

## Carbon Dioxide Reduction by Terminal Tantalum Hydrides: Formation and Isolation of Bridging Methylene Diolate Complexes

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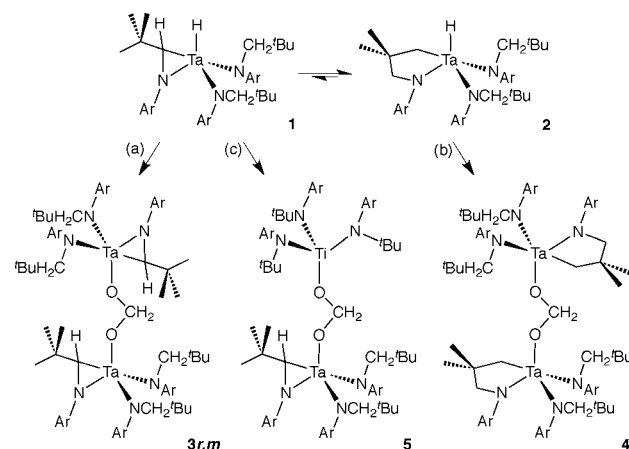
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**Abstract:** The preparation of tantalaziridine–hydride complex  $(\text{Ar}[\text{tBuCH}_2\text{N}])_2(\eta^2\text{-tBu(H)CNAr})\text{TaH}$  (**1**) is reported ( $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$ ). While stable for months in the solid state at  $-35^\circ\text{C}$ , in solution this complex undergoes partial conversion to isomeric hydride  $(\text{Ar}[\text{tBuCH}_2\text{N}])_2(\kappa^2\text{-CH}_2\text{C}(\text{Me})_2\text{CH}_2\text{NAr})\text{TaH}$  (**2**). Although **1** and **2** exist in equilibrium in benzene solution, complex **2** can be isolated cleanly from **1** by selective precipitation using cold *n*-pentane; solid-state structures for both **1** and **2** are presented. Exposure of **1** to *ca.* 1 atm of  $\text{CO}_2$  results in the production of methylene diolate complex  $\{(\text{Ar}[\text{tBuCH}_2\text{N}])_2(\eta^2\text{-tBu(H)CNAr})\text{Ta}\}_2(\mu\text{-OCH}_2\text{O})$  as a mixture of *rac* and *meso* diastereomers (**3r,m**). Similar reactivity for the Nb congener of **1** is reported herein. Furthermore, methylene diolate complex  $\{(\text{Ar}[\text{tBuCH}_2\text{N}])_2(\kappa^2\text{-CH}_2\text{C}(\text{Me})_2\text{CH}_2\text{NAr})\text{Ta}\}_2(\mu\text{-OCH}_2\text{O})$  (**4**) is produced from **2** upon treatment with  $\text{CO}_2$  and was characterized crystallographically. Complexes **3r,m** (and the Nb analogues) as well as **4** establish the feasibility of the formation of methylene diolate products from  $\text{CO}_2$  and two terminal transition-metal hydrides. Reaction of formate  $(\text{Ar}[\text{tBu}]\text{N})_3\text{TiOC}(\text{O})\text{H}$  with **1** generates the related, structurally characterized heterobimetallic complex  $(\text{Ar}[\text{tBuCH}_2\text{N}])_2(\eta^2\text{-tBu(H)CNAr})\text{TaOCH}_2\text{OTi}(\text{N}[\text{tBu}]\text{Ar})_3$  (**5**), which further contributes to the class of complexes reported herein that effectively stabilizes an unusual  $\text{H}_2\text{CO}_2^{2-}$  ligand between two metal centers.

