo-Wei Huang's laboratory, King Abdullah University of Science and Technology in Saudi Arabia.**

**Diverse catalytic reactivity of a dearomatized PN³P*−nickel hydride pincer complex towards CO$_2$ reduction**

The Huang group has demonstrated that the PN³(P)-pincer platform offers unique kinetic and thermodynamic properties compared to their analogs with CH$_2$ arms. This concept is further illustrated in PN³P*−nickel hydride that catalyzes hydrosilylation of CO$_2$ with unprecedented reactivity unseen in all other existing nickel hydride systems.

**As featured in:**
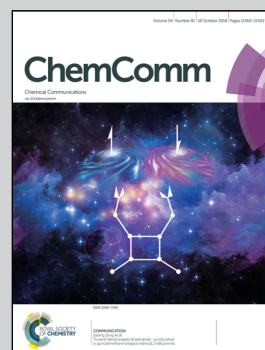


See Kuo-Wei Huang *et al.*,
*Chem*. *Commun*., 2018, **54**, 11395.

ROYAL SOCIETY
OF **CHEMISTRY**

# rsc.li/chemcomm

# ChemComm

## COMMUNICATION

# Diverse catalytic reactivity of a dearomatized PN$^3$P*–nickel hydride pincer complex towards CO$_2$ reduction†

Huaifeng Li,[a] Théo P. Gonçalves,[a] Qianyi Zhao,[a] Dirong Gong, [ID][a] Zhiping Lai, [ID][b] Zhixiang Wang, [ID][c] Junrong Zheng [ID][d] and Kuo-Wei Huang *[a]

A dearomatized PN$^3$P*–nickel hydride complex has been prepared using an 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 a PN$^3$P*–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 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 hydrogenation[4] and the hydroboration of CO$_2$ to methanol,[5] examples of hydrosilylation of CO$_2$ to methanol are still rare. Ir(CN)(CO)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, the 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] Oestreich[9] and Abu-Omar[10] 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 a 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 low reactivity or poor selectivity, especially for the methylation reaction. Interestingly, both formylation and methylation reactions could be achieved by using an inorganic salt (*e.g.* Cs$_2$CO$_3$)[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.

[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*
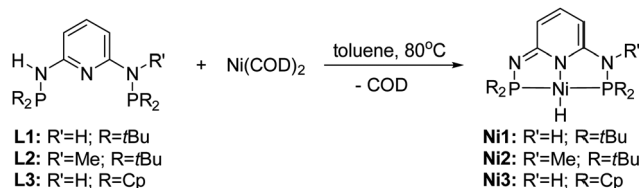
**Scheme 1** Synthesis of the dearomatized Ni–H pincer complexes *via* oxidative addition.

As part of our ongoing interest in the PN$^3$-pincer complexes for their unique kinetic and thermodynamic properties,[16] we report herein the preparation of well-defined dearomatized PN$^3$P*–nickel hydride complexes and their applications for hydrosilylation of CO$_2$. To the best of our knowledge, this catalytic system represents the first nickel-catalyzed hydrosilylation of CO$_2$ to methanol, with the highest TON reported to date. To further extend the diverse range of products accessible from CO$_2$ and silanes, this dearomatized PN$^3$P*–nickel hydride catalytic system is employed for the reductive functionalization of CO$_2$ with amines as well to offer a methodology for the selective formation of formamides and methylamines.

The dearomatized PN$^3$P*–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 $^1$H 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 $^{31}$P NMR spectra show two doublets, corresponding to the two magnetically different phosphorus atoms of the dearomatized pincer ligands. **Ni1**, **Ni2** and **Ni3** were characterized by single crystal X-ray diffraction, exhibiting a similar coplanar geometry with a shorter C–N bond distance for the imine arm of the dearomatized pyridine ring (Fig. 1).

The catalytic studies of the PN$^3$P*–Ni hydride complexes commenced with the reduction of 1 atm of CO$_2$ in DMF using Ph$_2$SiH$_2$ 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 CO$_2$-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 were observed, although Ph$_2$SiH$_2$ was completely

**Table 1** Hydrosilylation of CO$_2$ with diphenylsilane catalyzed by PN$^3$P*–Ni hydride complexes[a]

$$CO_2 + Ph_2SiH_2 \xrightarrow[\text{DMF, RT to 60 °C}]{\text{[Ni-H] catalyst}} \xrightarrow[\text{rt, 24 h}]{\text{NaOH/H}_2\text{O}} CH_3OH$$

| Entry | Catalyst | Catalyst loading [%Si–H] | Time[b] [h] | 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] Condition: CO$_2$ balloon, catalyst, 1.0 mmol of Ph$_2$SiH$_2$, 2.0 mL of DMF. [b] Time required for the full consumption of Ph$_2$SiH$_2$ monitored by GC/MS. [c] Yields of CH$_3$OH determined by GC based on Si–H. [d] Without catalyst. [e] 2.0 mmol of Ph$_2$SiH$_2$ was used.

