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Metal β-diketonate complexes as highly efficient catalysts for chemical fixation of CO_2 into cyclic carbonates under mild conditions†

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The potential of metal β-diketonate complexes for the catalysis of the chemical fixation of CO_2 into cyclic carbonates at 1 atm CO_2 and near room temperature was demonstrated. Their potential for the capture and simultaneous conversion of CO_2 in a dilute CO_2 stream was also determined. The catalysts were easily synthesized and commercially available. Therefore, this CO_2 transformation was less energy- and material-consuming, which made this reaction closer to true "green" chemistry.

Introduction

Carbon dioxide is an abundant, economical, nontoxic, and renewable C1 feedstock in organic synthesis. The coupling reaction of CO_2 with epoxides to afford cyclic carbonates is one of the most promising reactions for the utilization of CO_2, because this transformation is 100% atom economical, and the products can be widely used. A wide range of catalytic systems[1] have been developed for these reactions over the past decades. The early catalytic systems used simple quaternary ammonium/phosphonium salts (including ionic liquids),[2] organic bases,[3] inorganic or organic metal halides,[3a,4] and transition metal complexes[5] alone or in a physical mix. Then, the structures of catalysts became more and more exquisite, the materials became more and more advanced, and the catalytic activity became more and more efficient. To date, catalysts with multiple functionality in one molecule and a variety of new materials have been explored, including various metal–organic frameworks (MOFs),[6] porous materials,[7] multifunctional or polymerized ammonium/phosphonium salts,[8] functional transition metal complexes,[9] and some other special catalysts such as metal- and halide-free catalysts,[10] N-doped carbons,[11] and metal–organic nanotubes.[12] However, given that CO_2 is a highly oxidized and stable molecule, in addition to the participation of catalysts and solvents, its conversion usually requires high temperatures (>100 °C) and pressures (>1 MPa).

Moreover, CO_2 utilization is so attractive, because CO_2 is recognized as a primary greenhouse gas, and CO_2 conversion may contribute to mitigating climate change.[13] However, whether more CO_2 is emitted than converted in the transformation of CO_2 is debatable. The entire process should be considered, including the following: costs for capture, storage, and transportation of purified CO_2; the material and energy consumption for catalyst preparation; and the energy consumption in the course of CO_2 transformation.[14] The harsh temperatures and pressures required for the reactions are highly energy consuming. Therefore, as traditional catalyst research is relatively mature, less energy-consuming processes should be explored. Fortunately, a number of catalysts have been developed for CO_2 conversion under mild conditions (low temperature and pressure, even at atmospheric pressure[15]) in recent years. Hydrogen-bond donor ammonium salts, which were functionalized with –OH,[16] $-NH_2$,[17] or both,[18] and metal-based catalysts,[19] including functionalized metal complexes[20] and metal–organic frameworks (MOFs),[6a,c,21] were studied for their use in the transformation of CO_2 into cyclic carbonates at 1 atm CO_2 (Table S1†). Nevertheless, most of the catalysts were not sufficiently effective, because most of the turnover frequencies (TOFs) were lower than 8 h^{-1}. Although the TOFs of some catalysts were higher than 8 h^{-1} (Table S1,† entries 18, 21, and 26), the costs for catalyst preparation were relatively high. Thus, there is still plenty of room for improvement, such as reducing catalyst loading or lowering the cost for catalyst preparation.

In the area of metal complex-catalyzed chemical fixation of CO_2, metal(salen) complexes have attracted attention since their first use in the transformation of CO_2 into cyclic carbonates.[22] Over the past two decades, modifications and functionalizations have been made in metal centers, the diamine framework of ligands, and substituents on phenyl rings of salicylaldehydes to improve their performance in the chemical fixation of CO_2 into cyclic carbonates or polycarbonates (the products of the copolymerization of CO_2 with epoxides, which is another route for the reaction of CO_2 with epoxides).[1b,23] Metal β-diketonate complexes, which have similar coordination struc-

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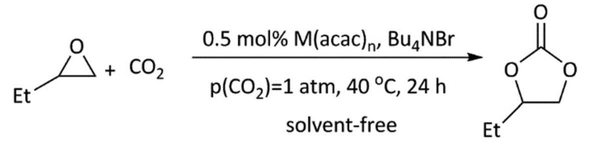
tures to metal(salen) complexes and the possibility of functionalization in three positions of the ligand,[24] were widely used in catalytic chemistry. However, in spite of their facile preparation and chemical stability, their application in the chemical fixation of CO_2 did not attract much attention. M(acac)$_n$, the simplest metal β-diketonate complexes, are easily synthesized[25] or commercially available. In the present study, we tap into their potential for catalyzing reactions under extremely mild conditions.

Results and discussion

We first examined the catalytic performances of several commercially available M(acac)$_n$ with 0.5 mol% catalyst loading combined with tetrabutylammonium bromide (Bu_4NBr) for the cycloaddition of CO_2 to 1,2-butene oxide (BO) at atmospheric pressure and 40 °C (Table 1). When Bu_4NBr was used alone, just 13% yield of 1,2-butylene carbonate (BC) was obtained after 24 h (Table 1, entry 1), whereas the addition of Co(acac)$_2$ enhanced the yield to 95% (Table 1, entry 2). The valence state of cobalt had a pronounced effect on catalytic activity, as Co(acac)$_3$ showed extremely low catalytic activity (Table 1, entry 3). It was reported that metal halide/n-Bu_4NOAc systems were effective for the conversion of epoxides into cyclic carbonates at 10–15 bar CO_2.[26] Herein, $CoCl_2·4H_2O$ and $CoAc_2·4H_2O$ were combined with Bu_4NBr and their catalytic activity was found to be almost the same as that of Bu_4NBr alone (Table 1, entries 4 and 5). Some other M(acac)$_n$ such as V(acac)$_3$, VO(acac)$_2$, Ni(acac)$_2$, and Zn(acac)$_2$ exhibited excellent to moderate catalytic activity (Table 1, entries 6–9), and the rest of the M(acac)$_n$ showed low catalytic activity at 40 °C (Table 1, entries 10–16). The solubility of the complexes in the monomer was investigated to confirm whether there was a relationship between the catalytic activity and the solubility of the complexes. Among the catalysts used above, no or very small amounts of precipitates were observed in the reaction mixture during the reaction at 40 °C, except for $CoCl_2·4H_2O$, $CoAc_2·4H_2O$, Cd(acac)$_2$, and La(acac)$_3$. Since the catalytic activities of these four catalysts were relatively low, it might be concluded that some catalysts with poor solubility exhibited poor catalytic activity. But it could not be proved that the reason for the poor catalytic activity was poor solubility, because it was observed during the experiments that the solubility of Al(acac)$_3$ was very good, but its catalytic activity was very low.

