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Dimetalloxycarbene Complexes

A Dimetalloxycarbene Bonding Mode and Reductive Coupling Mechanism for Oxalate Formation from CO_2**

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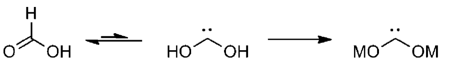
Abstract: *We describe the stable and isolable dimetalloxycarbene* $[(TiX_3)_2(\mu_2\text{-}CO_2\text{-}\kappa^2C,O{:}\kappa O')]$ **5**, *where* $X = N$*-(tert-butyl)-3,5-dimethylanilide, which is stabilized by fluctuating* $\mu_2\text{-}\kappa^2C,O{:}\kappa^1O'$ *coordination of the carbene carbon to both titanium centers of the dinuclear complex* **5**, *as shown by variable-temperature NMR studies. Quantum chemical calculations on the unmodified molecule indicated a higher energy of only* $+10.5\ \text{kJ mol}^{-1}$ *for the* $\mu_2\text{-}\kappa^1O{:}\kappa^1O'$ *bonding mode of the free dimetalloxycarbene compared to the* $\mu_2\text{-}\kappa^2C,O{:}\kappa^1O'$ *bonding mode of the masked dimetalloxycarbene. The parent cationic bridging formate complex* $[(TiX_3)_2(\mu_2\text{-}OCHO\text{-}\kappa O{:}\kappa O')][B(C_6F_5)_4]$, **4**$[B(C_6F_5)_4]$, *was simply deprotonated with the strong base* $K(N(SiMe_3)_2)$ *to give* **5**. *Complex* **5** *reacts smoothly with* CO_2 *to generate the bridging oxalate complex* $[(TiX_3)_2(\mu_2\text{-}C_2O_4\text{-}\kappa O{:}\kappa O'')]$, **6**, *in a C–C bond formation reaction commonly anticipated for oxalate formation by reductive coupling of* CO_2 *on low-valent transition-metal complexes.*

Fundamental transformations of CO_2 are of inherent interest in connection with the utilization of this greenhouse gas and waste product as a C_1 building block for the synthesis of useful chemicals.[1] In particular, reactions leading to C–C bond formation feature prominently, and the selective coupling of CO_2 to produce oxalate has been the target of efforts to control reductive processes that proceed by way of the CO_2 radical anion.[2] Recent mechanistic and theoretical investigations on oxalate formation as mediated by metal complexes have ruled out the CO_2 radical anion coupling pathway, focusing attention instead on a bimetallic intermediate featuring a $\mu\text{-}\kappa^2{:}\kappa^1$ CO_2 sandwich complex to which a second molecule of CO_2 can add.[3] Importantly, the proposed $\mu\text{-}\kappa^2{:}\kappa^1$ bimetallic CO_2 species that has been implicated by quantum chemical calculations has never been experimentally verified with an isolated and characterized example as it has for CS_2.[4] Herein, beginning from a titanium formate complex,[5] we provide an independent synthesis of the first example of such a $\mu\text{-}\kappa^2{:}\kappa^1$ bimetallic complex including full spectroscopic and structural characterization. Additionally, we demonstrate that the $\mu\text{-}\kappa^2{:}\kappa^1$ complex reacts with carbon dioxide to generate oxalate.[6] Quantum chemical mechanistic investigations reveal rearrangement of the unsymmetrical bridging carbondioxo ligand to an intriguing $\mu\text{-}\kappa^1{:}\kappa^1$ dimetalloxycarbene isomer[7,8] which enables the aforementioned indirect reduction of CO_2 by formic acid to give oxalate.