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, ESI†). Further optimization revealed that DMF was a better solvent. The reaction could also work well in polar solvents such as THF, and CH$_3$CN, albeit with slower reaction rates. No methanol was formed when the solvent was changed to the nonpolar solvents, such as CH$_2$Cl$_2$ and toluene (Table S1, ESI†). Other hydrosilanes were also investigated when using the same equivalent of Si–H groups. Reactions with PhSiH$_3$ 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, ESI†). 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 CO$_2$ with silane to methanol.

We next further explored the reductive functionalization of CO$_2$ with amines. The reaction of dibenzylamine **1a** was chosen as a model substrate when employing Ph$_2$SiH$_2$ as the reducing agent and CO$_2$ as a C1 source (Table S4, ESI†). To our delight, the notable reactivity afforded methylamine **2a** in 85% and formamide **3a** in 11% yield, observed when using 3 mol% **Ni1**,
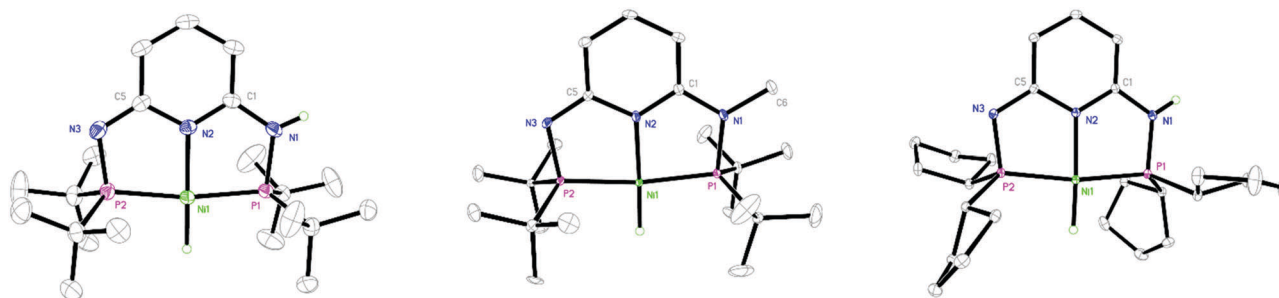


**Fig. 1** ORTEP diagram of PN$^3$P*–Ni hydride complexes **Ni1**, **Ni2** and **Ni3** at 30% ellipsoid probability. Hydrogen atoms (except for pincer arms and Ni–H) are omitted for clarity.

5 equiv. of $Ph_2SiH_2$ and 2.7 atm of $CO_2$ at 100 °C for 24 h (Table S3, entry 1, ESI†). Only a small amount of **3a** was detected in the absence of the catalyst (Table S3, entry 2, ESI†). We found that a higher reaction temperature was favorable for the formation of the methylation product (**2a**). Finally, the highest activity towards the formation of **2a** was provided at 120 °C under 2.7 atm of $CO_2$ (Table S3, entry 3, ESI†). Interestingly, with an increase of the $CO_2$ pressure or a decrease of the reaction temperature, improved yields of **3a** were achieved (Table S3, entries 4 and 5, ESI†). Meanwhile, the decreased amount of the reducing agent and solvent has a positive influence on the selectivity for the formylation reaction (Table S3, entry 6, ESI†). By increasing the $CO_2$ pressure to 8.2 atm, the formylation reaction could be performed at room temperature with 96% yield of **3a** (Table S3, entry 7, ESI†). On the basis of the reaction conditions of entries 3 and 7, the use of the other two $PN^3P^*$–Ni hydride complexes **Ni2** and **Ni3** showed lower selectivities or yields in comparison with **Ni1** (Table S3, entries 8–11, ESI†).