Table 1 Screening of catalysts for the synthesis of cyclic carbonate from CO_2 and BO at atmospheric pressure[a]



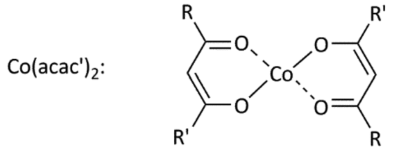
Entry	M(acac)$_n$	Yield[b] (%)
1	—[c]	13
2	Co(acac)$_2$	95
3	Co(acac)$_3$	21
4	$CoCl_2·4H_2O$	14
5	$CoAc_2·4H_2O$	20
6	V(acac)$_3$	95
7	VO(acac)$_2$	88
8	Ni(acac)$_2$	76
9	Zn(acac)$_2$	43
10	Fe(acac)$_2$	18
11	Fe(acac)$_3$	22
12	Al(acac)$_3$	16
13	Zr(acac)$_4$	21
14	MoO_2(acac)$_2$	24
15	Cd(acac)$_2$	13
16	La(acac)$_3$	25

[a] Reaction conditions: BO (40 mmol), M(acac)$_n$ (0.2 mmol), Bu_4NBr (0.2 mmol), 40 °C, 1 atm CO_2 (balloon), 24 h. [b] Determined by GC and the selectivities are >99%. [c] Bu_4NBr alone for the reaction.

The catalytic activity can be greatly influenced by minor alterations in ligands.[27] Several similar Co(β-diketonato)$_2$ complexes with the $-C(CH_3)_3$, $-CF_3$, or –Ph group substituted for $-CH_3$ in ligands were applied for the reaction (Table 2). The performance of bis(dipivaloylmethanato)cobalt(ɪɪ) (Co(dpm)$_2$) was equal to that of Co(acac)$_2$ (Table 2, entries 1 and 2). The catalytic activities of bis(benzoylacetonato)cobalt(ɪɪ) (Co(bac)$_2$) and bis(dibenzoylmethanato)cobalt(ɪɪ) (Co(dbm)$_2$) were slightly lower than that of Co(acac)$_2$ (Table 2, entries 3 and 4). When one or two $-CH_3$ groups in acetylacetonate were replaced by $-CF_3$, the catalytic activity was cut down so sharply that bis(hexafluoroacetonato)cobalt(ɪɪ) (Co(F_6-acac)$_2$) did not contribute to the catalytic activity anymore (Table 2, entries 5 and 6). These results might be attributed to the electronic effect of substituents. The addition of an electron-withdrawing group such as $-CF_3$ reduced the electron density of the oxygen atoms in the ligand, which would result in the loss of the coordination bond of the ligand to the metal center, thereby reducing the stability of the metal complex and leading to lower catalytic activity.

Reaction temperature had a significant effect on the reaction activity (Table 3, entries 1–5). The reaction of CO_2 with BO

Table 2 Catalytic activities of Co(β-diketonato)$_2$ [a]



Entry	Co(acac′)$_2$	R	R′	Yield[b] (%)
1	Co(acac)$_2$	CH_3	CH_3	95
2	Co(dpm)$_2$	$C(CH_3)_3$	$C(CH_3)_3$	95
3	Co(bac)$_2$	CH_3	Ph	87
4	Co(dbm)$_2$	Ph	Ph	90
5	Co(F_3-acac)$_2$	CH_3	CF_3	19
6	Co(F_6-acac)$_2$	CF_3	CF_3	12

[a] Reaction conditions: BO (40 mmol), Co(acac′)$_2$ (0.2 mmol), Bu_4NBr (0.2 mmol), 40 °C, 1 atm CO_2 (balloon), 24 h. [b] Determined by GC and the selectivities are all >99%.

Table 3 Effects of reaction parameters in the synthesis of cyclic carbonate from CO_2 and BO catalyzed by $Co(acac)_2$ [a]

Entry	Cocat.	Equiv. of cocat.	Temp. (°C)	Time (h)	Yield[b] (%)
1	Bu_4NBr	1	20	24	37
2	Bu_4NBr	1	30	24	70
3	Bu_4NBr	1	40	24	95
4	Bu_4NBr	1	50	24	>99
5	Bu_4NBr	1	50	12	99
6	None	0	40	12	0
7	Bu_4NBr	0.1	40	12	14
8	Bu_4NBr	0.2	40	12	20
9	Bu_4NBr	1	40	12	71
10	Bu_4NBr	2.5	40	12	85
11	Bu_4NBr	5	40	12	97
12	Bu_4NBr	7.5	40	12	98
13	Bu_4NBr	10	40	12	98
14	Bu_4NBr	2.5	40	4	51
15	Bu_4NBr	5	40	4	64
16	Bu_4NBr	7.5	40	4	63
17	Bu_4NBr	10	40	4	47
18	Bu_4NCl	5	40	12	20
19	Bu_4NI	5	40	12	>99
20	Bu_4NI	5	40	8	97(41[c])
21	BuMIMBr	5	40	12	60
22	$BuPh_3PBr$	5	40	12	43
23	BuPyBr	5	40	12	55

