Inorganic Chemistry
Communication
pubs.acs.org/IC

Reduction of Carbon Dioxide Promoted by a Dinuclear Tantalum Tetrahydride Complex

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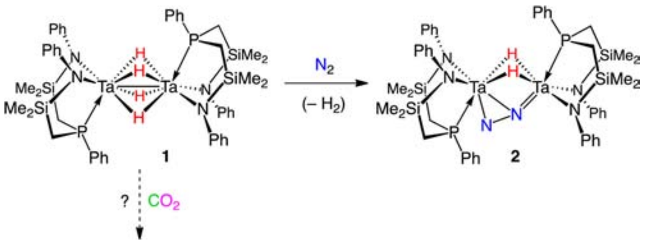
Supporting Information

ABSTRACT: The reaction of 1 equiv of carbon dioxide with the dinuclear tetrahydride complex $([NPN]Ta)_2(\mu\text{-}H)_4$ [where NPN = $PhP(CH_2SiMe_2NPh)_2$] results in the formation of $([NPN]Ta)_2(\mu\text{-}OCH_2O)(\mu\text{-}H)_2$ via a combination of migratory insertion and reductive elimination. The identity of the ditantalum complex containing a methylene diolate fragment was confirmed by single-crystal X-ray analysis, NMR analysis, and isotopic labeling studies. Density functional theory calculations were performed to provide information on the structure of the initial adduct formed and likely transition states and intermediates for the process.

Carbon dioxide (CO_2) is potentially a plentiful C_1 source that continues to occupy discussions related to climate change.[1] While conversion of CO_2 to higher-value carbon-based materials is a worthy goal, it is clear that these kinds of approaches are not realistic as a way to sequester this greenhouse gas,[2] particularly if dihydrogen (H_2) derived via steam reforming is involved. Nevertheless, from a fundamental point of view, discovering systems that can transform CO_2 with[3−5] or without H_2[6] is of considerable interest[7−9] and may provide hints on ways to better utilize this ever-more-abundant resource.[10]

We have described the facile activation of dinitrogen (N_2) by dinuclear tantalum tetrahydride, $([NPN]Ta)_2(\mu\text{-}H)_4$ (**1**, where NPN = $PhP(CH_2SiMe_2NPh)_2$), to generate the side-on end-on ditantalum dinitrogen complex $([NPN]Ta)_2(\mu\text{-}\eta^2{:}\eta^1\text{-}N_2)(\mu\text{-}H)_2$ (**2**;[11,12] Scheme 1). Given that N_2 is a very stable, inert molecule, the question arose as to what the outcome would be in the reaction of tetrahydride **1** with the very stable CO_2 molecule. Herein we report our efforts to examine the reactivity of CO_2 with the strongly reducing ditantalum tetrahydride complex **1**.

Scheme 1



What emerges from this work is a rare example of a dinuclear metal hydride system that functionalizes CO_2 and retains its dinuclearity.

Our initial inspiration to examine the activation of CO_2 was based on the report that certain zirconium and hafnium dinitrogen complexes react productively with CO_2 to generate new N−C bonds and regioisomeric hydrazides.[13] However, the reaction of CO_2 and the tantalum side-on end-on N_2 complex **2** led to the formation of a multitude of products even when the stoichiometry of added CO_2 was controlled. Undaunted, we turned to the reaction of the ditantalum tetrahydride **1** with CO_2 and discovered that a single product could be obtained provided that strict control of the stoichiometry was followed. For example, if excess CO_2 is used, very complicated spectra are obtained, indicative of a mixture of products, perhaps a consequence of migratory insertion of CO_2 in the tantalum−amido linkages of the NPN ligand. However, if exactly 1 equiv of CO_2 is employed, a clean reaction ensues with the formation of only one very symmetrical product (60% recrystallized yield) on the basis of a singlet at δ −13.1 observed in the ^{31}P NMR spectrum. The corresponding ^{1}H NMR spectrum shows a triplet resonance downfield at δ 6.81, which simplifies to a singlet upon ^{31}P decoupling and integrates to two H atoms. Analysis by heteronuclear single quantum coherence indicates that these H atoms are not C-bound, consistent with the presence of bridging tantalum hydrides, and are likely a $Ta_2(\mu\text{-}H)_2$ moiety. Also diagnostic in the ^{1}H NMR spectrum is a singlet at δ 6.11 that again integrates for two H atoms. That these two sets of proton resonances are derived from the bridging hydrides of **1** was confirmed by the use of **1**-d_{12}, in which all four bridging hydrides and all eight of the *o*-NPh protons are deuterated (see the Supporting Information); in this reaction, the peaks at δ 6.81 and 6.11 both disappear in the ^{1}H NMR spectrum, as does a peak at δ 6.89 due to the *o*-H atoms of the NPh moiety of the NPN ligand. When ^{13}C-labeled CO_2 was utilized, the resonance at δ 6.11 becomes a doublet with $^{1}J_{CH}$ = 110 Hz. Given our earlier publication[14] of the complete disassembly of CS_2 to generate the ditantalum species with a bridging methylene, an analogous structure was considered. However, there are no bridging hydrides in the CS_2 disassembly product, and the chemical shift of the resonance due to the bridging methylene of this material occurs at δ 4.5 in the ^{1}H NMR spectrum, which is considerably

