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Carboxylation of *N*-heterocyclic carbenes with carbon dioxide and their tantalum complexes with high oxidation

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ABSTRACT

Carboxylation of two free *N*-heterocyclic carbenes (NHCs) 1,3-dimesitylimidazol-2-yliden (IMes) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) with CO_2 led to two adducts [IMes:CO_2] and [IPr:CO_2], which were further reacted with $TaCl_5$ to afford the finial metal complexes [(IMes:CO_2)$TaCl_5$] (**1**) and [$(IPr:CO_2)_2TaCl_3$][$TaCl_6$]$_2$ (**2**), respectively. NMR spectroscopy, elemental analysis and single crystal X-ray diffraction proved that the carboxylate groups were retained in complexes **1** and **2**. Crystallography revealed that the metal centers in complexes **1** and **2** adopted the distorted octahedral and pentagonal bipyramidal geometries, respectively, in which complex **1** was constructed with one [IMes:CO_2] adducts, while complex **2** with two [IPr:CO_2] adducts. In addition, the catalytic properties of complexes **1**–**2** on the cycloaddition between CO_2 and propylene oxide to synthesize cyclic carbonate at the mild condition were investigated.

1. Introduction

N-heterocyclic carbenes (NHCs) as strong σ electron donors have attracted intense interest due to their unique structure and chemical properties [1–3]. Since the first stable NHC was isolated by Arduengo in 1991 [4], using these free NHCs as ligands for coordination to various metals has attracted tremendous attention because they often enhance the performance and selectivity in organometallic and catalytic chemistry [5–10].

It is known the metal NHCs complexes have been primarily focused on the late transition metals with low and medium valences. Conversely, the early transition metal NHC complexes [11–20], particularly the group 5 NHC metal complexes with high oxidation are scarce [21–24]. The low popularity may origin from the fact that the early metals have few d electrons, always in high valences, strong oxophilic property and extreme moisture sensitivity. Until now only Hollis [21] and Fryzuk [22] reported the chelating pincers NHC–Ta complexes.

Recently, we focused our interesting in the reaction of two free NHCs 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) and 1,3-dimesitylimidazol-2-yliden (IMes) with $TaCl_5$, we isolated a neutral NHC complex [(IPr)$TaCl_5$] and an ionic NHC complex [$(IMes)_2TaCl_4$][$TaCl_6$] [see ESI]. As our continued work on the catalytic properties of both complexes in the cycloaddition reaction between CO_2 and propylene oxide to synthesize cyclic carbonate, the adduct [NHC:CO_2] was considered to be the intermediate formed by inserting of CO_2 in the middle of complex [(IPr)$TaCl_5$] in the catalytic circle. This proposal mechanism was originated from the facts that the neutral NHCs are highly nucleophilic and can be reacted with CO_2 to form zwitterionic imidazolium carboxylate biphasic systems [NHC:CO_2] [25–30], as well as CO_2 group can be released from the adducts during the coordination [31–39]. But when we carried out the reaction of CO_2 with NHC complexes [(IPr)$TaCl_5$] and [$(IMes)_2TaCl_4$][$TaCl_6$] in NMR tubes, we did not find the sign of carboxylate carbon in ^{13}C NMR spectra.

On the other hand, reactions of free carbenes IMes and IPr with CO_2 gave the stable adducts [NHCs:CO_2], which were further reacted with $TaCl_5$ to lead to two metal complexes [(IMes:CO_2)$TaCl_5$] (**1**) and [$(IPr:CO_2)_2TaCl_3$][$TaCl_6$]$_2$ (**2**), respectively. In both complexes the carboxylates were not decomposed from adducts [NHC:CO_2], they are only the [(NHC:CO_2)Ta] complexes. These results also proved adducts [NHC:CO_2] are not the intermediates in the catalytic reaction of CO_2 with propylene oxide by complexes [(IPr)$TaCl_5$] and [$(IMes)_2TaCl_4$][$TaCl_6$]. Herein we reported the synthesis, characterization, crystal structures and catalytic properties of complexes **1** and **2**.