Currently, eleven coordination modes of CO_2 at metal centers in various oxidation states are known.[9] Low-valent transition-metal complexes react with CO_2 to yield end-on coordinated $CO_2^{\bullet-}$, bridging carbonate, or oxo complexes.[9b,10] In d^1 titanium tris(anilide) ($[TiX_3]$, with $X = N$-$[t\text{Bu}](3,5\text{-}Me_2C_6H_3)$, **1**),[11] CO_2 inserts into the Ti–N bonds rather than being reduced by the electron-donating metal.[12] In cooperation with $[MoX_3]$ however, **1** reductively cross-couples CO_2 with benzonitrile,[13] a process which could involve an intermediate radical $CO_2^{\bullet-}$ complex.[9b]

Because its presumed complex with CO_2 has been elusive and would contain at most a singly reduced form of the small molecule, we opted for an independent synthesis method to extend the CO_2 ligand chemistry of titanium tris(anilide). To reveal the fundamental transformations available for further reduced CO_2 in the coordination sphere of titanium tris(anilide), we decided to employ formic acid as an already two-electron-reduced form of CO_2. The twofold deprotonation and metalation of a higher energy tautomer of formic acid, which is dihydroxycarbene,[14] would render a dimetalloxycarbene [Eq. (1)].



(1)

One-electron oxidation of **1** with *tert*-butylformate introduces a formato ligand to render $[TiX_3(OCHO)]$, **2**.[5] Attempts to obtain a CO_2 anion stabilized by coordination to the titanium center via deprotonation of the formate ligand with a strong Brønsted base resulted in loss of carbon

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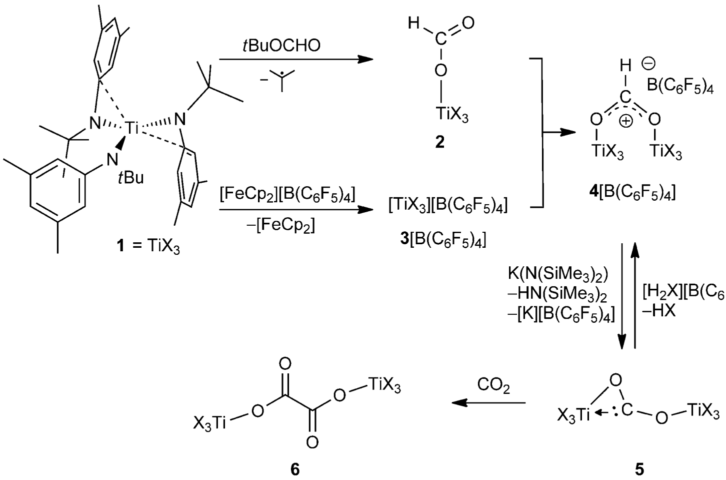
monoxide to form an anionic oxo complex;[5] this reacts with CO_2 to form a carbonate complex.[15] To retain the CO_2 framework, **2** needed to be stabilized against CO cleavage upon deprotonation. We envisioned a bimetallic structure to provide sufficient stabilization. This architecture was constructed via addition of $[TiX_3][B(C_6F_5)_4]$, **3**$[B(C_6F_5)_4]$,[16] yielding the formally symmetric cationic bridging formate complex with a weakly coordinating counter anion $[(TiX_3)_2(\mu_2\text{-OCHO-}\kappa O{:}\kappa O')][B(C_6F_5)_4]$, **4**$[B(C_6F_5)_4]$ (Scheme 1).[17]



Scheme 1. Synthesis strategy for the dimetalloxycarbene **5**.

The ^{1}H NMR spectrum of **4**$[B(C_6F_5)_4]$ shows a distinct upfield shift of the formate proton from 8.00 ppm for **2** to 6.25 ppm[18] in [D$_1$]chloroform. This assignment is confirmed by the ^{1}H–^{13}C coupling visible in the ^{1}H NMR spectrum of ^{13}C-labeled ^{13}C-**4**$[B(C_6F_5)_4]$ in which the formate proton signal appears as a doublet ($^1J_{CH} = 214$ Hz). Single crystals of **4**$[B(C_6F_5)_4]$ conducive to an X-ray diffraction study were obtained at −35 °C from a saturated diethyl ether solution (Figure 1).[19] The molecule adopts an unsymmetrical conformation with two inward directed aryl residues for one of the two titanium centers. This orientation of the aryl groups is otherwise a common motif for anionic metal tris(anilide) complexes with basic terminal ligands such as oxo ligands.[20] The positive charge of **4** is delocalized over Ti1-O1-C1-O2-Ti2 as evidenced by the similar C–O bond lengths of 1.257(3) Å (here and below, values in parentheses are errors in the last significant digit) and 1.239(3) Å, respectively, and their contraction compared to the O1–C1 single bond in **2** of 1.285(8) Å.[5]

