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An efficient and environmentally benign tungstate catalysis for reductive functionalization of CO₂ with amines and phenylsilane was developed. By simply varying the pressure, 2-electron or 6-electron reduction of CO₂ successfully approached with simultaneous C-N bond formation, thus leading to the formation of formamides and methylamines, respectively. That is, secondary and primary amines furnished the corresponding methylamines or dimethylamines in excellent yields under atmospheric pressure of CO₂, while various formamides were formed in yields ranging from 52% to 98% when increasing the CO₂ pressure to 2 MPa. ¹H NMR studies and control experiments demonstrate that the *N*-formylation undergoes the formation of silyl formate while the *N*-methylation proceeds through an aminal intermediate generated by 4-electron reduction of CO₂.

Introduction

CO2 has been attracting much attention as an abundant, nontoxic and renewable C1 building block.¹ Many procedures have been developed towards cost-effective chemical fixation of CO₂ to value-added chemicals via the construction of C-C, C-N and C-O bond.² In most of these processes, CO₂ is only functionalized but there is no reduction of the carbon atom and therefore no significant energy storage. On the other hand, extensive research efforts have also been devoted to CO₂ reduction, which can achieve energy-related molecules such as formic acid, methanol, methane or light alkanes.³ Even so, the scope of chemicals directly available from CO₂ remains very narrow. To further expand the scope of CO₂ recycling, novel processes for CO₂ conversion that combine both reduction of CO₂ and the formation of C-C, C-N or C-O bond, namely reductive functionalization of CO2 by Cantat et al., were explored.⁴ Notably, using amine as the functionalizing reagent, the reductive functionalization of CO₂ can output formamide and methylamine derivatives, which are widely applied as important solvent and intermediates in organic synthesis and material science.5

Among the established methods of reductive functionalization of CO_2 with amine, transition metal catalytic systems such as Ru,⁶ Rh,⁷ Re,⁸ Ir,⁹ Fe,¹⁰ Ni,¹¹ Cu,¹² Zn,¹³ Pd,¹⁴ Au¹⁵ and Pt¹⁶ have been employed using hydrosilane, hydroborane or hydrogen as reductant. Organocatalysis such as

organic superbases,^{4b, 17} carbene,¹⁸ 1,3,2-diazaphospholene,¹⁹ $B(C_6F_5)_{3,2}^{20}$ cesium formate,²¹ ionic liquids,²² γ -valerolactone,²³ DMSO²⁴ as well as DMF²⁵ have also been a research hotspot. In 2014, Cantat et al. described the temperature-tuned reductive functionalization of CO₂ with amine catalyzed by Fe(acac)₂ in combination with tris[2-(diphenylphosphino)ethyl]phosphine.^{10b} Although the chemoselectivity is moderate, this work represents the first example for reductive functionalization of CO₂ to respectively obtain methylamines and formamides. By tuning the temperature, Dyson et al. also realized the selective fixation of CO₂ onto amines.^{18c} Changing both the temperature and the type of hydrosilane, the Nmethylation and formylation can proceed as well with Cs₂CO₃²⁶ or TBAF²⁷ as a catalyst. Recently, our group has achieved the betaine-catalyzed hierarchical reduction of CO2 with amine and hydrosilane by tuning the reaction temperature and the CO₂ amount, giving products with various energy contents i.e. formamide, aminal and methylamine.²⁸ In spite of the above few examples for selectively reductive functionalization of CO₂ with amine, exploring catalytic system with distinctive conditions to respectively form methylamine and formamide appears to be pregnant. Especially, through regulating single variable of reaction conditions, e.g. CO₂ pressure, to control the chemoselectivity would be interesting and challenging.

On the other hand, the oxygen atoms of tungstate have a high charge density,²⁹ we speculated the tungstate anion could facilitate the hydrosilylation of CO₂ via interacting with the Si atom of hydrosilane to promote hydride transfer from hydrosilane to CO₂. In addition, the CO₂ pressure may influence the reductive level associated with CO₂ hydrosilylation.^{28, 30} Understandably, high CO₂ pressure represents a high molar fraction of CO₂, thus the hydrosilane can be rapidly consumed up, thus the further reduction is suppressed and terminated in the initial stage of forming silyl

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formate. While a decrease in CO_2 pressure may lower the reaction rate of hydrosilane with CO_2 , thereby leading to further reduction of the silyl formate by hydrosilane to bis(silyl)acetal or silylmethoxide.³¹ As a result, various products e.g. formamide, aminal and methylamine may be generated in the presence of an amine,^{7b, 21, 27, 28, 32} thus achieving selectively reductive functionalization of CO_2 . Herein, we developed an intriguing method using tungstate i.e. K_2WO_4 as efficient catalyst for the 2-electron or 6-electron reduction of CO_2 along with C-N bond formation in the presence of amine and phenylsilane (PhSiH₃). Only by varying the CO_2 pressure, methylamine and formamide derivatives were attained respectively, as shown in Scheme 1.