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2. Experimental

2.1. Instrument and materials

All manipulations were performed under an atmosphere of dry oxygen-free argon or nitrogen by means of standard Schlenk or glove box techniques. Solvents were freshly distilled by using appropriate drying agents prior to use. Deuterium reagents were purchased from Cambridge Isotopes and dried over activated 4 Å molecular sieves and stored under N_2. $TaCl_5$ was purchased from Alfa Aesar and freshly sublimed prior to use. CO_2 (purity ≥ 99.999%) was dried by going through anhydrous $CaCl_2$ and activated 4 Å molecular sieves. NMR-scale reactions were conducted in Teflon-valve-sealed J. Young-type NMR tubes on a DD2 400MR (Agilent) or a Bruker 600 Avance III spectrometer with TMS as internal standard. Elemental analysis was performed in the Analytical Laboratory of Shanghai Institute of Organic Chemistry. The free NHCs IMes and IPr were prepared according to the literature procedures [32].

2.2. Synthesis

2.2.1. Adduct [IMes:CO_2]

To a solution of free carbene IMes (0.6 g, 2 mmol) in THF (20 mL) was bubbled with CO_2 to give a white precipitate immediately. After the reaction was being stirred for 5 h at room temperature, the mixture was filtered. The obtained white solid was washed with THF for 3 times, and dried in vacuum. Yield: 0.45 g, 65%. IR: 1672 cm^{-1} (C═O). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.10 (s, 2H, NCH═), 7.04 (s, 4H, *m*-C_6H_2), 2.36 (s, 6H, *p*-CH_3), 2.17 (s, 12H, *o*-CH_3). ^{13}C NMR (DMSO-*d*$_6$, ppm): δ 16.8 (*ortho*-CH_3), 20.6 (*para*-CH_3), 121.6, 128.8 (*meta*-CH), 131.9, 134.6, 139.5, 146.4, 152.8 (CO_2).

2.2.2. Adduct [IPr:CO_2]

According to the similar procedures to synthesize [IMes:CO_2] by charging CO_2 into the solution of free carbene IPr (0.66 g, 2 mmol) in THF (20 mL) gave the white solid. Yield: 0.87, 68%. IR: 1676 cm^{-1} (C═O). ^1H NMR (601 MHz, CD_2Cl_2): δ 7.53 (t, *J* = 7.8 Hz, 1H, *p*-C_6H_3), 7.33 (d, *J* = 7.8 Hz, 2H, *m*-C_6H_3), 7.15 (s, 1H, NC*H*═), 2.52 (hept, *J* = 6.9 Hz, 2H, C*H*), 1.27 (d, *J* = 6.8 Hz, 6H, CH_3), 1.21 (d, *J* = 6.9 Hz, 6H, CH_3). ^{13}C NMR (CD_2Cl_2, ppm) δ: 23.3 (CH_3), 24.2 (CH_3), 29.3 ($(CH_3)_2CH$), 122.6, 124.3, 130.9, 132.6, 145.1, 147.8, 152.3 (CO_2).

2.2.3. Complex [(IMes:CO_2)$TaCl_5$]·2CH_2Cl_2 (**1**)

Into a cold CH_2Cl_2 (20 mL, −60 °C), solids [IMes:CO_2] (0.35 g, 1 mmol) and $TaCl_5$ (0.54 g, 1.5 mmol) were added. After the reaction was stirred for 30 min, the temperature was raised to 0 °C. The reactions were kept stirring at this temperature for one night and then filtered. The filtrate was concentrated and placed at −30 °C to give light yellow crystals in two days. Yield: 0.50 g, 70%. IR: 1686 cm^{-1} (C═O). Anal. cacld for $C_{22}H_{24}Cl_5N_2O_2Ta$(%): C, 37.39; H, 3.42; N, 3.96. Found(%): C, 37.47; H, 3.56; N, 3.91. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.46 (s, 2H, NCH═), 7.10 (s, 4H, *m*-C_6H_2), 2.37 (s, 6H, *p*-CH_3), 2.15 (s, 12H, *o*-CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 151.0 (C═O), 142.3 (*N*–C_6H_2), 134.1 (*p*-C_6H_2), 131.2 (*m*-C_6H_2), 130.5 (*o*-C_6H_2), 125.4 (NCH═), 21.4 (*p*-CH_3), 17.7 (*o*-CH_3).

