

## Hydrogenation of Carbon Dioxide and Aryl Isocyanates by a Tetranuclear Tetrahydrido Yttrium Complex. Isolation, Structures, and CO<sub>2</sub> Insertion Reactions of Methylene Diolate and $\mu_3$ -Oxo Yttrium Complexes

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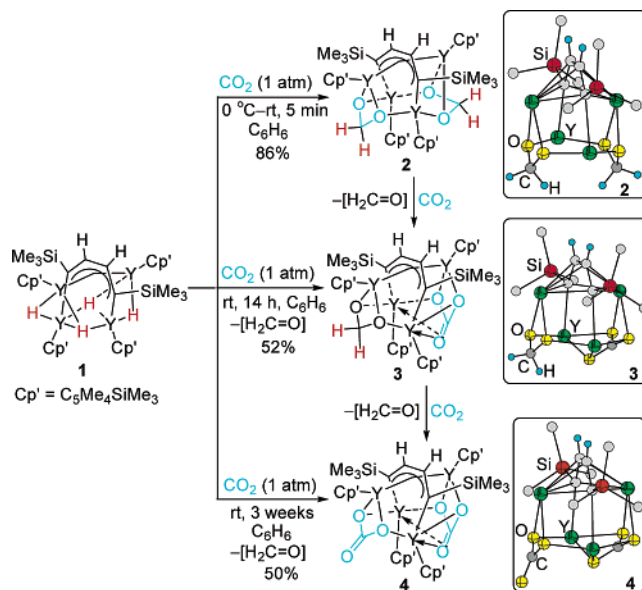
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The use of carbon dioxide (CO<sub>2</sub>) as a C1 building block for chemical synthesis has received continued interest, not only because of the value of the products but also because of its potential contribution to the reduction of the greenhouse gas.<sup>1</sup> The homogeneous hydrogenation of CO<sub>2</sub> by transition metal hydrides is among the most extensively studied CO<sub>2</sub>-transformation reactions, which usually yields metal formates as a key intermediate that can lead to catalytic formation of formic acid or its derivatives under appropriate conditions. Further hydrogenation of a metal formate species could, in principle, afford a methylene diolate. The latter is believed to be a key intermediate in the industrial catalytic hydrogenation of CO<sub>2</sub> to methanol over heterogeneous catalysts.<sup>2</sup> However, although a large number of metal formate complexes have been isolated and structurally characterized, observation of a methylene diolate species in either homogeneous or heterogeneous hydrogenation of CO<sub>2</sub> remained scarce,<sup>2a,3</sup> and none were structurally characterized. The reaction behavior of a methylene diolate species toward CO<sub>2</sub> remained almost unknown.

During our recent studies on polyhydrido rare earth metal complexes,<sup>4</sup> we obtained a tetranuclear tetrahydrido yttrium complex [(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Y( $\mu$ -H)]<sub>4</sub>(Me<sub>3</sub>SiCC(H)C(H)CSiMe<sub>3</sub>) (**1**), which possesses a novel butene-tetraanion ligand (a six- $\pi$ -electron system) bonding to all four Y atoms to form a robust tetranuclear Y skeleton.<sup>4a</sup> In this Communication, we report the reactions of this new polyhydrido complex with CO<sub>2</sub> and aryl isocyanates, from which structurally characterizable methylene diolate and oxo yttrium complexes were isolated, respectively. The CO<sub>2</sub> insertion reactions of the resulting methylene diolate and oxo complexes are also described. Most of these reactions are unprecedented and could shed new light on the mechanism of the hydrogenation of CO<sub>2</sub> on heterogeneous catalysts.