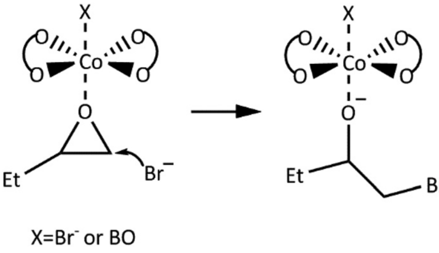
[a] Reaction conditions: BO (40 mmol), $Co(acac)_2$ (0.2 mmol, 0.5 mol%), 1 atm CO_2 (balloon). [b] Determined by GC and the selectivities are >99%. [c] $Co(acac)_2$ (0.04 mmol, 0.1 mol%) and Bu_4NI (0.2 mmol, 0.5 mol%).

can still be carried out at 20 °C at a reasonable rate. When the temperature was raised to 50 °C, the substrate could be almost completely converted to a cyclic carbonate after 12 h.

The boiling point of BO is 63 °C at atmospheric pressure. Thus, 40 °C was chosen for the sake of convenience and safety as the main operating temperature for further study.

Increasing the ratio of Bu_4NBr to $Co(acac)_2$ from 0 to 5 had a pronounced positive effect on the catalytic activity (Table 2, entries 6–11). Unsurprisingly, the reaction did not occur when Bu_4NBr was not present in the catalytic system. Comparison of the catalytic activity of Bu_4NBr alone and that of $Co(acac)_2$–Bu_4NBr showed that $Co(acac)_2$ and Bu_4NBr catalyzed the reaction synergistically. When the ratio was increased to 5, 97% yield of BC was obtained after 12 h. When the ratios were 5, 7.5, and 10, the conversion of BO was all nearly complete, and the difference between these ratios was unremarkable (Table 2, entries 11–13). As seen from Table 1, entry 1, Bu_4NBr could catalyze the reaction alone, and a long reaction time might level out the difference. Therefore, the reaction time was shortened to 4 h (Table 2, entries 14–17) to highlight the difference. The yield of BC with 10 equiv. of Bu_4NBr was lower than that with 5 or 7.5 equiv. of Bu_4NBr, which meant that the addition of excess cocatalyst was not conducive to the reaction, and this phenomenon was consistent with some relevant reports.[22,23a]

In the process of the reaction of CO_2 with epoxides catalyzed by metal complexes, a coordination bond was formed between the metal center and the oxygen atom of the epoxide, thereby activating the epoxide and prompting its ring opening (Scheme 1).[28] In addition to being a nucleophile in the ring opening of the epoxide, Br^- could also coordinate with the metal center. Therefore, Br^- competed with the epoxide in bonding to the metal center. When excess Br^- was loaded, coordinated epoxides would be displaced from the metal center, and the last two coordination sites of $Co(acac)_2$ might be occupied by Br^-, thereby leading to the reduction of reaction activity. This reason explains why the reaction activity with 10 equiv. of the cocatalyst was lower than that with 5 or 7.5 equiv. of the cocatalyst. Nevertheless, in the absence of metal complexes, Br^- alone can also promote the ring-opening reaction of epoxides. Considering this aspect, excess Br^- had a positive effect on the reaction activity. Therefore, the addition of excess catalysts did not reduce the catalytic activity significantly.



Scheme 1 The proposed pathway for epoxide ring opening by $Co(acac)_2/Bu_4NBr$.

The process described above, which especially took place in solution, had no prior direct evidence. As the reaction took place in a transparent glass container, the color of the reaction mixture noticeably changed from red to purple gradually when the equiv. of Bu_4NBr was increased (Fig. 1). According to the relationship between the absorption of visible light and the observed color, red, fuchsia, and purple colors can be observed when the light at wavelengths of 490–500, 500–560, and 560–580 nm was absorbed, respectively. Thus, the mixtures of

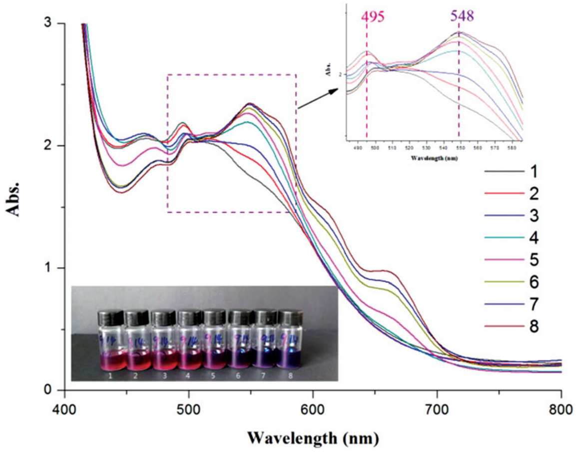


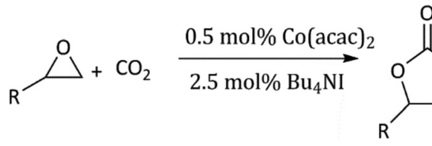
Fig. 1 The UV-vis absorption spectrum of the reaction mixtures. The amount of each material in the mixtures was in accordance with Table 2 entries 6–13: BO (40 mmol), $Co(acac)_2$ (0.2 mmol), the ratio of $Bu_4NBr/Co(acac)_2$: (1) 0, (2) 0.1, (3) 0.2, (4) 1, (5) 2.5, (6) 5, (7) 7.5, and (8) 10.