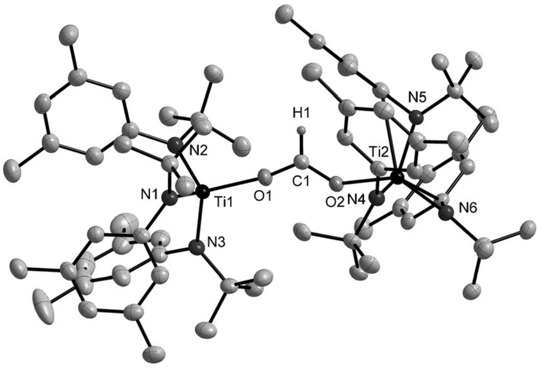


Figure 1. Molecular structure of **4**. Ellipsoids are set at 50% probability; two interstitial diethyl ether molecules and hydrogen atoms, except H1, are omitted for clarity. Selected interatomic distances [Å] and angles [°]: C1–O1 1.257(3), C1–O2 1.239(3), Ti1–O1 1.9592(16), Ti2–O2 2.0750(15); Ti1-O1-C1 167.47(16), Ti2-O2-C1 137.11(15), O1-C1-O2 124.6(2).

Treatment of **4**$[B(C_6F_5)_4]$ with the Brønsted base potassium hexamethyldisilazide $K(N(SiMe_3)_2)$ in diethyl ether at 25 °C produces $[(TiX_3)_2(\mu_2\text{-}CO_2)]$, **5**, which precipitates as an orange crystalline solid from the reaction mixture (Scheme 1). Red–orange single crystals of **5** suitable for X-ray diffraction studies were grown at −35 °C from a concentrated 10:1 solution of dichloromethane and benzene. Compound **5** is best described as $[(TiX_3)_2(\mu_2\text{-}CO_2\text{-}\kappa^2 O,C{:}\kappa O')]$ (Figure 2), with the bridging CO_2 ligand adopting an unsymmetrical $\kappa^2{:}\kappa^1$ coordination mode. Compound **5** crystallizes in the centrosymmetric space group $P2_1/n$, with C1 and O1 of the bridging carbondioxo ligand being disordered across the inversion center. The refinement was carried out with split positions (Supporting Information, Figure S42). A related disorder has already been described for CS_2-bridged diuranium complexes;[4] for example in $[(U(RC_5H_4)_3)_2(\mu_2\text{-}CS_2\text{-}\kappa^2 S,C{:}\kappa S')]$ the bridging ligand features a $\kappa^2{:}\kappa^1$ coordination mode.[4a] The angle O1-C1-O2 of 114.9(6)° of **5** is smaller than the corresponding angle of **4**$[B(C_6F_5)_4]$ and very similar to the O-C-O angle of structurally related μ_2-κ^3 metallocarboxylate rhenium complexes, such as $[\{Cp^*Re(CO)(NO)\}(\mu_2\text{-}CO_2)\{Re(CO)_2(PPh_3)_2\}]$ ($Cp^* = C_5Me_5$) with 112.7(7)° or $[\{Cp^*Re(CO)(NO)\}(\mu_2\text{-}CO_2)Mo(CO)_2Cp]$ ($Cp = C_5H_5$) with 112.8(10)°.[21] The interatomic distances of Ti1–C1 (2.066(8) Å), Ti1–O2 (2.092(4) Å), and Ti1′–O1 (1.914(6) Å) lie in the range of the respective single