Results and Discussion

The experiment was initially explored at atmospheric pressure of CO₂ using N-methylaniline 1a as the substrate and 4 equivalents of PhSiH₃ (relative to 1a) as the reductant in acetonitrile. The reaction could hardly proceed without any catalyst (Table 1, entry 1). Then several representative sodium polyoxometalates and sodium tungstate were primarily screened (entries 2-5). The methylated product i.e. N,Ndimethylaniline (2a) was obtained in 90% yield along with small amount of N-methyl-formanilide (3a) when using sodium tungstate as catalyst, indicating that tungstate with a stronger basicity²⁹ is more efficient for the reductive functionalization of CO₂ to methylamine (hereafter referred to as N-methylation) (entry 5 vs. 2-4). Then various tungstates with different counter cations were further investigated (entries 6-9), of which potassium tungstate (K2WO4) exhibited excellent catalytic activity towards the N-methylation. This result illustrates that the counter cation with lower electronegativity is more favourable for the tungstate catalysis. Yields over 90% can still be obtained when the amount of K₂WO₄ was reduced to 7.5 mol% (relative to 1a, entry 10). Further reducing the dosage of K₂WO₄ gave a good conversion of **1a** but caused a decrease in the product selectivity (entries 11, 12). Subsequently, we tried to validate our hypothesis that the reductive functionalization of CO_2 could be switched by adjusting the CO_2 pressure on basis of the methylated conditions. Delightedly, the formylated product 3a was generated in 93% yield along with trace of 2a in 1.5 MPa CO_2 (entry 13). Further raising the pressure of CO_2 to 2 MPa, 3a was exclusively obtained in 95% yield (entry 14).

In addition, we also found that $PhSiH_3$ was a more active reductant than other hydrosilanes e.g. PMHS, Ph_2SiH_2 or $(EtO)_3SiH$ (Table S1, entry 9 vs. 1-8, ESI^{\dagger}). The discriminatory activity of various hydrosilanes may be ascribed to the different electronic and steric effects.²⁰ Moreover, both the *N*-methylation and *N*-formylation can still proceed efficiently with

HN 1a	^{°CH} 3 + CO ₂ + PhSiH ₃	Cat. CH ₃ CN, 70 °C	CH₃ ^N CH₃ + 2a	CHO N CH ₃ 3a
Entry	Cat./(mol%)	Conv./%	Yield of $2a/\%^b$	Yield of 3a /% ^b
1	-	0	-	_
2	Na ₃ PW ₁₂ O ₄₀ (10)	0	0	0
3	Na ₆ SiW ₁₂ O ₄₀ (10)	0	0	0
4	Na4SiW10O32(10)	11	0	7
5	Na ₂ WO ₄ (10)	>99	90	7
6	K ₂ WO ₄ (10)	>99	99	0
7	Li ₂ WO ₄ (10)	6	0	5
8	NiWO ₄ (10)	0	0	0
9	CoWO ₄ (10)	7	0	5
10	$K_2WO_4(7.5)$	>99	97	trace
11	$K_2WO_4(5)$	>99	90	8
12	$K_2WO_4(2.5)$	92	53	33
13 ^c	$K_2WO_4(7.5)$	>99	7	93
14^d	K ₂ WO ₄ (7.5)	>99	trace	95

 a Reaction conditions: **1a** (0.0535 g, 0.5 mmol), catalyst, PhSiH₃ (248 μ L, 2 mmol), 1 bar CO₂, CH₃CN (2 mL), 70 K, 12 h. b Determined by GC using 1,3,5-trimethyoxybenzene as an internal standard. c 1.5 MPa CO₂. d 2 MPa CO₂.

high chemoselectivity, even decreasing the amount of $PhSiH_3$ to 1.5 mmol (Table S1, entries 10, 11, ESI†). While, inadequate amount of $PhSiH_3$ caused tremendous decrease in both yield and the product selectivity (Table S1, entries 12, 13, ESI†), perhaps because only one hydride of $PhSiH_3$ plays the role in reduction.