$Co(acac)_2$ and Bu_4NBr in BO, the compositions of which were consistent with those of reaction mixtures, were characterized by ultraviolet-visible (UV-Vis) spectroscopy. As shown in Fig. 1, solution 1 (with no Bu_4NBr) exhibits a significant absorption peak near 495 nm and no obvious absorption near 548 nm. With the increasing dosage of Bu_4NBr, the absorbance at around 495 nm decreased gradually and the absorbance at around 548 nm increased accordingly. This indicates that the peaks at around 495 nm and 548 nm might be caused by the Co–BO and Co–Br coordination bonds, respectively. With the increasing dosage of Bu_4NBr, the BO bonded to the Co center was replaced by Br^-. The increase of the absorbance at around 548 nm was pronounced in the ratio range of 0 to 2.5, and then gradually slowed down. When the ratio of Bu_4NBr to $Co(acac)_2$ increased to 7.5, adding more Bu_4NBr did not lead to a pronounced increase in the absorbance at around 548 nm. In addition, an absorption peak appeared at 450–490 nm, which decreased in intensity when the equiv. of Bu_4NBr was more than 2.5. Consequently, a new absorption peak appeared at 650–700 nm, whose intensity continuously enhanced with the increasing dose of Bu_4NBr. These two absorption peaks might correspond to the second Co–BO and Co–Br coordination bonds, respectively, and when the equiv. of Bu_4NBr was more than 2.5, the second BO bonded to the Co center began to be replaced by Br^-.

The effect of anions and cations of the cocatalyst was further studied with 5 equiv. of the cocatalyst. As to the anions of Bu_4NX (Table 3, entries 11, 18–20), the order of activity was $I^- > Br^- > Cl^-$, which was consistent with the order of their nucleophilicity.[29] When Bu_4NCl was used, BC yield was only 20% after 12 h, but when Bu_4NI was used, a BC yield of 97% was obtained after 8 h (TOF = 24.2 h^{-1}). $Co(acac)_2$ still showed good catalytic activity and led to 41% yield of BC after 8 h even when the amount was reduced to 0.1 mol% (Table 3, entry 20). The TOF value of $Co(acac)_2$ was 51.2 h^{-1}, which exceeded the TOF values of most of the catalytic systems reported previously under similar reaction conditions (Table S1†). The order of cocatalysts with different cations was Bu_4NBr > BuMIMBr > BuPyBr > $BuPh_3PBr$ (Table 3, entries 11, 21–23). The solubility and the electrostatic interactions between anions and cations of cocatalysts in BO (BO itself acted as solvent in the reaction), which influenced the concentration of Br^- disassociated from the bromide salt,[30] might affect the performance of the catalytic system. As observed in the experiment, a certain amount of $BuPh_3PBr$ was not soluble in BO. As seen, this value of TOF exceeded the TOF values of most of the catalytic systems reported previously. Considering the low cost and easy preparation of metal β-diketonate complexes, this method has the potential for CO_2 utilization.

The catalytic system was effective for the coupling reaction of CO_2 with a variety of terminal epoxides, including aliphatic and aromatic epoxides (Table 4, entries 1–5). The transformation of CO_2 commonly uses purified CO_2, thereby resulting in high energy and capital costs for its capture, storage, and transportation. Thus, the activity of this system for the capture and simultaneous conversion of CO_2 in a dilute CO_2 stream (a gas mixture containing 10% v/v CO_2 and 90% v/v N_2) was studied briefly. The boiling point of BO is low, and the raw materials could be easily carried away by the excess gas. Thus, non-volatile 1,2-hexene oxide (HO) was chosen as the substrate. The reaction was operated at 70 °C to shorten the time and thus reduce the loss of raw materials. The result showed that 92% of CO_2 in a dilute CO_2 stream could be captured and simultaneously converted into cyclic carbonate when the total flow of the dilute CO_2 stream was 10 sccm (Table 4, entry 8), which meant that the catalyst was also effective for the capture and simultaneous conversion of CO_2 in flue gas.

Table 4 The conversion of CO_2 (or CO_2 in flue gas) with various epoxides at atmospheric pressure[a]



Entry	R	Temp. (°C)	Time (h)	Yield[b] (%)
1	Me	40	8	97[c]
2	Et	40	8	97
3	Ph	40	8	58
4	CH_2Cl	40	8	67
5	Bu	40	8	82
6	Bu	70	2	85
7	Bu	70	4	>99
8[d]	Bu	70	4	49[e]

[a] Reaction conditions: Epoxides (40 mmol), $Co(acac)_2$ (0.2 mmol, 0.5 mol%), Bu_4NI (1 mmol, 2.5 mol%), 1 atm CO_2 (balloon). [b] Determined by GC. [c] Operating pressure: 2 atm. Since the boiling point of 1,2-propylene oxide (PO) is 34 °C, the pressure caused by the substrate gas is about 1 atm at 40 °C. Therefore, 2 atm pressure is required to make sure that CO_2 gets into the reaction system and the partial pressure of CO_2 is about 1 atm. [d] HO (20 mmol), $Co(acac)_2$ (0.1 mmol), Bu_4NI (0.5 mmol), and a dilute CO_2 stream (a gas mixture containing 10% v/v CO_2 and 90% v/v N_2) with a total flow of 10 sccm. [e] Conversion of CO_2 was 92%. Conversion of CO_2 calculated as the ratio between the moles of cyclic carbonate formed and the moles of CO_2 that flowed through the reaction (1 sccm = 7.43×10^{-7} mol s^{-1}; 10.7 mmol of CO_2 flowed for 4 h).