Received: November 12, 2012
Published: January 29, 2013

upfield of the methylene resonance observed for the CO_2 product **3**. In fact, a recent report of the reaction of CO_2 with a mononuclear tantalum hydride to generate a ditantalum species with a methylene diolate fragment proved to be a better analogy.[15]

The solid-state structure of this complex is shown in Figure 1, along with the transformation in eq 1; the most notable feature of **3** is the bridging methylene diolate unit between the two Ta centers. The Ta1−O1 bond length of **3** of 1.980(5) Å is slightly longer that the Ta−O bonds of 1.929(5) and 1.917(2) Å found in two dinuclear methylene diolate complexes formed via intermolecular processes.[15] The other parameters of this μ-OCH_2O unit compare unremarkably to other examples of this rare kind of fragment with the exception that the O−C−O angle in **3** of 117.0(9)° is larger than the aforementioned dinuclear systems [cf. 111.4(7) and 109.7(3)°][15] and a tetrayttrium cluster [cf. 107.6(3)°][16] that contain this unit.

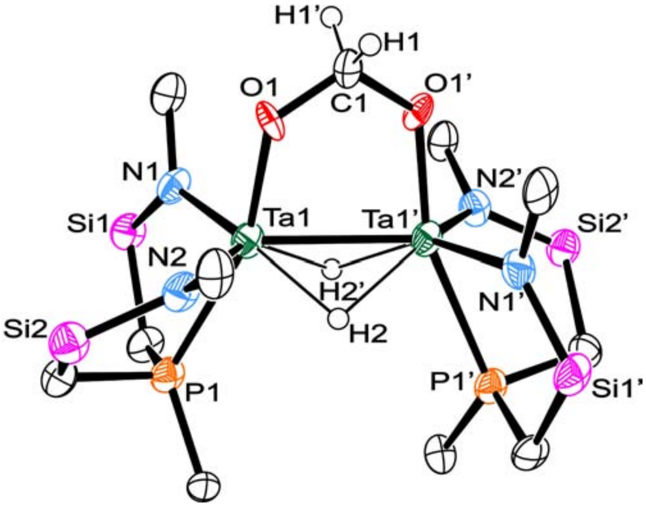
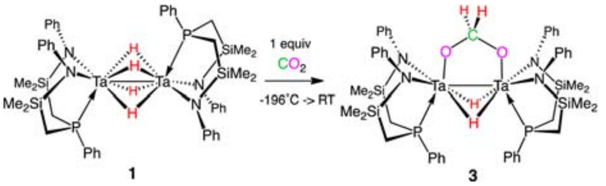


Figure 1. Selected bond lengths (Å) and bond angles (deg) for **3**: Ta1−N1 2.091(7), Ta1−N2 2.062(6), Ta1−P1 2.628(2), Ta1−O1 1.980(5), Ta1−Ta1 2.7688(7), N1−Si1 1.742(7), N2−Si2 1.739(7), C1−O1 1.384(7); O1−C1−O1′ 117.0(9), Ta1−O1−C1 126.4(5), O1−Ta1−O1′ 117.0(9), O1−Ta1−N1 91.6(2), O1−Ta1−N2 91.6(2), N1−Ta1−N2 118.2(3), O1−Ta1−P1 160.99(15), N1−Ta1−P1 77.82(19), N2−Ta1−P1 79.08(19), O1−Ta1−Ta1′ 83.45(14).



