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 CO₂ led to two adducts [IMes:CO₂] and [IPr:CO₂], which were further reacted with TaCl₅ to afford the final metal complexes [(IMes:CO₂)TaCl₅] (**1**) and [(IPr:CO₂)₂TaCl₃][TaCl₆]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:CO₂] adducts, while complex **2** with two [IPr:CO₂] adducts. **In addition, the catalytic properties of complexes 1–2 on the**

cycloaddition between CO₂ and propylene oxide to synthesize cyclic carbonate at the mild condition were investigated.

Keywords: *N*-heterocyclic carbene; Tantalum; Carboxylation; Crystal structure; Carbon dioxide fixation

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 TaCl₅, we isolated a neutral NHC complex [(IPr)TaCl₅] and an ionic NHC complex [(IMes)₂TaCl₄][TaCl₆] [see ESI]. As our continued work on the catalytic properties of both complexes in the cycloaddition reaction between CO₂ and propylene oxide to synthesize cyclic carbonate, the adduct [NHC:CO₂] was considered to be the intermediate formed by inserting of CO₂ in the middle of complex [(IPr)TaCl₅] in the catalytic circle. This proposal mechanism was originated from the facts that the neutral NHCs are highly nucleophilic and can be reacted with CO₂ to form zwitterionic imidazolium carboxylate biphasic systems [NHC:CO₂] [25-30], as well as CO₂ group can be released from the adducts during the coordination[31-39]. But when we carried out the reaction of CO₂ with NHC complexes [(IPr)TaCl₅] and [(IMes)₂TaCl₄][TaCl₆] in NMR tubes, we did not find the sign of carboxylate carbon in ¹³C NMR spectra.

On the other hand, reactions of free carbenes IMes and IPr with CO₂ gave the stable adducts [NHCs:CO₂], which were further reacted with TaCl₅ to lead to two metal complexes [(IMes:CO₂)TaCl₅] (**1**) and [(IPr:CO₂)₂TaCl₃][TaCl₆]₂ (**2**), respectively. In both complexes the carboxylates were not decomposed from adducts [NHC:CO₂], they are only the [(NHC:CO₂)Ta] complexes. These results also proved adducts [NHC:CO₂] are not the intermediates in the catalytic reaction of CO₂ with propylene

oxide by complexes [(IPr)TaCl₅] and [(IMes)₂TaCl₄][TaCl₆]. Herein we reported the synthesis, characterization, crystal structures and catalytic properties of complexes **1** and **2**.

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 N₂. TaCl₅ was purchased from Alfa Aesar and freshly sublimed prior to use. CO₂ (purity ≥ 99.999%) was dried by going through anhydrous CaCl₂ 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:CO₂]

To a solution of free carbene IMes (0.6 g, 2 mmol) in THF (20 mL) was bubbled with CO₂ 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, CD₂Cl₂): δ 7.10 (s, 2H, NCH=), 7.04 (s, 4H, *m*-C₆H₂), 2.36 (s, 6H, *p*-CH₃), 2.17 (s, 12H, *o*-CH₃). ¹³C NMR (DMSO-d₆, ppm): δ 16.8 (ortho-CH₃), 20.6 (para-CH₃), 121.6, 128.8 (meta-CH), 131.9, 134.6, 139.5, 146.4, 152.8 (CO₂).

2.2.2 Adduct [IPr:CO₂]

According to the similar procedures to synthesize [IMes:CO₂] by charging CO₂ 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, CD₂Cl₂): δ 7.53 (t, *J* = 7.8 Hz, 1H, *p*-C₆H₃), 7.33 (d, *J* = 7.8 Hz, 2H, *m*-C₆H₃), 7.15 (s, 1H, NCH=), 2.52 (hept, *J* = 6.9 Hz, 2H, CH), 1.27 (d, *J* = 6.8 Hz, 6H, CH₃), 1.21 (d, *J* = 6.9 Hz, 6H, CH₃). ¹³C NMR (CD₂Cl₂, ppm) δ: 23.3 (CH₃), 24.2 (CH₃), 29.3 ((CH₃)₂CH), 122.6, 124.3, 130.9, 132.6, 145.1, 147.8, 152.3 (CO₂).