Conclusions

In conclusion, the catalytic potential of $M(acac)_n$-based catalytic systems was tapped for the synthesis of cyclic carbonates from CO_2 and epoxides under extremely mild conditions. The transformation could be achieved under the conditions of 1 atm CO_2, near room temperature, and without additional solvents. With 0.5 mol% $Co(acac)_2$, 97% yield of 1,2-butylene carbonate was obtained after 8 h (TOF = 24.2 h^{-1}) at 1 atm CO_2 and 40 °C. When the loading of the catalyst was reduced to 0.1 mol%, the yield of 1,2-butylene carbonate was 41% (TOF = 51.2 h^{-1}). Furthermore, this system with 1,2-hexene oxide as the substrate could capture and simultaneously convert 92% of CO_2 in a dilute CO_2 stream (a gas mixture containing 10% v/v CO_2 and 90% v/v N_2). In addition to being less energy consuming, the preparation of the catalyst was facile and less material consuming, which made this transformation of CO_2 closer to true "green" chemistry. Tetrabutylammonium halide was used as a cocatalyst, and its excess dosage had a negative effect on the reaction activity. The UV-Vis spectrum of the reaction mixture was used to investigate the mechanism, and to the best of our knowledge, this evidence has not been provided in other studies. Three positions in the ligand of $M(acac)_n$ can be modified or functionalized to highlight the great value of this catalyst system in further studies.

Experimental

General information

NMR spectra were recorded with a 500 MHz Bruker spectrometer and calibrated with tetramethylsilane (TMS) as the internal reference. Infrared spectra measurements were performed on a Thermo 470 FT-IR spectrometer. UV-Vis spectra measurements were performed on an Agilent Cary 5000 spectrometer. GC/MS analysis was performed on an Agilent 7890A gas chromatograph with an Agilent 5975C mass-selective detector. GC analysis was performed on an Agilent 6890 gas chromatograph with an HP-5 column and an FID detector. ESI-MS analyses were performed on a Waters LCT premier XE mass spectrometer. The catalysts were dissolved in CH_3OH for ESI-MS analyses. The carbon and the hydrogen contents of Co(β-diketonato)$_2$ were analysed on a Thermo Fisher Flash 2000 elemental analyser (EA) and the cobalt contents were analysed on an Agilent 720 inductively coupled plasma atomic emission spectrometer (ICP-AES). Both the EA and the ICP-AES were performed at Shanghai Huiming Testing Equipment Co., Ltd. Reagents and starting materials were all used as received unless otherwise stated.

Synthesis of cobalt(II) β-diketonate complexes

Bis(benzoylacetonato)cobalt(II) ($Co(bac)_2$), bis(dibenzoylmethanato)cobalt(II) ($Co(dbm)_2$), bis(trifluoroacetonato)cobalt(II) ($Co(F_3\text{-}acac)_2$), and bis(hexafluoroacetonato)cobalt(II) ($Co(F_6\text{-}acac)_2$) were synthesized as described.[25] Bis(dipivaloylmethanato) cobalt(II) ($Co(dpm)_2$) was purchased from Alfa Aesar Co., Ltd.

$Co(bac)_2$. Cobalt(II) acetate tetrahydrate (1.49 g, 6 mmol) in 6 mL of water was added into benzoylacetone (1.62 g, 10 mmol) in 6 mL of ethanol. 3 mol L^{-1} aqueous ammonia was added dropwise until the solution was slightly basic. A large amount of yellow-brown product precipitated immediately. Then the reaction mixture was stirred for 2 hours at 50 °C. The product was filtered off, washed alternately with water and ethanol, and then dried under vacuum overnight to yield 1.30 g (68%) of pinkish brown powder.

IR (KBr): ν/cm^{-1} 1592, 1559, 1515, 1486, 1453 and 1405.

MS (ESI^+): m/z 382.0661 (calcd for $[Co(C_{10}H_9O_2)_2 + H]^+$ 382.0615).

Anal. calcd for $Co(C_{10}H_9O_2)_2{\cdot}H_2O$: C, 60.16; H, 5.05; Co, 14.76. Found: C, 60.85; H, 4.67; Co, 14.21. The ratio of C/Co calcd for $Co(C_{10}H_9O_2)_2{\cdot}nH_2O$: 4.08. Found: 4.28.

The synthesis of $Co(dbm)_2$, $Co(F_3\text{-}acac)_2$ and $Co(F_6\text{-}acac)_2$ was similar to that of $Co(bac)_2$.

$Co(dbm)_2$. Yellow solid, yield 91%.

IR (KBr): ν/cm^{-1} 1594, 1547, 1524, 1480, 1454 and 1395.

MS (ESI^+): m/z 506.0893 (calcd for $[Co(C_{15}H_{11}O_2)_2 + H^+]$ 506.0928).

Anal. calcd for $Co(C_{15}H_{11}O_2)_2{\cdot}2H_2O$: C, 66.55; H, 4.84; Co, 10.88. Found: C, 66.80; H, 4.52; Co, 10.32. The ratio of C/Co calcd for $Co(C_{15}H_{11}O_2)_2{\cdot}nH_2O$: 6.12. Found: 6.47.

$Co(F_3\text{-}acac)_2$. Dark purple powder, yield 87%.

IR (KBr): ν/cm^{-1} 1625, 1531, 1465 and 1401.

MS (ESI^-): m/z 395.9830 (calcd for $[Co(C_5H_4F_3O_2)_2{\cdot}CH_3OH\text{-}H]^-$ 395.9843).

Anal. calcd for $Co(C_5H_4F_3O_2)_2$: C, 32.90; H, 2.21; Co, 16.14. Found: C, 33.20; H, 2.42; Co, 15.85. The ratio of C/Co calcd for $Co(C_5H_4F_3O_2)_2{\cdot}nH_2O$: 2.04. Found: 2.09.

$Co(F_6\text{-}acac)_2$. Reddish brown powder, yield 81%.

IR (KBr): ν/cm^{-1} 1645, 1534, 1483 and 1400.

MS (ESI^-): m/z 503.9269 (calcd for $[Co(C_5HF_6O_2)_2{\cdot}CH_3OH\text{-}H]^-$ 503.9277).

Anal. calcd for $Co(C_5HF_6O_2)_2$: C, 25.39; H, 0.43; Co, 12.46. Found: C, 26.65; H, 0.54; Co, 12.09. The ratio of C/Co calcd for $Co(C_5HF_6O_2)_2{\cdot}nH_2O$: 2.04. Found: 2.20.