With the optimized reaction conditions in hand, we began to examine the substrate scope for each transformation (Tables 2 and 3). As shown in Table 2, 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 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

**Table 2** Methylation of various amines using $CO_2$ and $Ph_2SiH_2$ catalyzed by **Ni1**[a]



*a* Condition: complex **Ni1** (0.015 mmol), amine (0.50 mmol), $Ph_2SiH_2$ (2.5 mmol), $CH_3CN$ (15.0 mL), 2.7 atm of $CO_2$, 120 °C. Isolated yield unless otherwise noted. *b* Determined by $^1H$ NMR of the crude product using $CH_2Br_2$ as the internal standard.

**Table 3** Formylation of various amines using $CO_2$ and $Ph_2SiH_2$ catalyzed by **Ni1**[a]



*a* Condition: complex **Ni1** (0.015 mmol), amine (0.50 mmol), $Ph_2SiH_2$ (1.25 mmol), $CH_3CN$ (5.0 mL), 8.2 atm of $CO_2$, room temperature. Isolated yield unless otherwise noted. *b* Determined by $^1H$ NMR of the crude product using $CH_2Br_2$ as the internal standard.

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 $CO_2$ 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 $CO_2$ usually involve the insertion of $CO_2$ into a metal–H bond and generate $CH_4$ as the final product.[18] However, this pathway was ruled out since no reaction was observed

between complex **Ni1** and $CO_2$ at 125 °C. This observation suggests that $CO_2$ insertion into the Ni–H bond of **Ni1** might not be a catalysis related event. Catalyst **Ni2** bearing an NMe arm showed some similar reactivity (Table 1, entry 4; Table S4, entries 8 and 10, ESI†), implying that the N–H gorup of **Ni1** was not necessary for the activation of $CO_2$. Although we have not identified the active catalyst in the above $CO_2$ reduction reactions, we speculate that an alternative pathway for $CO_2$ activation may involve the nucleophlic attack of $CO_2$ by the iminic 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 $PN^3P^*$–nickel hydride pincer complexes *via* an oxidative addition process. The first example of nickel catalyzed hydrosilylation of $CO_2$ to methanol has been achieved, with an unprecedentedly high turnover number of 4900. Moreover, these $PN^3P^*$–nickel hydride pincer complexes are capable of selectively catalyzing reductive methylation and formylation of amines with $CO_2$ with a very broad substrate scope.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

1 For selected reviews of $CO_2$ transformation, see: (*a*) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387; (*b*) S. N. Riduan and Y. Zhang, *Dalton Trans.*, 2010, **39**, 3347–3357; (*c*) M. Aresta, *Carbon dioxide as chemical feedstock*, Wiley-VCH, Weinheim, 2010, p. 394; p. xix; (*d*) M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2014, **114**, 1709–1742; (*e*) C. Maeda, Y. Miyazaki and T. Ema, *Catal. Sci. Technol.*, 2014, **4**, 1482–1497; (*f*) Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 5933.
2 For selected examples, see: (*a*) P. G. Jessop, F. Joo and C.-C. Tai, *Coord. Chem. Rev.*, 2004, **248**, 2425–2442; (*b*) R. Tanaka, M. Yamashita and 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 and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 9777–9780; (*d*) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg and M. Beller, *J. Am. Chem. Soc.*, 2012, **134**, 20701–20704; (*e*) S. Bontemps, L. Vendier and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2014, **136**, 4419–4425.
3 G. A. Olah, A. Goeppert and G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, Weinheim, 2009.
4 For $CO_2$ hydrogenation to methanol, see recent reviews: (*a*) Y.-N. Li, R. Ma, L.-N. He and Z.-F. Diao, *Catal. Sci. Technol.*, 2014, **4**, 1498–1512; (*b*) E. Alberico and M. Nielsen, *Chem. Commun.*, 2015, **51**, 6714;