2.2.3 Complex [(IMes:CO₂)TaCl₅] $\cdot$ 2CH₂Cl₂ (**1**)

Into a cold CH₂Cl₂ (20 mL, -60°C), solids [IMes:CO₂] (0.35 g, 1 mmol) and TaCl₅ (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. calcd for C₂₂H₂₄Cl₅N₂O₂Ta(%): C, 37.39; H, 3.42; N, 3.96. Found(%): C, 37.47; H, 3.56; N, 3.91. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.46 (s, 2H, NCH=), 7.10 (s, 4H, *m*-C₆H₂), 2.37 (s, 6H, *p*-CH₃), 2.15 (s, 12H, *o*-CH₃). ¹³C NMR (101 MHz, CD₂Cl₂): δ 151.0 (C=O), 142.3 (*N*-C₆H₂), 134.1 (*p*-C₆H₂), 131.2 (*m*-C₆H₂), 130.5 (*o*-C₆H₂), 125.4 (NCH=), 21.4 (*p*-CH₃), 17.7 (*o*-CH₃).

2.2.4 Complex [(IPr:CO₂)₂TaCl₃][TaCl₆]₂ (**2**)

According to the similar procedures to **synthesize** complex **1** starting from [IPr:CO₂] (0.43 g, 1.0 mmol) and TaCl₅ (0.53 g, 1.5 mmol) at -40°C gave yellow solid. Yield: (0.54g, 56%). IR: 1698 cm⁻¹ (C=O). Anal. calcd. for C₅₆H₇₂Cl₁₅N₄O₄Ta₃(%): C, 34.60; H, 3.94; N, 2.88. Found: C, 34.61; H, 3.78; N, 2.91. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.71 (s, 2H, NCH=), 7.63 (t, *J* = 7.7 Hz, 2H, *p*-C₆H₃), 7.43 (d, *J* = 7.7 Hz, 4H, *m*-C₆H₃), 2.50–2.28 (m, 4H, CH), 1.32 (d, *J* = 6.5 Hz, 12H, CH₃), 1.25 (d, *J* = 6.8 Hz, 12H, CH₃). ¹³C NMR (101 MHz, CD₂Cl₂): 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 K α 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 [TaCl₆][−] 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.

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

Complexes	1	2
Chemical formula	C ₂₄ H ₂₈ Cl ₉ N ₂ O ₂ Ta	C ₅₆ H ₇₂ Cl ₁₅ N ₄ O ₄ Ta 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 K α , mm ⁻¹)	4.078	4.893
Total no. of reflns.	13824	28041
θ_{max}	27.44	26.87
No. of unique reflns.	5552 [$R_{\text{(int)}} = 0.0173$]	14254 [$R_{\text{(int)}} = 0.1383$]
No. of observed refns	7546	16322
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

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), CH₂Cl₂ (2 mL) and 1 MPa CO₂. After being stirred for 10 h at 20 °C, the reaction was taken to NMR detection. ¹H NMR (600 MHz, CD₂Cl₂): δ 4.83 (m, *J* = 7.4, 6.3 Hz, 1H, *CH*), 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 literatures[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 CO₂ (1 atm) afforded the corresponding zwitterionic imidazolium carboxylates [IMes:CO₂] and [IPr:CO₂] with quantitative yields, Scheme 1. The free carbenes IMes and IPr were unstable, and only can be kept at the low temperature and in an inert atmosphere. But after their combination with CO₂, the adducts [IMes:CO₂] and [IPr:CO₂] became stable, and even did not decompose in open air.

Scheme 1 the synthesis routes for complexes **1–2**.