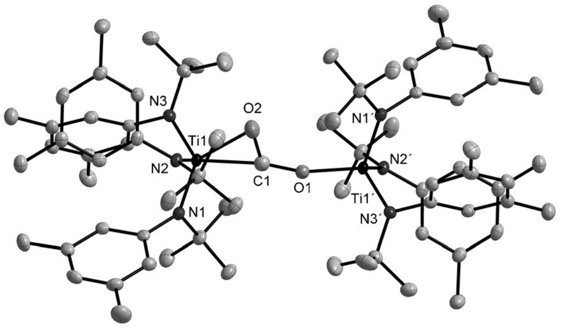
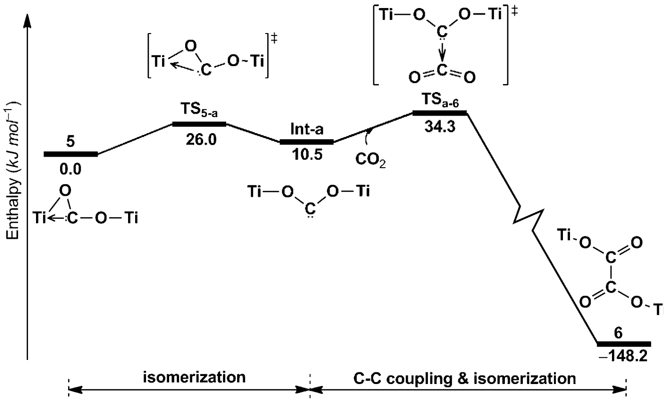


Figure 2. Molecular structure of **5**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: C1–O1 1.299(7), C1–O2 1.253(10), Ti1′–O1 1.914(6), Ti1–C1 2.066(8), Ti1–O2 2.092(4); Ti1-C1-O1 170.7(6), Ti1′-O1-C1 164.3(4), Ti1-C1-O2 73.6(4), O1-C1-O2 114.9(6).

bonds[22] while C1−O2 (1.253(10) Å) is in the range of typical C−O double bonds.[23] The reverse reaction to form back the bridging formate complex **4**$[B(C_6F_5)_4]$ from **5** required a very weak Brønsted acid because of the hydrolysis-sensitive anilide ligands. The corresponding ammonium salt of the anilide ligands, $[H_2X][B(C_6F_5)_4]$, was found to regenerate **4**$[B(C_6F_5)_4]$ in benzene in up to 68% yield of isolated product (Scheme 1).

The infrared (IR) spectrum of **5** exhibits a weak ν_{as}(^{12}C=O) absorption at 1683 cm^{-1} (Supporting Information, Figure S36), which shifts to 1645 cm^{-1} for ^{13}C-**5** (which is $[(TiX_3)_2(\mu_2\text{-}^{13}CO_2)]$) (Supporting Information, Figure S37). The ^{12}C/^{13}C isotopic ratio R(1683/1645) of 1.0231 is different from that of free CO_2 gas ($R = 1.0284$) as expected for a nonlinear CO_2^{2-} ligand.[9b]

The carbon signal of the CO_2 ligand of ^{13}C-**5** was observed at 252.2 ppm in the solution $^{13}C\{^1H\}$ NMR spectrum acquired in [D$_6$]benzene. The corresponding carbon signal in the solid-state ^{13}C CP/MAS (cross-polarization/magic-angle spinning) spectrum appears at 254 ppm, suggesting that the coordination mode of the bridging unit is similar both in solid state and in solution. Otherwise, the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **5** in [D$_6$]benzene at 24 °C exhibit signals corresponding to one chemical environment for all six anilide ligands which, at first appearance, seems to contradict the expectation induced by the solid-state structure of **5** that implies at least two different signal sets in the NMR spectra. Supposing a fluctuating behavior of the CO_2 ligand to cause a superposition of the expected signals to only one signal set, we turned to variable-temperature (VT) ^{1}H NMR experiments in [D$_8$]toluene. The first event, a splitting of the *o*-aryl and methyl aryl signals below −20 °C, is due to locking of the N−C$_{ipso}$ rotation.[24] Below a coalescence temperature of −55 °C, another splitting of the *o*-aryl and methyl aryl signals occurs in the ^{1}H NMR spectrum accompanied by splitting of the *p*-aryl singlet (Supporting Information, Figure S31). These findings suggested that the carbon of the CO_2 ligand alternately binds to each of the titanium centers. The activation barrier of 26.0 kJ mol^{-1} for this wagging motion is low enough to occur at room temperature, as calculated using DFT methods (Scheme 2). The wagging is prevented at temperatures lower than −55 °C which leads to chemically inequivalent environments on both sides of **5** (Supporting Information, Scheme S1). The then presumably unsymmetrical species **5** forms two atropisomers in an unequal ratio which is indicated by the concomitant splitting of the CO_2 carbon signal in the solution $^{13}C\{^1H\}$ NMR spectrum into two incongruent signals (Supporting Information, Figure S31).