Investigations concerning the chemical transformation of carbon dioxide into reduced  $\text{C}_1$ -molecules of higher value, such as methanol and formic acid, comprise a field of considerable interest.<sup>1</sup> Among processes effecting the hydrogenation of  $\text{CO}_2$ , soluble transition-metal hydride complexes as well as heterogeneous systems featuring surface-bound hydrides have emerged as capable catalysts.<sup>1</sup> A fundamental step of reaction sequences in each case is the insertion of a  $\text{C}=\text{O}$  bond of  $\text{CO}_2$  into a metal–hydride linkage to produce a metalformate species, i.e.,  $\text{L}_n\text{M}-\text{OC}(\text{O})\text{H}$ ; further reduction to generate the ultimate product from the bound formate may then occur by the action of additional metal hydride equivalents.<sup>1–3</sup> Seminal work by Floriani and co-workers<sup>2</sup> exemplified the stepwise reduction of  $\text{CO}_2$  to formaldehyde and methanol using Schwartz's reagent, i.e.,  $[\text{Cp}_2\text{Zr}(\text{Cl})\text{H}]_n$ , and ensuing studies have served to elucidate  $\text{CO}_2$  reduction pathways using metal hydrides.<sup>1,3</sup> In particular, spectroscopic evidence for a commonly alleged bridging intermediate within this class of reactions,  $\text{L}_n\text{M}-\text{OCH}_2\text{O}-\text{ML}_n$ , has been presented for both solid surfaces<sup>4</sup> and in solution,<sup>5,6</sup> yet reports describing the isolation and structural characterization of such methylene diolate complexes have remained limited.<sup>7,8</sup> In pursuit of  $\text{CO}_2$  reduction chemistry we targeted the preparation of tantalum hydride complexes, encouraged by their remarkable function in the hydrogenation of rather difficult substrates such as arenes,<sup>9</sup>  $\text{CO}$ ,<sup>10</sup> and  $\text{N}_2$ .<sup>11</sup> In the present work, we report the reactions

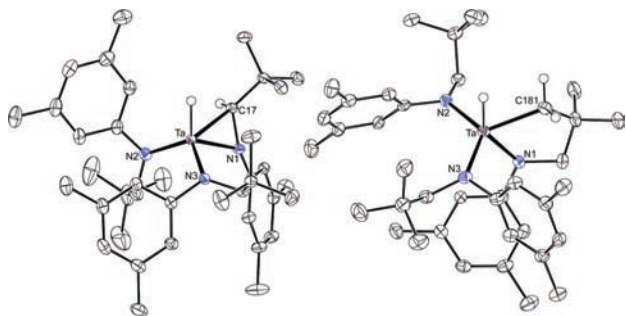
Scheme 1<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) and (b) *ca.* 1 atm of  $\text{CO}_2$ ,  $\text{C}_6\text{H}_6$ ,  $20^\circ\text{C}$ ; (c)  $(\text{Ar}[\text{tBu}]\text{N})_3\text{TiOC}(\text{O})\text{H}$ ,  $\text{C}_7\text{H}_8$ ,  $-35^\circ\text{C}$  ( $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$ ).

of new terminal Ta–H complexes with  $\text{CO}_2$  to give bimetallic methylene diolate complexes.

Our synthetic approach to generate a tantalum hydride complex was based upon metallaziridine–hydride ( $\text{M} = \text{Nb}, \text{Mo}$ ) chemistry featuring *N*-neopentylamide ligands (i.e.,  $\text{N}[\text{CH}_2\text{tBu}]\text{Ar}$ ,  $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$ ) previously disclosed by our laboratory.<sup>12</sup> Accordingly, tantalaziridine–hydride **1** (Scheme 1) was accessed via a similar sequence that led to the corresponding Nb-centered complex,<sup>12a</sup> treatment of  $(\text{Ar}[\text{tBuCH}_2\text{N}])_3\text{Ta}_2$  with  $\text{THF}_3\text{Mg}(\text{C}_{14}\text{H}_{10})$  in THF, followed by removal of salts and anthracene, led to isolation of  $(\text{Ar}[\text{tBuCH}_2\text{N}])_2(\eta^2\text{-tBu(H)CNAr})\text{TaH}$  as a pale yellow solid in 86% yield.<sup>13</sup> Characterization of  $\text{C}_1$ -symmetric **1** by  $^1\text{H}$  NMR spectroscopy revealed a diagnostic chemical shift for the Ta–H resonance at 17.1 ppm and an absorbance at  $1756\text{ cm}^{-1}$  was observed in the infrared spectrum, in good agreement with related terminal hydride complexes.<sup>14</sup> Further, the solid state structure of **1** (Figure 1) determined by single crystal X-ray diffraction closely resembles the Nb congener.<sup>12a</sup> While complexes containing comparable three-membered Ta–N–C rings have been structurally characterized,<sup>16</sup> **1** appears to be a unique example of an isolated tantalaziridine–hydride species.<sup>17</sup> If stored at  $-35^\circ\text{C}$ , **1** remains stable for months in the solid state. In solution however, **1** undergoes gradual but incomplete conversion (*ca.* 80% after 14 d,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ) to an isomeric terminal hydride complex  $(\text{Ar}[\text{tBuCH}_2\text{N}])_2(\kappa^2\text{-CH}_2\text{C}(\text{Me})_2\text{CH}_2\text{NAr})\text{TaH}$  (**2**, Ta–H:  $^1\text{H}$   $\delta$  19.2 ppm;  $\nu$   $1726\text{ cm}^{-1}$ ), in which the Ta–C of the five-membered metallacycle derives from a *t*Bu residue of an anilide ligand (Scheme 1).<sup>18</sup> Complexes **1** and **2** exist in equilibrium in  $\text{C}_6\text{D}_6$  ( $20^\circ\text{C}$ ,  $K_{\text{eq}} = 3.8$ ),<sup>13</sup> although the mechanistic nature of their interconversion remains unclear. Selective precipitation of **2** from equilibrium mixtures with **1** using cold *n*-pentane allowed for the clean isolation of **2** as a yellow solid in 55% yield; NMR