Having in hand the protocol for this kind of reductive functionalization of CO₂, the generality of the N-methylation was firstly examined with 7.5 mol% of K₂WO₄ and 3 equivalents of PhSiH₃ in acetonitrile under 1 bar CO₂ at 70 °C for 12 h, as shown in Table 2. Most of aromatic, heteroaromatic and aliphatic amines were successfully methylated in excellent yields. The para-substituted N-methylanilines with either electron donating or weak electron withdrawing groups are active to produce the corresponding N,N-dimethylanilines in over 90% yields (entries 1-4). N-alkyl anilines could be also converted to methylamines efficiently (entries 5-8). Particularly, N-allyl aniline delivered N-allyl-N-methylaniline without the reduction of the unsaturated bond (entry 5). This catalysis also worked effectively with heterocyclic amines such as 1,2,3,4-tetrahydroquinoline and morpholine (entries 9, 10). While due to the weak nucleophilicity against the formation of C-N bond, substrates with strong electron withdrawing groups, e.g. N-methyl-4-nitroaniline, are inert. Moreover, the reactivity of diphenylamine is suppressed perhaps owing to the dual effects of weak nucleophilicity and steric hindrance. In addition, dimethylated products were obtained dominantly by increasing the amount of PhSiH₃ in the cases of primary aromatic amines (entries 11-15).

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Table 2 Substrate scope for the N-methylation.^a

H - R ^{1-N} 1	$egin{array}{c} K_2W\\ PhS\\ R^2(H) & + & CO_2 & - & PhS\\ R^2(H) & 1 & bar & CH_3C \end{array}$	O₄(7.5 mol%) iH ₃ (3 equiv.) N, 70 °C, 12 h R ^{1-N} 2	H ₃ `R ² (CH ₃) 2
Entry	Substrate	Product	Yield of $2/\%^b$
	x ^H ⊂H ₃	X CH3	
1	X = H, 1a	X = H, 2a	97 ^c
2	X = Cl, 1b	X = Cl, 2b	90
3	X = CH ₃ , 1c	$X = CH_3, 2c$	97
4	$X = OCH_3, 1d$	$X = OCH_3, 2d$	92
	HN.R	CH ₃ N _R	
5	R = Allyl, 1e	R = Allyl, 2e	94
6	R = Et, 1f	R = Et, 2f	89
7	R = iPr, 1g	R = iPr, 2g	92
8	R = Bn, 1h	R = Bn, 2h	99
9		СН ₃ 2і	90
10	⊂ N 1j	O N CH₃ 2j	90
	X NH2	X CH3	
11^{d}	X = H, 1k	X = H, 2a	41
12^{d}	X = Cl, 11	X = Cl, 2b	63
13 ^d	X = Br, 1m	X = Br, 2m	42
14^d	$X = CH_3$, 1n	$X = CH_3$, 2c	45
15 ^d	X = OCH ₃ , 10	$X = OCH_3, 2d$	45

^{*a*} Unless otherwise specified, all of the reactions were performed with **1** (0.5 mmol), K₂WO₄ (0.0122 g, 7.5 mol%), PhSiH₃ (186 μL, 1.5 mmol), 1 bar CO₂, CH₃CN (2 mL), 70 K, 12 h. ^{*b*} The yield was determined by ¹H NMR technique using 1,3,5-trimethyoxybenzene as an internal standard. ^{*c*} Determined by GC using 1,3,5-trimethyoxybenzene as an internal standard. ^{*d*} PhSiH₃ (372 μL, 3 mmol).

Subsequently, the utility of *N*-formylation was also explored by tuning the pressure of CO₂ to 2 MPa, as shown in Table 3. Most of secondary aromatic amines were converted into the corresponding formamides in good yields (entries 1-8). Unlike *N*-methylation, diphenylamine can be formylated in 52% yield (entry 9), probably because the intermediate of silyl formate in *N*-formylation has lower steric hindrance than the *N*-methylation intermediate i.e. bis(silyl)acetal (Scheme 2, intermediate II). Heterocyclic amines 1,2,3,4-tetrahydroquinoline and morpholine were transformed into formamide derivatives efficiently as well (entries 10,11). *N*-benzyl-*N*-methylformamide can also be obtained in 98% yield with aliphatic *N*-methyl-1-phenylmethanamine as substrate (entry 12). However, electron-deficient primary amines are not so nucleophilic enough to trap the weak electrophilic silyl formate intermediate that the primary amines become inert towards *N*-formylation.^{32c}

To explore the reaction mechanism, a mixture of K_2WO_4 (0.0375 mmol), PhSiH₃ (1.5 mmol) and CO₂ (2 MPa) was treated at 70 °C for 4 h in the absence of amine. The silyl