(*c*) J. Klankermayer, S. Wesselbaum, K. Beydoun and W. Leitner, *Angew. Chem., Int. Ed.*, 2016, **55**, 7296 and references therein.
5 (*a*) C. Das Neves Gomes, E. Blondiaux, P. Thuéry and T. Cantat, *Chem. – Eur. J.*, 2014, **20**, 7098 and references therein; (*b*) R. Pal, T. L. Groy and R. J. Trovitch, *Inorg. Chem.*, 2015, **54**, 7506–7515; (*c*) Y. Yang, M. Xu and D. Song, *Chem. Commun.*, 2015, **51**, 11293–11296; (*d*) A. Aloisi, J.-C. Berthet, C. Genre, P. Thuery and T. Cantat, *Dalton Trans.*, 2016, **45**, 14774–14788; (*e*) Q.-Q. Ma, T. Liu, S. Li, J. Zhang, X. Chen and H. Guan, *Chem. Commun.*, 2016, **52**, 14262–14265; (*f*) T. J. Hadlington, C. E. Kefalidis, L. Maron and C. Jones, *ACS Catal.*, 2017, **7**, 1853–1859; (*g*) T. Liu, W. Meng, Q.-Q. Ma, J. Zhang, H. Li, S. Li, Q. Zhao and X. Chen, *Dalton Trans.*, 2017, **46**, 4504–4509.
6 T. C. Eisenschmid and R. Eisenberg, *Organometallics*, 1989, **8**, 1822–1824.
7 S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2009, **48**(3322–3325), S3322.
8 M.-A. Courtemanche, M.-A. Legare, E. Rochette and F.-G. Fontaine, *Chem. Commun.*, 2015, **51**, 6858–6861.
9 T. T. Metsänen and M. Oestreich, *Organometallics*, 2015, **34**, 543–546.
10 M. G. Mazzotta, M. Xiong and M. M. Abu-Omar, *Organometallics*, 2017, **36**, 1688–1691.
11 (*a*) A. Tlili, E. Blondiaux, X. Frogneux and T. Cantat, *Green Chem.*, 2015, **17**, 157 and references therein; (*b*) Y. Li, X. Cui, K. Dong, K. Junge and M. Beller, *ACS Catal.*, 2017, **7**, 1077 and references therein.
12 C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine and T. Cantat, *Angew. Chem., Int. Ed.*, 2012, **51**, 187–190.
13 (*a*) Y. Li, X. Fang, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2013, **52**, 9568–9571; (*b*) O. Jacquet, X. Frogneux, C. Das Neves Gomes and T. Cantat, *Chem. Sci.*, 2013, **4**, 2127–2131.
14 (*a*) X. Frogneux, O. Jacquet and T. Cantat, *Catal. Sci. Technol.*, 2014, **4**, 1529–1533; (*b*) C. Fang, C. Lu, M. Liu, Y. Zhu, Y. Fu and B.-L. Lin, *ACS Catal.*, 2016, 7876–7881; (*c*) S. Das, F. D. Bobbink, S. Bulut, M. Soudani and P. J. Dyson, *Chem. Commun.*, 2016, **52**, 2497–2500.
15 X.-F. Liu, X.-Y. Li, C. Qiao, H.-C. Fu and L.-N. He, *Angew. Chem., Int. Ed.*, 2017, **56**, 7425–7429.
16 (*a*) H. Li, B. Zheng and K.-W. Huang, *Coord. Chem. Rev.*, 2015, **293–294**, 116–138 and references therein; (*b*) Y. Pan, C.-L. Pan, Y. Zhang, H. Li, S. Min, X. Guo, B. Zheng, H. Chen, A. Anders, Z. Lai, J. Zheng and K.-W. Huang, *Chem. – Asian J.*, 2016, **11**, 1357–1360; (*c*) D. Gong, X. Zhang and 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 and K.-W. Huang, *Inorg. Chem.*, 2017, **56**, 438–445; (*e*) H. Li, Y. Wang, Z. Lai and K.-W. Huang, *ACS Catal.*, 2017, **7**, 4446–4450; (*f*) T. P. Gonçalves and K.-W. Huang, *J. Am. Chem. Soc.*, 2017, **139**, 13442–13449.
17 (*a*) N. A. Eberhardt and 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 and D. Milstein, *Organometallics*, 2018, **37**, 2217–2221.
18 (*a*) S. Chakraborty, J. A. Krause and H. Guan, *Organometallics*, 2009, **28**, 582–586; (*b*) S. Chakraborty, Y. J. Patel, J. A. Krause and H. Guan, *Polyhedron*, 2012, **32**, 30–34; (*c*) L. Gonzalez-Sebastian, M. Flores-Alamo and J. J. Garcia, *Organometallics*, 2013, **32**, 7186–7194; (*d*) K. Motokura, N. Takahashi, A. Miyaji, Y. Sakamoto, S. Yamaguchi and T. Baba, *Tetrahedron*, 2014, **70**, 6951–6956; (*e*) S. Chakraborty, P. Bhattacharya, H. Dai and H. Guan, *Acc. Chem. Res.*, 2015, **48**, 1995–2003; (*f*) O. Santoro, F. Lazreg, Y. Minenkov, L. Cavallo and C. S. J. Cazin, *Dalton Trans.*, 2015, **44**, 18138–18144.