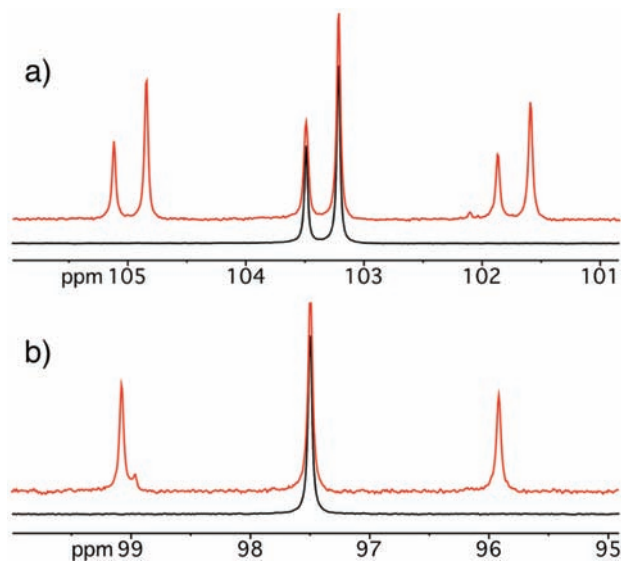


**Figure 1.** ORTEP renderings<sup>15</sup> of **1** (left) and **2** (right) with thermal ellipsoids at 50% probability with selected H atoms omitted for clarity. Selected distances (Å) and angles (deg): **1**: Ta–N1 1.9571(14), Ta–N2 2.0016(15), Ta–N3 1.9907(14), Ta–C17 2.1808(15), N1–C17 1.433(2), N1–Ta–C17 40.07(6), C17–N1–Ta 78.39(9); **2**: Ta–N1 2.077(2), Ta–N2 1.960(2), Ta–N3 1.967(2), Ta–C181 2.207(3), C181–C18 1.536(5), Ta–C181–C18 117.0(2).

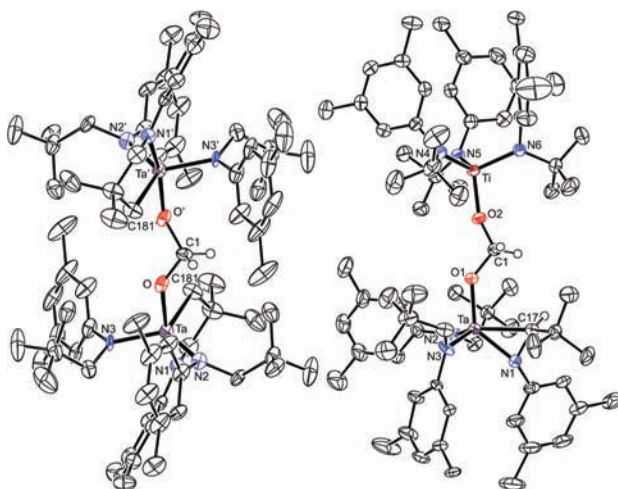
characterization showed the expected  $C_s$ -symmetry of **2** in  $C_6D_6$  solution, while the crystal structure of **2** served to substantiate our spectroscopic assignments (Figure 1).<sup>13</sup> Solution molecular weight measurements<sup>19</sup> on mixtures of **1** and **2** in  $C_6H_6$  were consistent with both hydride complexes retaining their monomeric forms as depicted in Scheme 1.