1 3 (1)

The formation of **3** likely involves hydride addition reactions most probably through a formate-type intermediate.[3,17] In an effort to shed light on this process, possible structures of intermediates and transition states were examined computationally. Density functional theory [B3PW91//SDDALl(Ta,P)/6-31G** (other atoms)] calculations were carried out on the full system.

The Gibbs free-energy profile of the reaction between **1** and CO_2 is presented in Figure 2. For each minimum, singlet and triplet spin states have been considered, and the singlet spin states are always the most stable, by 20−50 kcal/mol. Thus, the reactivity takes place on the singlet potential energy surface.

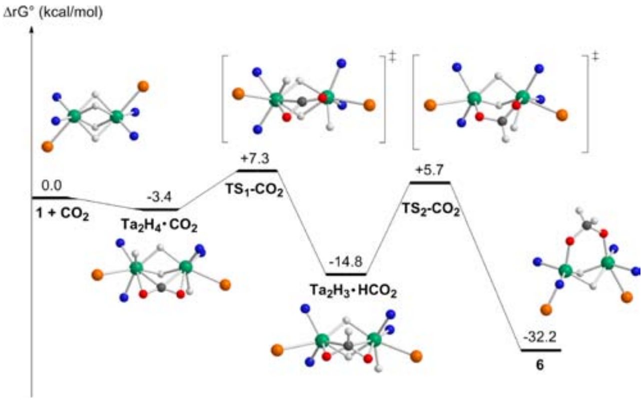


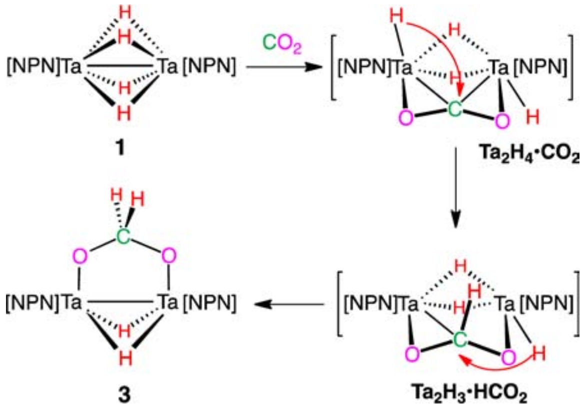
Figure 2. Gibbs free-energy profile of the reaction between the tetrahydride complex **1** and CO_2. NPN ligands have been simplified for clarity. Atoms colors: Ta, green; P, orange; N, blue; O, red; C, black; H, white. For atom numbering, Ta1 is on the left, while Ta2 is on the right.

The first step of the reaction is coordination of CO_2 to complex **1**, involving the two Ta centers. In $Ta_2H_4{\cdot}CO_2$, two bridging hydride groups have become terminal in order to liberate one coordination site on each Ta center and thus allow the μ-η^2:η^2-coordination mode of CO_2, all of which happens in a concerted fashion. The computed O−C−O angle is 132.8° and both C−O bonds are equal to 1.26 Å, suggesting that CO_2 has been reduced by complex **1**. The Ta−Ta distance has increased from 2.59 to 3.01 Å, so that the Ta−Ta bond has been broken. This is confirmed by natural bond order (NBO) analysis, which gives an oxidation state of +5 for each Ta, suggestive of the presence of CO_2^{2-}, at least formally. NPA charges show that the C atom of CO_2 is strongly positively charged (+0.70). The formation of this adduct is slightly exergonic by −3.4 kcal/mol, but it readily transforms to give the dinuclear μ-η^2:η^2-formato $Ta_2H_3{\cdot}HCO_2$. Indeed, the transition state corresponding to the hydrogen transfer from one Ta center to CO_2 lies at only +10.7 kcal/mol with respect to $Ta_2H_4{\cdot}CO_2$, while the formation of $Ta_2H_3{\cdot}HCO_2$ is exergonic by −11.4 kcal/mol with respect to the adduct. The geometry of the first transition state is standard because one O atom of CO_2 has just moved away from the Ta−Ta−CO_2 plane of $Ta_2H_4{\cdot}CO_2$ in order to allow the terminal hydride to bridge from the Ta center to the C atom of CO_2. All other bond lengths or angles are mostly unchanged.