Scheme 2. Energy profile of the reaction of **5** with CO_2 calculated with DFT methods on B3PW91 level with D3 corrections. Anilide ligands X were omitted for clarity.

Computationally, two isomers of **5** are located, namely the μ_2-κ^2O,C:κ^1O' species characterized by X-ray and a μ_2-κ^1O:κ^1O' dimetalloxycarbene species, **5′**.[25] The latter one lies only slightly higher in energy (10.5 kJ mol^{-1}) than the former (Scheme 2). We infer that the dimetalloxycarbene is short-lived since the observed $^{13}C\{^1H\}$ NMR signal at 252.2 ppm is almost identical to that predicted using DFT methods for the μ_2-κ^2O,C:κ^1O' isomer, and quite far from the calculated shift of 356 ppm for the μ_2-κ^1O:κ^1O' dimetalloxycarbene (see the Supporting Information).[26]

Frontier molecular orbital analysis on the hypothetical dimetalloxycarbene **5′** ("**Int-a**", Scheme 2) indicates that the highest occupied molecular orbital (HOMO) is predominantly a lone pair located at the carbon center of the CO_2 moiety (Supporting Information, Scheme S3). Furthermore, the natural bonding orbital (NBO) analysis locates two lone pairs on each oxygen atom and one lone pair on the central carbon, while also indicating single bond character for both C−O bonds (Supporting Information, Scheme S4). Thus, the predominant bonding mode of this CO_2 ligand comprises titanium–oxygen single bonds and a lone pair at the carbenoid carbon atom. The bridging CO_2 ligand can be formally regarded as CO_2^{2-}.

Cyclic voltammetry of **5** in dichloromethane (CH_2Cl_2) at 25 °C features an irreversible oxidation at $E^\circ_{ox} = 0.41$ V (vs. ferrocene) in the electrochemical window of the solvent (Supporting Information, Figure S41). The oxidation event might be correlated to one of the electrons of the bridging CO_2 ligand since d^0 titanium centers are already in their highest oxidation state.

Exposure of a degassed solution of **5** in toluene to an excess of CO_2 gas (0.3 bar, 25 °C) results in the formation of the bridging oxalate complex $[(TiX_3)_2(\mu_2\text{-}C_2O_4\text{-}\kappa O{:}\kappa O'')]$, **6**, as indicated by ^{1}H NMR spectroscopy. The CO_2 carbon atom signal of **5** at 252.2 ppm disappears in the $^{13}C\{^1H\}$ NMR spectrum in favor of a new signal at 162.8 ppm, which resembles that of free oxalic acid at 160.1 ppm in [D$_8$]dioxane[27] rather than that of chelating oxalato ligands in the region of 200 ppm.[6c]

Single crystals of **6** were grown at 25 °C as yellow–orange square plates by slow evaporation from a mixture of diethyl ether and benzene. The solid-state structure of **6** is centrosymmetric with an oxalato ligand bridging two titanium atoms in a κ^1:κ^1 fashion (Figure 3).[28] Absence of chelation is most likely due to the steric bulk provided by the three ancillary anilide ligands. Steric congestion at the titanium centers is also indicated by the orientation of the anilide ligands, the aryl moieties of which all point away from the metal centers. The κ^1 coordination mode effects a clear distinction between the localized double C1−O2 (1.194(10) Å)[23] and single C1−O1 (1.287(10) Å)[22] bonds which is also confirmed by DFT calculations.