Exposure of a  $C_6D_6$  solution of **1** to *ca.* 1 atm of  $CO_2$  led to the complete consumption of the starting hydride complex within 10 min, as indicated by  $^1H$  NMR spectroscopy (Scheme 1). Examination of the NMR data from the reaction mixture gave no evidence for the anticipated formate  $(Ar[{}^tBuCH_2]N)_2(\eta^2-{}^iBu(H)CNAr)TaOC(O)H$  but rather showed the presence of two closely related species of low symmetry that appeared both to retain stereogenic tantalaziridine moieties. The ultimate identification of the products as a diastereomeric mixture of methylene diolate complexes,  $\{(Ar[{}^tBuCH_2]N)_2(\eta^2-{}^iBu(H)CNAr)Ta\}_2(\mu-OCH_2O)$  (**3r,m**; *rac*( $C_2$ ): *meso*( $C_s$ ), 1.68:1), was facilitated by DEPT and HSQC experiments which evinced spectroscopic features in keeping with an O–CH<sub>2</sub>–O linkage in each diastereomer.<sup>13</sup> Additionally, prepared via **1** and  $^{13}CO_2$ , **3r,m**- $^{13}C$  manifests a pair of triplets in the  $^{13}C$  NMR spectrum at  $\delta$  103.5 ( $^1J_{CH} = 163.5$  Hz, *meso*) and 103.2 ( $^1J_{CH} = 163.6$  Hz, *rac*), each a signature for a methylene fragment of this type (Figure 2a).<sup>5</sup> Combustion analysis for pale yellow solid **3r,m**, isolated in 94% yield supported this formulation. In accord with **1**, isomeric tantalum hydride complex **2** produced methylene diolate complex **4** upon treatment with  $CO_2$  (Scheme 1, 91% yield). With diagnostic spectroscopic features comparable to those of **3r,m**, this complex exhibits NMR spectra considerably less complex than those of **3r,m** as a consequence of the effective  $C_s$  symmetry of **4** ( $C_6D_6$ , 20 °C).<sup>13</sup> Preparation of **4**- $^{13}C$  from  $^{13}CO_2$  gave the anticipated triplet ( $^1J_{CH} = 158.9$  Hz) in the  $^{13}C$  NMR spectrum (Figure 2b). Pale yellow crystals of **4** suitable for X-ray diffraction studies were grown from  $Et_2O$  at  $-35$  °C. The solid-state structure of **4** revealed geometric parameters consistent with a ‘TaOCH<sub>2</sub>OTa’ core (Figure 3); **4** represents a unique example of a structurally characterized complex wherein a methylene diolate unit spans just two metal centers.<sup>7a,8,20</sup> Despite possessing such an unusual bimetallic tether, complexes **3r,m** and **4** each appear to have appreciable thermal stability, as neither shows signs of decomposition for a period of 48 h at 70 °C (monitored by  $^1H$  NMR,  $C_6D_6$ ).

Given that complexes **3r,m** and **4** arise from net di-insertion of a molecule of  $CO_2$  into two terminal Ta–H bonds, the driving force for their formation can be partially attributed to the generation of two strong Ta–O bonds.<sup>21</sup> Further, it is thought that the bulky anilide frameworks surrounding the methylene diolate bridges



**Figure 2.** Partial  $^{13}C\{^1H\}$  (black) and  $^{13}C$  (red) NMR spectra displaying the  $\{O^{13}CH_2O\}$  region for a) **3r,m**- $^{13}C$ , and b) **4**- $^{13}C$ .



**Figure 3.** ORTEP renderings<sup>15</sup> of **4** (left) and **5**·2.5 $C_5H_{12}$  (right) with thermal ellipsoids at 50% probability. Selected H atoms and the pentane solvates in **5**·2.5 $C_5H_{12}$  have been omitted for clarity. Selected distances (Å) and angles (deg): **4**: Ta–O 1.929(5), Ta–C181 2.190(8), O–C1 1.408(17), C1–O–Ta 142.3(7), O–C1–O' 111.4(10); **5**·2.5 $C_5H_{12}$ : Ta–C17 2.165(4), Ta–N1 1.962(3), N1–C17 1.438(5), Ta–O1 1.917(2), O1–C1 1.409(4), Ti–O2 1.810(3), O2–C1 1.395(4), C1–O–Ta 138.2(2), O2–C1–O1 109.7(3), C1–O2–Ti 154.7(3).

confer kinetic stability to the observed products **3r,m** and **4**. As the likely reaction course in each case involves the reduction of a  $L_nTaOC(O)H$  intermediate by an additional Ta–H complex, we endeavored to find experimental support for this supposed pathway.<sup>2,3,5,7</sup> Ultimately, these efforts served to underscore a marked tendency for each of the starting hydrides **1** and **2** to react rapidly with  $CO_2$  to form their respective methylene diolate products, **3r,m** and **4**. Variances in reaction conditions (e.g., stoichiometry, temperature) meant to bias formation of the putative formate intermediate  $(Ar[{}^tBuCH_2]N)_2(\eta^2-{}^iBu(H)CNAr)TaOC(O)H$  have been rather unsuccessful. Even the treatment of **1** in the solid state with  $CO_2$  produced the target formate in only 13% yield, with the remainder of the reaction mixture identified as **3r,m** (quantified by  $^1H$  NMR after 24 h). Turning to a lighter congener of **1** we found that our previously reported niobaziridine–hydride,<sup>12a</sup> upon exposure to *ca.* 0.6 equiv of  $CO_2$ , cleanly produced a diastereomeric