Table 3 Substrate scope for the Λ	-formylation.a
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	H R ^{1-N} R ² + CO ₂ 1 2 MPa	K ₂ WO ₄ (7.5 mol%) PhSiH ₃ (3 equiv.) CH ₃ CN, 70 °C, 12 h	CHO R ^{1-N} `R ² 3
Entry	Substrate	Product	Yield of $3/\%^b$
	CH3	CHO N-CH3	
1	X = H, 1a	X = H, 3a	94 ^c
2	X = Cl, 1b	X = Cl, 3b	85
3	$X = CH_3$, 1c	$X = CH_3, 3c$	93
4	$X = OCH_3, 1d$	$X = OCH_3, 3d$	92
	R R	CHO N.R	
5	R = Allyl, 1e	R = Allyl, 3e	81
6	R = Et, 1f	R = Et, 3f	90
7	R = iPr, 1g	R = iPr, 3g	76 (dr=31:5)
8	R = Bn, 1h	R = Bn, 3h	70
9	R = Ph, 1p	R = Ph, 3p	52
10		СТО Зі	83 (dr=10.8:5)
11	⊂ N 1j	С Кно 3ј	90
12	N ^{CH3}	CHO 30	98 (dr=4:3)

^a Conditions: 1 (0.5 mmol), K₂WO₄ (0.0122 g, 7.5 mol%), PhSiH₃ (186 μL, 1.5 mmol), 2 MPa CO₂, CH₃CN (2 mL), 70 K, 12 h. ^b The yield was determined by ¹H NMR technique using 1,3,5-trimethyoxybenzene as an internal standard.^c Determined by GC using 1,3,5-trimethyoxybenzene as an internal standard.

formate was obviously detected by NMR technique (Fig. S1, ESI†), which is consistent with the reports by Liu^{22} and Chung^{33} . When **1a** (0.5 mmol) was added into the above reaction mixture, **3a** was obtained in 90% yield with a reaction time of 8 h. The above results confirmed that the CO₂ is reduced by PhSiH₃ to silyl formate which subsequently reacts with an amine to produce the formamide under 2 MPa CO₂. That is to say, the *N*-formylation undergoes a 2-electron reduction of CO₂ and then the C-N bond coupling, almost simultaneously.

To gain insight into the mechanism of *N*-methylation, the reaction of atmospheric CO₂ with **1a** and PhSiH₃ in deuterated acetonitrile was studied by the ¹H NMR technique. As shown in Fig.1, in the first three hours of the reaction, a group of new signals assigned to the intermediate emerged at $\delta = 7.25$, 6.84, 6.78, 4.77, 2.88 ppm (triangles in Fig. 1); meanwhile the signals of **1a** disappeared progressively. As the time went on, signals of the intermediate gradually disappeared and **2a** finally generated. According to the analysis for the above ¹H NMR monitoring, we quenched the reaction after three hours with large amount of acetonitrile, and then the intermediate was isolated by column chromatography, thus identified as *N*,*N*-

C)

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dimethyl-*N*,*N*-diphenylmethanediamine (aminal, Fig.1, compound **III**) by NMR and GC-MS (See the Supporting Information).^{32c} We used the aminal (0.5 mmol) replacing **1a** to react with CO₂ and PhSiH₃ under the standard *N*-methylation conditions (Scheme 3, eq. a). As expected, **2a** was obtained quantitatively. As a result, the *N*-methylation goes through the formation of an aminal intermediate. It is also suggested that the CO₂ is reduced by hydrosilane in *N*-methylation to a C⁰ species, i.e. bis(silyl)acetal which reacts with amine to generate the aminal.³¹

Furthermore, the transformation of aminal to methylamine may occur via two possible pathways (Scheme 2). Path A: With the silanol in situ formed as a proton donor, the aminal reacts with hydrosilane to give methylamine and siloxane, regenerating the amine substrate simultaneously. Path B: The aminal is reduced by hydrosilane with the aid of bis(silyl)acetal, giving methylamine, siloxane and aminosilylacetal derivative (Scheme 2, intermediate IV) which is the precursor of aminal. Because the ¹H NMR peaks corresponding to the reactant **1a** disappeared after 3 h (Fig. 1); and no reaction was observed for aminal with PhSiH₃ and triphenylsilanol catalyzed by K₂WO₄ (Scheme 3, eq. b), therefore the path A is ruled out. On the other hand, there is no conversion of aminal and PhSiH₃ in the absence of CO₂ (Scheme 3, eq. c), indicating that the reduction of aminal to methylamine involves CO₂ or the CO₂ reductive species, of which the bis(silyl)acetal is most likely. Accordingly, the path B is reasonable. In addition, the formylamide, methoxysilanes and N,N-dimethyl-N,N-diphenylurea can be ruled out as the intermediate (Scheme 3, eq. d-f).