2.2.4. Complex [(IPr:CO_2)$_2$$TaCl_3$][$TaCl_6$]$_2$ (**2**)

According to the similar procedures to synthesize complex **1** starting from [IPr:CO_2] (0.43 g, 1.0 mmol) and $TaCl_5$ (0.53 g, 1.5 mmol) at −40 °C gave yellow solid. Yield: (0.54 g, 56%). IR: 1698 cm^{-1} (C═O). Anal. calcd. for $C_{56}H_{72}Cl_{15}N_4O_4Ta_3$(%): C, 34.60; H, 3.94; N, 2.88. Found:C, 34.61; H, 3.78; N, 2.91. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.71 (s, 2H, NC*H*═), 7.63 (t, *J* = 7.7 Hz, 2H, *p*-C$_6H_3$), 7.43 (d, *J* = 7.7 Hz, 4H, *m*-C$_6H_3$), 2.50–2.28 (m, 4H, C*H*), 1.32 (d, *J* = 6.5 Hz, 12H, CH_3), 1.25 (d, *J* = 6.8 Hz, 12H, CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 144.31, 132.71, 131.02, 127.93, 127.05, 126.22, 125.69, 30.03, 24.93, 23.50.

2.3. X-ray crystallography

X-ray diffraction data for single crystals of complexes **1**–**2** were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å). The structures were solved by the direct methods routines in the *SHELXS* program and refined on F^2 in *SHELXL* [40]. In structure of **2**, four chlorine atoms in the equatorial position of one $[TaCl_6]^-$ anion were severely disordered, and were split into two fragments with an occupancy factors of 0.47/0.53. In crystals **1**–**2**, except that the carbon atoms in complex **2** were refined isotropically and other non-hydrogen atoms were modeled anisotropically. All hydrogen atoms were placed in idealized positions and treated as riding atoms. Details of the data collection and refinement are given in Table 1. CCDC numbers for compounds **1**–**2** are 1413431 and 938868, respectively.

2.4. Typical procedures for the synthesis of propylene carbonate

Into a Schlenk tube was charged with catalyst (0.1 mmol), 1,2-propylene oxide (1 mmol), CH_2Cl_2 (2 mL) and 1 MPa CO_2. After being stirred for 10 h at 20 °C, the reaction was taken to NMR detection. ^1H NMR (600 MHz, CD_2Cl_2): δ 4.83 (m, *J* = 7.4, 6.3 Hz, 1H, C*H*), 4.53 (dd, *J* = 8.4, 7.7 Hz, 1H, CH_2), 4.00 (dd, *J* = 8.4, 7.3 Hz, 1H, CH_2), 1.44 (d, *J* = 6.3 Hz, 3H, CH_3).

3. Results and discussion

3.1. Synthesis and characterization

The free *N*-heterocyclic carbenes IMes and IPr were synthesized according to the literature [12] through the simply deprotonating of the corresponding imidazole hydrochloride salts IMesHCl and IPrHCl with potassium *tert*-butoxide. Carboxylation of IMes, or IPr with atmospheric CO_2 (1 atm) afforded the corresponding

Table 1
Crystallographic data for complexes **1**–**2**.

Complexes	**1**	**2**
Chemical formula	$C_{24}H_{28}Cl_9N_2O_2Ta$	$C_{56}H_{72}Cl_{15}N_4O_4Ta_3$
Fw	876.48	1939.78
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	P-1
a (Å)	11.3376(7)	14.160(4)
b (Å)	13.6268(10)	14.349(4)
c (Å)	11.6256(7)	19.955(6)
α (°)	90	71.955(4)
β (°)	113.059(2)	89.663(4)
γ (°)	90	79.704(4)
V (Å^3)	1652.59(19)	3787.8(19)
Z	2	2
D_{calc} (g·cm^{-3})	1.761	1.701
F(000)	856	1884
μ (Mo Kα, mm^{-1})	4.078	4.893
Total no. of reflns.	13,824	28,041
θ_{max}	27.44	26.87
No. of unique reflns.	5552 [$R_{(int)}$ = 0.0173]	14,254 [$R_{(int)}$ = 0.1383]
No. of observed refns	7546	16,322
No. of variables	343	776
R_1, wR_2 (obsd data)	0.0302, 0.0836	0.0832, 0.2047
R_1, wR_2 (all data)	0.0313, 0.0926	0.1461, 0.2384
GOF, S	1.125	1.005
Max./min. peak (e. Å^{-3})	1.436, −1.170	3.683, −3.743