Synthesis of [BuMIM]Br and [BuPy]Br

1-Butyl-3-methylimidazolium bromide (BuMIMBr) and 1-butylpyridin-1-ium bromide ([BuPy]Br) were synthesized as described.[31]

[BuMIM]Br. The synthesis of $[C_4MIM]Br$ was carried out in a 100 mL round-bottomed flask, which was immersed in a recirculating heated water bath and fitted with a reflux condenser. 1-Bromobutane (41.1 g, 0.3 mol) was dropped into *n*-methylimidazole (20.5 g, 0.25 mol) at 80 °C for 1 h. After the addition, the reaction mixture was stirred for another period of 4 h at 80 °C. The remaining 1-bromobutane was removed by heating the residue at 80 °C under high vacuum until the weight of the residue remained constant. ^1H NMR ($CDCl_3$): δ (ppm) 10.20 (s, 1H), 7.77 (s, 1H), 7.66 (s, 1H), 4.35–4.39 (t, 2H), 4.15 (s, 3H), 1.98–1.86 (m, 2H), 1.45–1.32 (m, 2H), 0.95–0.98 (t, 3H).

[BuPy]Br. The synthesis of [BuPy]Br was similar to that of $[C_4MIM]Br$. ^1H NMR ($CDCl_3$): δ (ppm) 9.26 (t, 2H), 8.37–8.34 (t, 1H), 7.95–7.93 (d, 2H), 4.73–4.67 (m, 2H), 1.78–1.73 (m, 2H), 1.12–1.09 (m, 2H), 0.68–0.62 (m, 3H).

The coupling reaction of CO_2 with epoxide

A typical procedure for the reaction of CO_2 with epoxide was carried out in a 25 mL Schlenk tube with a magnetic stir bar. For a typical run, the epoxide (40 mmol) and the catalyst (appropriate amount) were introduced into the tube and the tube was vacuum-sealed and then purged with CO_2 3 times. The tube which was connected to a balloon filled with CO_2 was then placed in a preheated water bath and allowed to stir (at 400 rpm) for a designated time frame. The product yields and selectivity were determined by GC analysis. Some typical products were analyzed by GC/MS.

The reaction of CO_2 with 1,2-propylene oxide was carried out in a 25 mL stainless steel autoclave. The operating pressure was maintained at 0.2 MPa during the reaction.

The capture and simultaneous conversion of CO_2 in a dilute CO_2 stream

The capture and conversion of CO_2 was carried out in a 25 mL glass flask with a magnetic stir bar and a low-temperature alcohol-cooled condenser. 1,2-Hexene oxide (20 mmol), $Co(acac)_2$ (0.1 mmol), and Bu_4NI (0.5 mmol) were introduced into the flask. The flask was vacuum-sealed and then purged with the dilute CO_2 stream (a gas mixture containing 10% v/v CO_2 and 90% v/v N_2) 3 times. Then the dilute CO_2 stream was bubbled through the reaction solution and the flask was placed in a preheated water bath and allowed to stir (at 400 rpm) for 4 h. The flow of the dilute CO_2 stream was 10 sccm.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (*a*) C. Martin, G. Fiorani and A. W. Kleij, *ACS Catal.*, 2015, **5**, 1353; (*b*) S. Dagorne and R. Wehmschulte, *ChemCatChem*, 2018, **10**, 2509; (*c*) S. Kumar, M. Y. Wani, C. T. Arranja, J. D. E. Silva, B. Avula and A. Sobral, *J. Mater. Chem. A*, 2015, **3**, 19615; (*d*) S. B. Wang and X. C. Wang, *Angew. Chem., Int. Ed.*, 2016, **55**, 2308; (*e*) J. W. Comerford, I. D. V. Ingram, M. North and X. Wu, *Green Chem.*, 2015, **17**, 1967; (*f*) R. R. Shaikh, S. Pornpraprom and V. D'Elia, *ACS Catal.*, 2018, **8**, 419; (*g*) M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing and C. Detrembleur, *Catal. Sci. Technol.*, 2017, **7**, 2651.

2 (*a*) W. L. Wong, P. H. Chan, Z. Y. Zhou, K. H. Lee, K. C. Cheung and K. Y. Wong, *ChemSusChem*, 2008, **1**, 67; (*b*) E. H. Lee, J. Y. Ahn, M. M. Dharman, D. W. Park, S. W. Park and I. Kim, *Catal. Today*, 2008, **131**, 130; (*c*) T. Chang, H. W. Jing, L. Jin and W. Y. Qiu, *J. Mol. Catal. A: Chem.*, 2007, **264**, 241; (*d*) W. N. Sit, S. M. Ng, K. Y. Kwong and C. P. Lau, *J. Org. Chem.*, 2005, **70**, 8583; (*e*) H. Z. Yang, Y. L. Gu, Y. Q. Deng and F. Shi, *Chem. Commun.*, 2002, **48**, 274; (*f*) V. Calo, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561.

3 (*a*) H. W. Jing and S. T. Nguyen, *J. Mol. Catal. A: Chem.*, 2007, **261**, 12; (*b*) K. Mori, Y. Mitani, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, *Chem. Commun.*, 2005, **51**, 3331; (*c*) Y. M. Shen, W. L. Duan and M. Shi, *Adv. Synth. Catal.*, 2003, **345**, 337; (*d*) H. Kawanami and Y. Ikushima, *Chem. Commun.*, 2000, **46**, 2089.

4 (*a*) S. S. Wu, X. W. Zhang, W. L. Dai, S. F. Yin, W. S. Li, Y. Q. Ren and C. T. Au, *Appl. Catal., A*, 2008, **341**, 106; (*b*) J. L. Song, Z. F. Zhang, B. X. Han, S. Q. Hu, W. J. Li and Y. Xie, *Green Chem.*, 2008, **10**, 1337; (*c*) H. S. Kim, J. J. Kim, H. N. Kwon, M. J. Chung, B. G. Lee and H. G. Jang, *J. Catal.*, 2002, **205**, 226.