Fig. 1 ¹H NMR spectra for the methylation of 1a (0.0535 g, 0.5 mmol), PhSiH₃ (186 μ L, 1.5 mmol) and CO₂ (1 bar) in CD₃CN.



a)
$$Ph \cdot N \cap Ph + CO_2 + PhSiH_3 \frac{K_2WO_4 (7.5 \text{ mol}\%)}{CH_3CN, 70 \circ C, 12 h}$$
 2 $Vh^3 CH_3$
Quantitative yield

$$\stackrel{\text{Ph.}}{\underset{\text{CH}_3}{}} \stackrel{\text{Ph.}}{\underset{\text{CH}_3}{}} \stackrel{\text{Ph.}}{\underset{\text{CH}_3}{}} + \text{PhSiH}_3 \xrightarrow{} \frac{K_2 WO_4 (7.5 \text{ mol}\%)}{CH_3 CN, 70 \text{ }^{\circ}\text{C}, 12 \text{ h}} \stackrel{\text{N.R.}}{\longrightarrow} \text{N.R.}$$



Scheme 3 Control experiments.

On basis of the above experimental results and previous reports,^{28,30,31} a possible pathway for the present potassium tungstate-promoted and pressure-switched reductive functionalization of CO2 with amine and PhSiH3 was proposed, as illustrated in Scheme 4. At 2 MPa CO₂, the PhSiH₃ is rapidly consumed up in the hydrosilylation of CO₂ to form the silyl formate $(I)^{30a}$ which reacts with amine to yield formamide. While at atmospheric pressure of CO₂, the rate of CO₂ hydrosilation to silvl formate decreased and the silvl formate can be further reduced by PhSiH₃ to bis(silyl)acetal (II).^{30b} The further reduction of silvl formate to silvlacetal has been also demonstrated by Zhang in the research of N-heterocyclic carbene catalyzed conversion of carbon dioxide with silanes.³¹ Subsequently, nucleophilic attack of amine towards II delivers the aminosilylacetal derivative (IV) which is successively converted into aminal (III). Then the aminal is further reduced by PhSiH₃ with the assistance of II, giving the methylated product, siloxane and IV.28 The intermediate IV can be regenerated to III. In the whole process, the tungstate may play a vital role in the hydride transfer from hydrosilane to CO₂ or the reductive species via a nucleophilic interaction with the Si atom of hydrosilane (Scheme S1). In short, the pressure of CO_2 dominates the hierarchical reduction levels of CO₂ i.e. the formation of silvl formate at 2 MPa or bis(silvl)acetal at atmospheric pressure, and successive generation of the aminal, and thereby tunes the product selectivity i.e. formamide or methylamine.

Scheme 2 Two possible pathways of aminal to methylamine

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Scheme 4 Proposed pathways for the pressure-switched reductive functionalization of CO_2 with amine.

Conclusions

In summary, we have found that tungstate, a kind of abundant and environmentally benign inorganic salts, could efficiently catalyze the reductive functionalization of CO_2 with amine and phenylsilane under mild conditions. Simply by tuning the pressure of CO_2 , this protocol achieves the selective synthesis of formamides and methylamines. From a mechanistic standpoint, the pressure of CO_2 controls the hierarchical reduction levels of CO_2 , i.e. the formation of silyl formate at 20 bar or bis(silyl)acetal at atmospheric pressure, and successive generation of the aminal. Through ¹H NMR studies and control experiments, a presumable pathway through the aminal intermediate for *N*-methylation and the silyl formate for *N*formylation is demonstrated. Further studies on the reductive functionalization of CO_2 with amines, other nucleophiles and various reductants are in progress in our laboratory.

Experimental

General procedure for the reductive functionalization of CO₂ with amines to methylamines

Potassium tungstate (12.2 mg, 7.5 mol% relative to amine), amine (0.5 mmol), CH₃CN (2 mL) and phenylsilane (186 μ L, 1.5 mmol) was added successively into a 10 mL over-dried Schlenk tube equipped with a stir-bar. The reaction mixture was stirred at 70 °C for 12 h under an atmosphere of CO₂ (99.999%, balloon). Upon completion, the conversion and yield were determined by GC or ¹H NMR technique using 1,3,5-trimethyoxybenzene (40.0 mg) as an internal standard. The reaction mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the corresponding methylamine. All of the products were characterized by GC-MS and NMR technique.