The intermediate $Ta_2H_3{\cdot}HCO_2$ presents a nearly symmetrical μ-η^2:η^2-HCO_2 moiety. The Ta−Ta distance is 2.95 Å, which is not consistent with a formate unit between two Ta^{IV} centers unless the two d electrons remain unpaired. NBO analysis shows that there are no unpaired electrons in the d orbitals of the Ta centers or the presence of a Ta−Ta bond. The Lewis configuration extracted from the NBO shows a covalent bond between Ta1 and the C atom and two dative bonds from both negatively charged O atoms to each Ta center. The system can thus be described with two electrons delocalized between both Ta−C bonds and formally Ta^V centers. The formation of the experimental product involves the transition state TS_2-CO_2, which corresponds to the transfer of the second terminal hydride to the C atom of the HCO_2 unit. The activation barrier is calculated to be +20.5 kcal/mol, which is high but still kinetically accessible. The geometry of this transition state looks like that of TS_1-CO_2, discussed above. The formation of **3** is calculated to be exergonic by −17.4 kcal/mol with respect to the dinuclear formate complex $Ta_2H_3{\cdot}HCO_2$. The computed structure of **3** is similar to the experimental one, for example, with C−O, Ta−O, and Ta−Ta bond lengths of 1.40 Å [1.388(10) Å exp], 1.95 Å [1.982(8) Å exp], and 2.80 Å [2.7693(9) Å exp], respectively. The highest occupied molecular orbital (HOMO) still corresponds to the σ interaction of the two d orbitals of Ta, confirming the Ta^{IV} oxidation state. The importance of the metal is clearly evident because calculations using copper surfaces detail quite different intermediates.[18]

The reaction of CO_2 with the highly reducing ditantalum tetrahydride complex **1** proceeds by a migratory insertion process followed by reductive elimination, as summarized in Scheme 2.

Scheme 2



Of particular interest is how CO_2 interacts with the starting hydride. By using a computational approach, a low-energy structure emerged, wherein CO_2 binds reductively with tetrahydride **1** to generate $Ta_2H_4\cdot CO_2$, wherein two of the bridging hydrides become terminal and the CO_2 unit is formally a CO_2^{2-} moiety. One of the interesting insights that result from these calculations is the importance of the terminal hydride unit in the transformation documented in this work. While the starting tetrahydride **1** contains four bridging hydrides in its ground state, each step in the process involves a terminal hydride interacting with a small organic moiety in a bridging position. In the first transfer, the μ-η^2:η^2-formato complex $Ta_2H_3\cdot HCO_2$ is generated and finally the methylene diolate product **3**; this latter process is formally a dinuclear C−H reductive elimination, wherein the two Ta^{V} centers of $Ta_2H_3\cdot HCO_2$ are converted to Ta^{IV} moieties in **3**.

While dinuclear complexes offer unique activation modes for small molecules, mainly by invoking simultaneous interactions with two metal centers, in this work, we show that the strongly reducing ditantalum complex in concert with available hydrides can convert the important C_1 source CO_2 to a reduced form, in this case, a methylene diolate fragment. We are presently examining the effect of new ligand designs on the overall reducing power of a series of ditantalum tetrahydrides with CO_2 and other hard-to-activate small molecules.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, X-ray data collection and refinement procedures for **3**, including the corresponding CIF file, computational details, Cartesian coordinates for optimized structures, schematic of HOMO−5 of the adduct $Ta_2H_4\cdot CO_2$, and representative NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.D.F. thanks the NSERC of Canada for a Discovery Grant. L.M. is member of the Institut Universitaire de France. CINES and CalMip are acknowledged for a generous grant of computing time. J.B., M.D.F., and L.M. are also grateful to the Alexander von Humboldt Foundation for fellowships.

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