5 (*a*) M. North and R. Pasquale, *Angew. Chem., Int. Ed.*, 2009, **48**, 29468; (*b*) X. B. Lu, Y. J. Zhang, K. Jin, L. M. Luo and H. Wang, *J. Catal.*, 2004, **227**, 537; (*c*) Z. W. Bu, G. Qin and S. K. Cao, *J. Mol. Catal. A: Chem.*, 2007, **277**, 35; (*d*) M. L. Man, K. C. Lam, W. N. Sit, S. M. Ng, Z. Y. Zhou, Z. Y. Lin and C. P. Lau, *Chem. – Eur. J.*, 2006, **12**, 1004; (*e*) D. J. Darensbourg, P. Ganguly and D. R. Billodeaux, *Organometallics*, 2004, **23**, 6025.

6 (*a*) B. Aguila, Q. Sun, X. Wang, E. O'Rourke, A. M. Al-Enizi, A. Nafady and S. Ma, *Angew. Chem., Int. Ed.*, 2018, **57**, 10107; (*b*) X. Y. Li, Y. Z. Li, Y. Yang, L. Hou, Y. Y. Wang and Z. Zhu, *Chem. Commun.*, 2017, **53**, 12970; (*c*) H. He, J. A. Perman, G. Zhu and S. Ma, *Small*, 2016, **12**, 6309; (*d*) B. Parmar, P. Patel, R. S. Pillai, R. K. Tak, R. I. Kureshy, N.-u. H. Khan and E. Suresh, *Inorg. Chem.*, 2019, **58**, 10084.

7 (*a*) H. H. Wang, L. Hou, Y. Z. Li, C. Y. Jiang, Y. Y. Wang and Z. Zhu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 17969; (*b*) D. Zhao, X. H. Liu, J. H. Guo, H. J. Xu, Y. Zhao, Y. Lu and W. Y. Sun, *Inorg. Chem.*, 2018, **57**, 2695; (*c*) Q. Yang, C. C. Yang, C. H. Lin and H. L. Jiang, *Angew. Chem., Int. Ed.*, 2019, **58**, 3511; (*d*) D. Liu, G. Li, J. Liu, Y. Wei and H. Guo, *ACS Appl. Mater. Interfaces*, 2018, **10**, 22119.

8 (*a*) L. G. Ding, B. J. Yao, W. L. Jiang, J. T. Li, Q. J. Fu, Y. A. Li, Z. H. Liu, J. P. Ma and Y. B. Dong, *Inorg. Chem.*, 2017, **56**, 2337; (*b*) M. Liu, J. Lan, L. Liang, J. Sun and M. Arai, *J. Catal.*, 2017, **347**, 138; (*c*) M. Ding and H. L. Jiang, *ACS Catal.*, 2018, **8**, 3194; (*d*) K. Hu, Y. Tang, J. Cui, Q. Gong, C. Hu, S. Wang, K. Dong, X. Meng, Q. Sun and F.-S. Xiao, *Chem. Commun.*, 2019, **55**, 9180.

9 (*a*) T. T. Liu, J. Liang, R. Xu, Y. B. Huang and R. Cao, *Chem. Commun.*, 2019, **55**, 4063; (*b*) K. A. Andrea, E. D. Butler, T. R. Brown, T. S. Anderson, D. Jagota, C. Rose, E. M. Lee, S. D. Goulding, J. N. Murphy, F. M. Kerton and C. M. Kozak, *Inorg. Chem.*, 2019, **58**, 11231; (*c*) Y. Kim, K. Hyun, D. Ahn, R. Kim, M. H. Park and Y. Kim, *ChemSusChem*, 2019, **12**, 4211; (*d*) F. de la Cruz-Martinez, J. Martinez, M. A. Gaona, J. Fernandez-Baeza, L. F. Sanchez-Barba, A. M. Rodriguez, J. A. Castro-Osma, A. Otero and A. Lara-Sanchez, *ACS Sustainable Chem. Eng.*, 2018, **6**, 5322; (*e*) E. Y. Seong, J. H. Kim, N. H. Kim, K.-H. Ahn and E. J. Kang, *ChemSusChem*, 2019, **12**, 409; (*f*) M. Cozzolino, V. Leo, C. Tedesco, M. Mazzeo and M. Lamberti, *Dalton Trans.*, 2018, **47**, 13229.

10 X. Wu, C. Chen, Z. Guo, M. North and A. C. Whitwood, *ACS Catal.*, 2019, **9**, 1895.

11 A. Samikannu, L. J. Konwar, P. Maki-Arvela and J. P. Mikkola, *Appl. Catal., B*, 2019, **241**, 41.

12 Z. Zhou, C. He, J. H. Xiu, L. Yang and C. Y. Duan, *J. Am. Chem. Soc.*, 2015, **137**, 15066.

13 N. Mac Dowell, P. S. Fennell, N. Shah and G. C. Maitland, *Nat. Clim. Change*, 2017, **7**, 243.

14 M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2014, **114**, 1709.

15 (*a*) G. Shi, K. Chen, Y. Wang, H. Li and C. Wang, *ACS Sustainable Chem. Eng.*, 2018, **6**, 5760; (*b*) K. H. Chen, G. L. Shi, W. D. Zhang, H. R. Li and C. M. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 14198; (*c*) X. Y. Luo, K. H. Chen, H. R. Li and C. M. Wang, *Int. J. Hydrogen Energy*, 2016, **41**, 9175; (*d*) K. Chen, G. Shi, R. Dao, K. Mei, X. Zhou, H. Li and C. Wang, *Chem. Commun.*, 2016, **52**, 7830.