General procedure for the reductive functionalization of CO₂ with amines to formylamides

Potassium tungstate (12.2 mg, 7.5 mol% relative to amine), amine (0.5 mmol), CH₃CN (2 mL) and phenylsilane (186 μ L, 1.5 mmol) was added successively into a 10 mL (inner volumes) stainless steel autoclave at room temperature. Then CO₂ was charged into the reactor up to 2 MPa. The autoclave was heated at 70 °C for 12 h. Upon completion, the reactor was cooled to 0 °C in ice-water bath and carefully depressurized to atmospheric pressure. The conversion

and yield were determined by GC or 1 H NMR technique using 1,3,5-trimethyoxybenzene (40.0 mg) as an internal standard. The reaction mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the desired formylamide. All of the products were characterized by GC-MS and NMR technique.

Conflicts of interest

The authors declare no conflicts of interest.

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References

- Select examples and reviews on carbon dioxide as a C₁ building block in organic synthesis: (a) M. He, Y. Sun, B. Han, Angew. Chem., Int. Ed., 2013, 52, 9620-9633; (b) Q. Liu, L. Wu, R. Jackstell and M. Beller, Nat. Commun., 2015, 6: 5933; (c) K. Dong and X.-F. Wu, Angew. Chem., Int. Ed., 2017, 56, 5399-5401; (d) M. Aresta, A. Dibenedetto and A. Angelini, Chem. Rev., 2014, 114, 1709-1742; (e) Q.-W. Song, Z.-H. Zhou and L.-N. He, Green Chem., 2017, 19, 3707-3728.
- 2 For selected examples or reviews on chemical fixation of CO₂ by forming C-C bond, see: (a) A. Banerjee, G. R. Dick, T. Yoshino and M. W. Kanan, Nature, 2016, 531, 215-219; (b) A.-H. Liu, B. Yu and L.-N. He, Greenhouse Gas Sci. Technol., 2015, 5, 17-33. (c) K. Sekine and T. Yamada, Chem. Soc. Rev., 2016, 45, 4524-4532; for selected reviews of chemical fixation of CO₂ by forming C-N bond, see: (d) Y. Li, X. Cui, K. Dong, K. Junge and M. Beller, ACS Catal., 2017, 7, 1077-1086; (e) Z.-Z. Yang, L.-N. He, J. Gao, A.-H. Liu and B. Yu, Energy Environ. Sci., 2012, 5, 6602-6639; for selected examples and reviews on chemical fixation of CO₂ by forming C–O bond, see: (f) J. Rintjema, R. Epping, G. Fiorani, E. Martín, E. C. Escudero-Adán and A. W. Kleij, Angew. Chem., Int. Ed., 2016, 55, 3972-3976; (g) B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang and S.-J. Zhang, Green Chem., 2015, 17, 108-122; (h) C. Martín, G. Fiorani and A. W. Kleij, ACS Catal., 2015, 5, 1353-1370.
- 3 For selected reviews or examples on CO₂ reduction, see: (a) W. Wang, S. Wang, X. Ma and J. Gong, Chem. Soc. Rev., 2011, 40, 3703-3727; (b) W.-H. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck and E. Fujita, Chem. Rev., 2015, 115, 12936-12973; (c) S. Gao, Y. Lin, X. Jiao, Y. Sun, Q. Luo, W. Zhang, D. Li, J. Yang and Y. Xie, Nature, 2015, 529, 68-71; (d) J. Schneidewind, R. Adam, W. Baumann, R. Jackstell and M. Beller, Angew. Chem., Int. Ed., 2017, 56, 1890-1893; (e) A. Bordet, L.-M. Lacroix, P.-F. Fazzini, J. Carrey, K. Soulantica and B. Chaudret, Angew. Chem., Int. Ed., 2016, 55, 15894-15898; (f) Y.-N. Li, R. Ma, L.-N. He and Z.-F. Diao, Catal. Sci. Technol., 2014, 4, 1498-1512.
- 4 (a) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine and T. Cantat, *Angew. Chem., Int. Ed.*, 2012, 51, 187-190. (b) A. Tlili, E. Blondiaux, X. Frogneux and T. Cantat, *Green Chem.*, 2015, 17, 157-168.