As shown in Scheme 1, reaction of $[\text{IMes}:\text{CO}_2]$ and $[\text{IPr}:\text{CO}_2]$ with TaCl_5 in CH_2Cl_2 give two complexes $[(\text{IMes}:\text{CO}_2)\text{TaCl}_5] \cdot 2\text{CH}_2\text{Cl}_2$ (**1**) and $[(\text{IPr}:\text{CO}_2)_2\text{TaCl}_3][\text{TaCl}_6]_2$ (**2**), respectively, in which the carboxylate group did not release from $[\text{NHC}:\text{CO}_2]$ adducts. Complexes **1–2** are stable and can be kept for over 1 month without decomposition at room temperature under an argon atmosphere. In addition, we conducted the inserted reactions of CO_2 into NHC-Ta complexes $[(\text{IPr})\text{TaCl}_5]$ and $[(\text{IMes})_2\text{TaCl}_4][\text{TaCl}_6]$ in Teflon-valve-sealed J. Young-type NMR tubes, but did not observe the new sign of carboxylate carbon in ^{13}C NMR spectra.

In IR spectra, the strong absorption bands at $1672, 1676 \text{ cm}^{-1}$ in $[\text{IMes}:\text{CO}_2]$ and $[\text{IPr}:\text{CO}_2]$ which are belonged to the $\text{C}=\text{O}$ asymmetric stretching vibrations were red

shifted to 1686, 1698 cm^{-1} in complexes **1** and **2**. From the ^1H NMR spectra it can be seen that the protons of the imidazolyl ring in adducts $[\text{IMes}:\text{CO}_2]$ and $[\text{IPr}:\text{CO}_2]$ were observed as a singlet resonance at 7.10 and 7.15 ppm, which have low-field shifted to 7.46 and 7.71 ppm in complexes **1** and **2**. This is because the electron density in imidazole was reduced after the ligands $[\text{IMes}:\text{CO}_2]$ and $[\text{IPr}:\text{CO}_2]$ being coordinated to TaCl_5 . In ^{13}C NMR spectra the free carbene $[\text{IMes}]$ and $[\text{IPr}]$ showed carbenic carbon resonance at 220 and 244 ppm, which have clear up-field shift on the bonding to a relevant Lewis acid CO_2 , indicating their chemical shifts were much affected by the nature of the Lewis acid. To be noted, in complexes **1** and **2**, the signals attributed to the carboxylate carbon were observed at 151 and 144 ppm, which were less affected compared with those in adducts $[\text{IMes}:\text{CO}_2]$ and $[\text{IPr}:\text{CO}_2]$.

3.2 Structural analysis

Compound **1** crystallizes in the monoclinic system with a space group of $P2_1$ and the asymmetric unit contains a neutral $[(\text{IMes}:\text{CO}_2)\text{TaCl}_5]$ molecule, and two CH_2Cl_2 solvated molecules. The metal centre in **1** chose a distorted octahedral geometry coordinated by five chlorine atoms and one oxygen atom of CO_2 , in which O(1) and Cl(4) atoms occupied the axis position with the angle $\angle\text{O}(1)\text{--Nb}(1)\text{--Cl}(4) = 176.68(14)^\circ$, and others occupied the equatorial position, Figure 1. As shown in Table 2, the bond length of O(1)–C(22) in CO_2 group is at 1.328(8) Å which is longer than the other at 1.200(8) Å. The unequivalent of C–O bond distances indicated that the

negative charge was not equally distributed between the central carbon and the two oxygen atoms, consistent with only one oxygen atom in a single carboxylate group being coordinated to Ta metal. In contrast, the bond lengths between the carbene carbon and nitrogen atoms are comparable to each other (1.346(8) Å vs. 1.340(8) Å) which suggested the delocalization of the positive charge in imidazole plane. The Ta–Cl(4) bond length at 2.3061(17) Å is shorter than the others, which is caused by John-Teller effect. The Ta(1)–O(1) bond length at 2.028(5) Å is common in the analogous Ta–O complexes[23].

Figure 1 the crystal structure of complex **1**.

Table 2 bond lengths (Å) and angles (°) for complex **1**.