16 (*a*) M. Hong, Y. Kim, H. Kim, H. J. Cho, M. H. Baik and Y. Kim, *J. Org. Chem.*, 2018, **83**, 9370; (*b*) A. Rostami, M. Mahmoodabadi, A. H. Ebrahimi, H. Khosravi and A. Al-Harrasi, *ChemSusChem*, 2018, **11**, 4262; (*c*) R. K. Tak, P. Patel, S. Subramanian, R. I. Kureshy and N. U. H. Khan, *ACS Sustainable Chem. Eng.*, 2018, **6**, 11200; (*d*) N. Liu, Y. F. Xie, C. Wang, S. J. Li, D. H. Wei, M. Li and B. Dai, *ACS Catal.*, 2018, **8**, 9945; (*e*) D. X. Ma, K. Liu, J. X. Li and Z. Shi, *ACS Sustainable Chem. Eng.*, 2018, **6**, 15050.

17 Y. Fan, M. Tiffner, J. Schorgenhumer, R. Robiette, M. Waser and S. R. Kass, *J. Org. Chem.*, 2018, **83**, 9991.

18 B. Y. Liu, F. X. Wei, J. J. Zhao and Y. Y. Wang, *RSC Adv.*, 2013, **3**, 2470.

19 (*a*) G. Bresciani, M. Bortoluzzi, F. Marchetti and G. Pampaloni, *ChemSusChem*, 2018, **11**, 2737; (*b*) L. Wang, R. L. Zhang, Q. X. Han, C. Xu, W. M. Chen, H. Yang, G. S. Gao, W. W. Qin and W. S. Liu, *Green Chem.*, 2018, **20**, 5311; (*c*) Z. F. Dai, Q. Sun, X. L. Liu, L. P. Guo, J. X. Li, S. X. Pan, C. Q. Bian, L. Wang, X. Hu, X. J. Meng, L. H. Zhao, F. Deng and F. S. Xiao, *ChemSusChem*, 2017, **10**, 1186; (*d*) S. Ghosh, P. Bhanja, N. Salam, R. Khatun, A. Bhaumik and S. M. Islam, *Catal. Today*, 2018, **309**, 253.

20 (*a*) J. Melendez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323; (*b*) W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem. – Eur. J.*, 2010, **16**, 6828; (*c*) A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212; (*d*) P. A. Carvalho, J. W. Comerford, K. J. Lamb, M. North and P. S. Reiss, *Adv. Synth. Catal.*, 2019, **361**, 345; (*e*) Y. Chen, R. C. Luo, Q. H. Xu, W. Y. Zhang, X. T. Zhou and H. B. Ji, *ChemCatChem*, 2017, **9**, 767; (*f*) Z. A. K. Khattak, H. A. Younus, N. Ahmad, H. Ullah, S. Suleman, M. S. Hossain, M. Elkadig and F. Verpoort, *Chem. Commun.*, 2019, **55**, 8274.

21 (*a*) G. Ji, Z. Yang, H. Zhang, Y. Zhao, B. Yu, Z. Ma and Z. Liu, *Angew. Chem., Int. Ed.*, 2016, **55**, 9685; (*b*) P. Patel, B. Parmar, R. I. Kureshy, N. U. Khan and E. Suresh, *ChemCatChem*, 2018, **10**, 2401.

22 R. L. Paddock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001, **123**, 11498.

23 (*a*) L. P. Guo, C. M. Wang, W. J. Zhao, H. R. Li, W. L. Sun and Z. Q. Shen, *Dalton Trans.*, 2009, 5406; (*b*) Y. Wang and D. J. Darensbourg, *Coord. Chem. Rev.*, 2018, **372**, 85; (*c*) K. Chen, G. Shi, H. Li, C. Wang and D. J. Darensbourg, *Macromolecules*, 2018, **51**, 6057.

24 T. V. Deepthi and P. Venugopalan, *Inorg. Chim. Acta*, 2016, **450**, 243.

25 (*a*) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, 1960, **82**, 2979; (*b*) G. S. Hammond, C. H. S. Wu and D. C. Nonhebel, *Inorg. Chem.*, 1963, **2**, 73.

26 T. Bok, E. K. Noh and B. Y. Lee, *Bull. Korean Chem. Soc.*, 2006, **27**, 1171.

27 C. Cohen, C. Thomas, K. Peretti, E. Lobkovsky and G. Coates, *Dalton Trans.*, 2006, 237.

28 (*a*) K. B. Hansen, J. L. Leighton and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1996, **118**, 10924; (*b*) D. J. Darensbourg, P. Ganguly and W. Choi, *Inorg. Chem.*, 2006, **45**, 3831; (*c*) M. H. Chisholm and Z. P. Zhou, *J. Am. Chem. Soc.*, 2004, **126**, 11030; (*d*) D. J. Darensbourg and R. M. Mackiewicz, *J. Am. Chem. Soc.*, 2005, **127**, 14026; (*e*) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388; (*f*) X. B. Lu, X. J. Feng and R. He, *Appl. Catal., A*, 2002, **234**, 25.

29 (*a*) X. B. Lu, Y. J. Zhang, K. Jin, L. M. Luo and H. Wang, *J. Catal.*, 2004, **227**, 537; (*b*) J. L. He, T. B. Wu, Z. F. Zhang, K. L. Ding, B. X. Han, Y. Xie, T. Jiang and Z. M. Liu, *Chem. – Eur. J.*, 2007, **13**, 6992.

30 L. P. Guo, C. M. Wang, X. Y. Luo, G. K. Cui and H. R. Li, *Chem. Commun.*, 2010, **46**, 5960.

31 (*a*) C. M. Wang, L. P. Guo, H. R. Li, Y. Wang, J. Y. Weng and L. H. Wu, *Green Chem.*, 2006, **8**, 603; (*b*) X. Q. Xu, C. M. Wang, H. R. Li, Y. Wang, W. L. Sun and Z. Q. Shen, *Polymer*, 2007, **48**, 3921.