DOI: 10.1039/C7GC03416D

- 5 (a) S. Ding and N. Jiao, Angew. Chem., Int. Ed., 2012, 51, 9226-9237; (b) D. K. Tosh, A. Janowsky, A. J. Eshleman, E. Warnick, Z.-G. Gao, Z. Chen, E. Gizewski, J. A. Auchampach, D. Salvemini and K. A. Jacobson, J. Med. Chem., 2017, 60, 3109-3123.
- 6 (a) O. Krocher, R. A. Koppel and A. Baiker, Chem. Commun., 1997, 453-454; (b) Y. Li, I. Sorribes, T. Yan, K. Junge and M. Beller, Angew. Chem., Int. Ed., 2013, 52, 12156-12160; (c) K. Beydoun, T. vom Stein, J. Klankermayer and W. Leitner, Angew. Chem., Int. Ed., 2013, 52, 9554-9557; (d) Y. Li, X. Fang, K. Junge and M. Beller, Angew. Chem., Int. Ed., 2013, 52, 9568-9571; (e) L. Zhang, Z. Han, X. Zhao, Z. Wang and K. Ding, Angew. Chem., Int. Ed., 2015, 54, 6186-6189.
- (a) T. V. Q. Nguyen, W.-J. Yoo and S. Kobayashi, Angew. 7 Chem., Int. Ed., 2015, 54, 9209-9212; (b) S. Itagaki, K. Yamaguchi and N. Mizuno, J. Mol. Catal. A: Chem., 2013, 366. 347-352.
- (a) D. S. Morris, C. Weetman, J. T. C. Wennmacher, M. Cokoja, M. Drees, F. E. Kuhn and J. B. Love, Catal. Sci. Technol, 2017, 7, 2838-2845. (b) T. Toyao, S. M. A. H. Siddiki, Y. Morita, T. Kamachi, A. S. Touchy, W. Onodera, K. Kon, S. Furukawa, H. Ariga, K. Asakura, K. Yoshizawa and K. Shimizu, Chem. Eur. J., 2017, 23, 14848-14859.
- (a) Q.-Y. Bi, J.-D. Lin, Y.-M. Liu, S.-H. Xie, H.-Y. He and Y. Cao, Chem. Commun., 2014, 50, 9138-9140. (b) K. Park, G. H. Gunasekar, N. Prakash, K.-D. Jung and S. Yoon, ChemSusChem, 2015, 8, 3410-3413.
- 10 (a) 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; (b) X. Frogneux, O. Jacquet and T. Cantat, Catal. Sci. Technol., 2014, 4, 1529-1533; (c) U. Jayarathne, N. Hazari and W. H. Bernskoetter, ACS Catal., 2018, 8, 1338-1345.
- 11 L. González-Sebastián, M. Flores-Alamo and J. J. García, Organometallics, 2015, **34**, 763-769. 12 (a) K. Motokura, N. Takahashi, D. Kashiwame, S.
- Yamaguchi, A. Miyaji and T. Baba, Cataly. Sci. Technol., 2013, 3, 2392-2396; (b) R. Shintani and K. Nozaki, Organometallics, 2013, 32, 2459-2462; (c) S. Zhang, Q. Mei, H. Liu, H. Liu, Z. Zhang and B. Han, RSC Adv., 2016, 6, 32370-32373; (d) O. Santoro, F. Lazreg, Y. Minenkov, L. Cavallo and C. S. J. Cazin, Dalton Trans., 2015, 44, 18138-18144; (e) X. Cui, X. Dai, Y. Zhang, Y. Deng and F. Shi, Chem. Sci., 2014, 5, 649-655.
- 13 (a) R. Luo, X. Lin, Y. Chen, W. Zhang, X. Zhou and H. Ji, ChemSusChem, 2017, 10, 1224-1232; (b) R. Luo, Y. Chen, Q. He, X. Lin, Q. Xu, X. He, W. Zhang, X. Zhou and H. Ji, ChemSusChem, 2017, 10, 1526-1533.
- 14 (a) R. A. Molla, P. Bhanja, K. Ghosh, S. S. Islam, A. Bhaumik and S. M. Islam, ChemCatchem, 2017, 9, 1939-1946; (b) X. Cui, Y. Zhang, Y. Deng and F. Shi, Chem. Commun., 2014, 50, 13521-13524.
- 15 (a) X.-L. Du, G. Tang, H.-L. Bao, Z. Jiang, X.-H. Zhong, D. S. Su and J.-Q. Wang, *ChemSusChem*, 2015, **8**, 3489-3496; (b) T. Mitsudome, T. Urayama, S. Fujita, Z. Maeno, T. Mizugaki, K. Jitsukawa and K. Kaneda, ChemCatchem, 2017, 9, 3632-3636; (c) G. Tang, H.-L. Bao, C. Jin, X.-H. Zhong and X.-L. Du, RSC Advances, 2015, 5, 99678-99687.
- 16 K. Kon, S. M. A. H. Siddiki, W. Onodera and K.-i. Shimizu, Chem. Eur. J., 2014, 20, 6264-6267.
- 17 E. Blondiaux, J. Pouessel and T. Cantat, Angew. Chem., Int. Ed., 2014, 53, 12186-12190.
- 18 (a) O. Jacquet, C. Das Neves Gomes, M. Ephritikhine and T. Cantat, J. Am. Chem. Soc., 2012, 134, 2934-2937; (b) S. Das, F. D. Bobbink, G. Laurenczy, P. J. Dyson, Angew. Chem., Int. Ed., 2014, 53, 12876-12879; (c) S. Das, F. D. Bobbink, S. Bulut, M. Soudani and P. J. Dyson, Chem. Commun., 2016,