Ta(1)–O(1)	2.028(5)	Ta(1)–Cl(4)	2.3061(17)
Ta(1)–Cl(1)	2.3245(17)	Ta(1)–Cl(5)	2.3455(15)
Ta(1)–Cl(3)	2.3449(17)	Ta(1)–Cl(2)	2.3524(19)

O(1)-C(22)	1.328(8)	O(2)-C(22)	1.200(8)
N(1)-C(19)	1.346(8)	N(2)-C(19)	1.340(8)
O(1)-Ta(1)-Cl(4)	176.68(14)	O(1)-Ta(1)-Cl(1)	86.66(14)
Cl(4)-Ta(1)-Cl(1)	90.97(6)	O(1)-Ta(1)-Cl(5)	86.89(13)
Cl(4)-Ta(1)-Cl(5)	90.91(6)	Cl(1)-Ta(1)-Cl(5)	92.79(6)
O(1)-Ta(1)-Cl(3)	89.12(14)	Cl(4)-Ta(1)-Cl(3)	93.18(6)
Cl(1)-Ta(1)-Cl(3)	89.34(7)	Cl(5)-Ta(1)-Cl(3)	175.36(7)
O(1)-Ta(1)-Cl(2)	89.17(14)	Cl(4)-Ta(1)-Cl(2)	93.28(7)
Cl(1)-Ta(1)-Cl(2)	175.27(7)	Cl(5)-Ta(1)-Cl(2)	89.21(7)
Cl(3)-Ta(1)-Cl(2)	88.36(8)	O(2)-C(22)-O(1)	125.8(6)

Compound **2** crystallizes in the triclinic system with a space group of *P*-1 and the asymmetric unit contains a [(IPr:CO₂)₂TaCl₃]²⁺ cation, and two [TaCl₆][−] anions. The metal centre in **2** chose a distorted pentagonal bipyramidal geometry coordinated by three chlorine atoms and four oxygen atoms of two carboxylate groups, in which the four O atoms and Cl(3) occupied the equatorial position and the other two Cl atoms occupied the axis position ($\angle\text{Cl}(1)\text{--Ta}(1)\text{--Cl}(2) = 170.35(15)^\circ$), Figure 2. As shown in Table 3, both pairs of carbene C–N bond distances were found to be identical, but were significantly different from one another in the neutral [IPr:CO₂] adduct[32], which is consistent with the formation of a zwitterionic imidazolium carboxylate and loss of the some carbene character at the carbon atom. Also the near equivalent C–O bond distances in complex **2** indicated that the negative charge was equally distributed

between the central carbon and the two oxygen atoms, yet are elongated with respect to uncoordinated [IPr:CO₂]. Obviously, there appeared to be some delocalization of the carboxylate charge into the imidazole ring as their planes were coplanar to each other. At last, the Ta–Cl bond lengths in the axis directions are longer than that in equatorial position, but all are shorter than those in complex **1**.

Figure 2 the crystal structure of cation [(IPr:CO₂)₂TaCl₃]²⁺ of complex **2**.

Table 3 bond lengths (Å) and angles (°) for complex **2**.

Ta(1)-O(1)	2.131(8)	Ta(1)-Cl(3)	2.279(4)
Ta(1)-O(4)	2.150(8)	Ta(1)-Cl(1)	2.300(4)
Ta(1)-O(3)	2.169(8)	Ta(1)-Cl(2)	2.318(4)