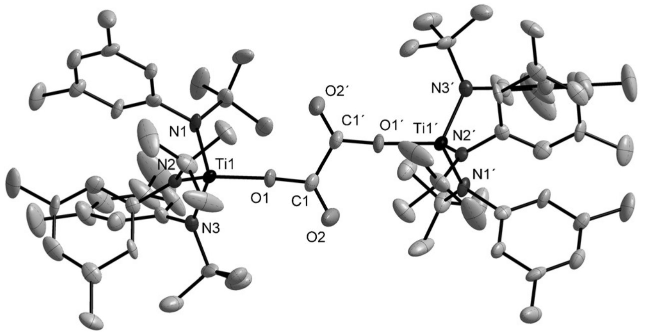


Figure 3. Molecular structure of **6**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: C1–O1 1.287(10), C1–O2 1.194(10), Ti1–O1 1.883(5), C1–C1′ 1.501(17); Ti1-O1-C1 174.7(6), O1-C1-O2 123.5(8), O1-C1-C1′ 115.1(8), O2-C1-C1′ 121.4(10).

In the IR spectrum of the oxalate complex **6** (Supporting Information, Figure S38), a new strong absorption at 1702 cm^{-1} was observed, which shifts to 1661 cm^{-1} for the product obtained from the treatment of ^{13}C-**5** with $^{13}CO_2$, $^{13}C_2$-**6** (Supporting Information, Figure S40). An analogous reaction of **5** with $^{13}CO_2$ gave ^{13}C-**6**, with both the ^{12}C=O and ^{13}C=O stretch absorption frequencies at 1699 cm^{-1} and 1658 cm^{-1} (Supporting Information, Figure S39), respectively, slightly shifted compared to those of homoisotopic **6** and $^{13}C_2$-**6**. Being conducted with excess $^{13}CO_2$, the latter reaction excludes the possibility that free CO_2 exchanges with bound CO_2 in **5** because, in that case, ν_{as}(C=O) of **6** and $^{13}C_2$-**6** would also have appeared in the IR spectrum of ^{13}C-**6**. Ligated and free CO_2 exclusively react to form irreversibly the oxalato fragment.

DFT calculations suggested a peculiar reaction path (Scheme 2), being very different from the one found for samarocenes or trivalent uranium complexes.[3d,e] Here, the CO_2 moiety of the metastable intermediate dimetalloxycarbene **5′** ("**Int-a**", Scheme 2) directly attacks free CO_2 in a nucleophilic manner known from carbene chemistry.[29] No activation of the incoming CO_2 molecule by coordination to the metal center is required. The process was calculated to have a low activation barrier of $\Delta H^{\neq} = 34.3\ kJ\,mol^{-1}$. The oxalate complex **6** is energetically favored by 148.2 $kJ\,mol^{-1}$ over CO_2 and μ_2-κ^2:κ^1 coordinated **5**. The carbenic nature of complex **5′** (**Int-a**) was further confirmed by computing the singlet–triplet gap. The gap accounts for 126.9 $kJ\,mol^{-1}$ with the singlet being the lowest-energy state.

In conclusion, we have isolated and fully characterized the first dimetalloxycarbene complex, **5**. Compound **5** is stabilized by a fluctuating coordination of the carbenic carbon atom to both metal centers and can be stored indefinitely at low temperatures in a dry and oxygen-free atmosphere. Reaction with CO_2 gave an oxalate complex, **6**, with DFT calculations inferring a nucleophilic attack on CO_2 by the free carbene species **5′**.

Keywords: anilides · carbene ligands · CO_2 fixation · structure elucidation · titanium

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[7] We coin the term dimetalloxycarbene in reference to the structural unit M-O-C(:)-O-M in which a doubly reduced CO_2 ligand (electron lone pair at carbon) bridges two metal centers. This term is introduced by analogy with the terms "zirconoxycarbene" or "titanoxycarbene" typically used to describe bimetallic oxycarbene systems brought about by reaction of a zirconium or titanium hydride or alkyl system with CO or with a CO complex of a transition metal.

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[18] See the Supporting Information.

[19] CCDC 953819 (**4**[$B(C_6F_5)_4$]), 953820 (**5**), and 953821 (**6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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