52, 2497-2500; (d) W.-C. Chen, J.-S. Shen, T. Jurca, C.-J. Peng, Y.-H. Lin, Y.-P. Wang, W.-C. Shih, G. P. A. Yap and T.-G. Ong, Angew. Chem., Int. Ed., 2015, 54, 15207-15212.

- 19 C. C. Chong and R. Kinjo, Angew. Chem., Int. Ed., 2015, 54, 12116-12120.
- 20 Z. Z. Yang, B. Yu, H. Y. Zhang, Y. F. Zhao, G. P. Ji, Z. S. Ma, X. Gao and Z. M. Liu, Green. Chem., 2015, 17, 4189-4193
- 21 X.-F. Liu, C. Qiao, X.-Y. Li and L.-N. He, Green Chem., 2017, 19, 1726-1731.
- 22 L. D. Hao, Y. F. Zhao, B. Yu, Z. Z. Yang, H. Y. Zhang, B. X. Han, X. Gao and Z. M. Liu, ACS Catal., 2015, 5, 4989-4993.
- 23 J. Song, B. Zhou, H. Liu, C. Xie, Q. Meng, Z. Zhang and B. Han, *Green Chem.*, 2016, **18**, 3956-3961. 24 H. Lv, Q. Xing, C. Yue, Z. Lei and F. Li, *Chem. Commun.*,
- 2016, 52, 6545-6548.
- 25 (a) H. Niu, L. Lu, R. Shi, C.-W. Chiang, A. Lei, Chem. Commun., 2017, 53, 1148-1151; (b) T. X. Zhao, G. W. Zhai, J. Liang, P. Li, X. B. Hu and Y. T. Wu, Chem. Commun., 2017. 53. 8046-8049.
- 26 C. Fang, C. Lu, M. Liu, Y. Zhu, Y. Fu and B.-L. Lin, ACS Catal., 2016, 6, 7876-7881.
- X.-F. Liu, R. Ma, C. Qiao, H. Cao and L.-N. He, Chem. Eur. J., 2016, 22, 16489-16493.
- 28 X.-F. Liu, X.-Y. Li, C. Qiao, H.-C. Fu and L.-N. He, Angew. Chem., Int. Ed., 2017, 56, 7425-7429.
- 29 T. Kimura, K. Kamata and N. Mizuno, Angew. Chem., Int. Ed., 2012, 51, 6700-6703
- 30 (a) S. N. Riduan, J. Y. Ying and Y. Zhang, ChemCatChem, 2013, 5, 1490-1496; (b) Z. Z. Yang, B. Yu, H. Y. Zhang, Y. F. Zhao, G. P. Ji and Z. M. Liu, RSC Adv., 2015, 5, 19613-19619
- 31 S. N. Riduan, Y. Zhang and J. Y. Ying, Angew. Chem., Int. Ed., 2009, 48, 3322-3325.
- 32 (a) G. Jin, C. G. Werncke, Y. Escudié, S. Sabo-Etienne and S. Bontemps, J. Am. Chem. Soc., 2015, 137, 9563-9566; (b) O. Jacquet, C. Das Neves Gomes, M. Ephritikhine, T. Cantat, ChemCatChem, 2013, 5, 117-120. (c) X. Frogneux, E. Blondiaux, P. Thuery and T. Cantat, ACS Catal., 2015, 5, 3983-3987
- 33 S. Chun, S. Yang and Y. K. Chung, Tetrahedron, 2017, 73, 3438-3442.

6 | J. Name., 2012, 00, 1-3

TOC Graphic

A tungstate catalysis for reductive functionalization of CO_2 with amines and phenylsilane is successfully developed by simply varying the pressure to respectively form formamides and methylamines.