Ta(1)-O(2)	2.194(8)	Ta(1)-C(44)	2.538(12)
Ta(1)-C(16)	2.542(11)	C(16)-O(1)	1.278(15)
C(16)-O(2)	1.260(14)	C(44)-O(3)	1.258(13)
N(1)-C(15)	1.342(16)	N(2)-C(15)	1.337(17)
N(3)-C(43)	1.364(15)	N(4)-C(43)	1.360(16)
C(44)-O(4)	1.248(14)	O(1)-Ta(1)-O(4)	162.2(3)
O(1)-Ta(1)-O(3)	138.6(3)	O(4)-Ta(1)-O(3)	59.1(3)
O(1)-Ta(1)-O(2)	59.9(3)	O(4)-Ta(1)-O(2)	137.9(3)
O(3)-Ta(1)-O(2)	78.8(3)	O(1)-Ta(1)-Cl(3)	81.0(2)
O(4)-Ta(1)-Cl(3)	81.2(3)	O(3)-Ta(1)-Cl(3)	140.4(2)
O(2)-Ta(1)-Cl(3)	140.8(2)	O(1)-Ta(1)-Cl(1)	91.3(3)
O(4)-Ta(1)-Cl(1)	91.1(3)	O(3)-Ta(1)-Cl(1)	86.5(3)
O(2)-Ta(1)-Cl(1)	85.9(3)	Cl(3)-Ta(1)-Cl(1)	95.17(16)
O(1)-Ta(1)-Cl(2)	90.5(3)	O(4)-Ta(1)-Cl(2)	90.1(3)
O(3)-Ta(1)-Cl(2)	85.9(3)	O(2)-Ta(1)-Cl(2)	86.7(3)
Cl(3)-Ta(1)-Cl(2)	94.48(15)	Cl(1)-Ta(1)-Cl(2)	170.35(15)

3.3 Catalysis on the formation of cyclic carbonate

The catalytic performances of complexes **1–2** on the synthesis of cyclic carbonate by reaction of 1 Mpa CO₂ with 1,2-propylene oxide at 20°C were assessed. After the reactions, ¹H NMR spectroscopic monitoring indicated the final results and shown in

Table 4. Due to the low reacted temperature, complexes **1** and **2** showed poor catalytic efficiencies with the conversion rate at 44% and selectivity at 61% for **1** (entry 1), and the conversion rate at 70% and selectivity at 84% for **2** (entry 2), which were less effective than the NHC-Ta complexes [(IPr)TaCl₅] and [(IMes)₂TaCl₄][TaCl₆]. At last, neither TaCl₅ nor adducts [IMes:CO₂] and [IPr:CO₂] showed catalytic activity on the cycloaddition reaction (entry 3-5), indicating the catalytic centers were in the Ta complexes.

Table 4 catalytic cyclization of 1,2-propylene oxide with 1 MPa CO₂ by complexes **1–2**.

Entry ^a	Catalyst	Conversion(%) ^b	Yield(%)	Selectivity(%)
1	1	44	27	61
2	2	70	59	84
3	TaCl ₅	0	trace	/
4	[IMes:CO ₂]	0	trace	/
5	[IPr:CO ₂]	0	trace	/

^a Reaction conditions: 20°C, 1 MPa CO₂, 10 h, 10 mol% catalyst.

^b Conversion rates were determined by comparing the ratio of product to substrate in the reacted mixture through the ¹H NMR spectra.

4. Conclusions

In conclusion, two free *N*-heterocyclic carbenes IMes and IPr were converted to their respective imidazolylidene carboxylates [IMes:CO₂] and [IPr:CO₂] by introducing them to CO₂. Compared to the free carbenes, the zwitterionic adducts displayed a much greater stability toward air and moisture in the solid state. Thus, they could be easily handled in organometallic synthesis and catalysis. In this paper, the adducts were found to readily react with TaCl₅ to give two VB group metal complexes [(IMes:CO₂)TaCl₅]·2CH₂Cl₂ (**1**) and [(IPr:CO₂)₂TaCl₃][TaCl₆]₂ (**2**) with high oxidation, in which the carboxylates were not decomposed from adduct [NHC:CO₂] to lead to Ta-carbene complexes, this may be due to the strong interaction between Ta and carboxylate group.

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Graphic abstract

Two imidazolylidene carboxylates [IMes:CO₂] and [IPr:CO₂], which were obtained by combination of CO₂ with *N*-heterocyclic carbenes, were reacted with VB group metal TaCl₅ to give a monomeric complex [(IMes:CO₂)TaCl₅] (**1**) and a dimeric complex [(IPr:CO₂)₂TaCl₃][TaCl₆]₂ (**2**) with high oxidation of metal.