mixture of methylene diolate complexes analogous to **3r,m**,  $\{(\text{Ar}[\text{BuCH}_2\text{N}]_2(\eta^2\text{-Bu(H)CNAr})\text{Nb})_2(\mu\text{-OCH}_2\text{O})\}$  as a brown powder in 93% yield (*rac:meso*, *ca.* 1:1).<sup>13</sup> In the presence of excess CO<sub>2</sub>, however, the Nb–H complex reacts less selectively than its Ta counterpart, and this property was exploited for the definitive spectroscopic identification of Nb-formate  $(\text{Ar}[\text{BuCH}_2\text{N}]_2(\eta^2\text{-Bu(H)CNAr})\text{NbOC(O)H}$  (up to 87% NMR yield).<sup>13</sup> Experiments addressing reactivity differences of these Ta and Nb metallaziridine complexes are ongoing.

Tantalaziridine–hydride **1** was treated with alternative carbonyl-containing substrates that were anticipated to undergo single insertion reactions to produce species reminiscent of the OCH<sub>2</sub>O complexes described above. Along these lines, the reaction between **1** and the organic formate <sup>t</sup>BuOC(O)H resulted in the isolation of colorless crystals of  $(\text{Ar}[\text{BuCH}_2\text{N}]_2(\eta^2\text{-Bu(H)CNAr})\text{TaOCH}_2\text{O}^t\text{Bu}$  (82% yield), which has been characterized crystallographically.<sup>13</sup> The spectroscopic and structural features associated with the ‘OCH<sub>2</sub>O’ segment of this complex are consistent with related complexes reported herein. A related insertion product was cleanly isolated upon workup of a reaction between **1** and <sup>t</sup>BuNCO; an X-ray diffraction study of pale yellow crystals of  $(\text{Ar}[\text{BuCH}_2\text{N}]_2(\eta^2\text{-Bu(H)CNAr})\text{TaOC(H)N}^t\text{Bu}$  (64% yield) affirmed our spectroscopic assignments.<sup>13,22</sup> Additional studies centered on the reduction of a preformed metalloformate with Ta–H complex **1**; the combination of **1** and  $(\text{Ar}[\text{Bu}]_3\text{TiOC(O)H})^{23}$  resulted in the production of the heterobimetallic methylene diolate complex  $(\text{Ar}[\text{BuCH}_2\text{N}]_2(\eta^2\text{-Bu(H)CNAr})\text{TaOCH}_2\text{OTi}(\text{N}^t\text{Bu})\text{Ar}_3$  (**5**, Scheme 1). Complex **5** was isolated as pale orange crystals (75% yield) and characterized spectroscopically and crystallographically (Figure 3). The <sup>13</sup>C DEPT spectrum of **5** displays a methylene resonance at 101.7 ppm, while the C<sub>1</sub>-symmetry for this complex renders the hydrogens of the ‘OCH<sub>2</sub>O’ moiety diastereotopic. In the solid-state structure for **5**, the metrical parameters within the Ta coordination sphere mirror those of the insertion products from <sup>t</sup>BuOC(O)H and <sup>t</sup>BuNCO,<sup>13</sup> while the titanium trisanilide portion is in accord with previously reported complexes of related makeup.<sup>23,24</sup> The M–O–C angle is considerably more obtuse (*ca.* 16°) in the case of M = Ti than for M = Ta, which may reflect the increased steric demands from the ligands in the Ti coordination sphere.

In summary, the synthesis and definitive characterization of complexes **3r,m** (and the Nb variants) as well as **4** establish the feasibility of the formation of methylene diolate products from CO<sub>2</sub> and two terminal transition-metal hydrides. Combined with the mixed Ta,Ti complex **5**, this class of complexes effectively stabilizes an unusual H<sub>2</sub>CO<sub>2</sub><sup>2-</sup> ligand between two metal centers. Current efforts are aimed at the chemical elaboration of this central bridging unit into reduced C<sub>1</sub> derivatives, ideally whereby the starting tantalum hydride is regenerated.

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**Supporting Information Available:** Complete experimental details, characterization data, a full author list for ref 1c, and crystallographic details, including crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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