The reaction of the tetrahydrido yttrium complex **1** with an atmosphere of CO<sub>2</sub> occurred rapidly between 0 °C and room temperature, which afforded the corresponding bis(methylene diolate) complex **2** as yellow crystals in 86% yield (Scheme 1).<sup>5</sup> The formation of the methylene diolate species ( $\delta$  5.74, 6.27) along with the disappearance of the hydride species ( $\delta$  4.39) in **1**<sup>4a</sup> could be easily monitored by the <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub>, while formation of a formate species was not observed. The overall structure of the tetranuclear yttrium skeleton in **2** is very similar to that of **1** as shown by X-ray analysis. The bond distances of the C–O bonds in the methylene diolate units (1.392(4)–1.410(4) Å) are significantly longer than those found in formate complexes such as [CpTi(OCHO)]<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>) (1.21(1)–1.30(2) Å),<sup>6a</sup> Cp<sub>2</sub>Zr(OCHO)( $\mu$ -H)( $\mu$ -N<sup>t</sup>Bu)IrCp\* (1.208(8)–1.276(8) Å),<sup>6b</sup> and Ru(dmpe)<sub>2</sub>(OCHO)H (1.204(9)–1.226(11) Å)<sup>6c</sup> and can be viewed as C–O single bonds. Each oxygen atom of the methylene diolate units is

**Scheme 1.** One-Step Reduction of CO<sub>2</sub> into Methylene Diolate Species and the Following CO<sub>2</sub> Insertion Reactions<sup>a</sup>



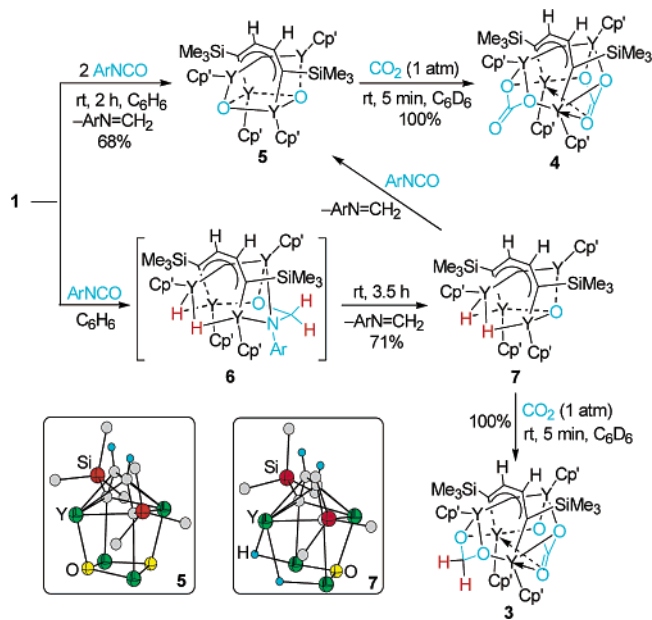
<sup>a</sup> C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub> ligands in the X-ray structures have been omitted for clarity.

asymmetrically bonded to two Y atoms, with one Y–O bond being significantly shorter than the other (cf. 2.154(2)–2.166(2) vs 2.330(2)–2.359(2) Å), but both being comparable with those reported for the Y–OH bridging bonds in [Cp<sub>2</sub>Y( $\mu$ -OH)]<sub>2</sub>(PhCCPh) (2.33(2) and 2.36(2) Å).<sup>8</sup> These data strongly suggest that both C–O double bonds of CO<sub>2</sub> have been completely reduced into C–O single bonds. This is in sharp contrast with what was observed previously for other transition metal polyhydrido complexes such as [CpTi( $\mu$ -H)]<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>),<sup>6a</sup> Cp<sub>2</sub>Zr(H)( $\mu$ -H)( $\mu$ -N<sup>t</sup>Bu)IrCp\*,<sup>6b</sup> Ru(dmpe)<sub>2</sub>H<sub>2</sub>,<sup>6c</sup> and Mo(dmpe)<sub>2</sub>H<sub>4</sub>,<sup>7</sup> which yielded either bis(formate),<sup>6a,7</sup> mixed hydrido/formate,<sup>6b,c</sup> or mixed hydrido/carbonate complexes,<sup>7</sup> without formation of a methylene diolate species being observed.

When the reaction of **1** with CO<sub>2</sub> was carried out at room temperature for 14 h, the mixed methylene diolate/carbonate complex **3** was isolated as orange-yellow crystals in 52% yield (Scheme 1). The reaction of **2** with CO<sub>2</sub> also afforded **3** similarly. Apparently, **3** must be formed by insertion of one molecule of CO<sub>2</sub> into a Y–O bond of the diolate units in **2**, followed by possible release of formaldehyde.<sup>9</sup> Further insertion of CO<sub>2</sub> into the methylene diolate unit in **3** was also possible, albeit much more slower, yielding the bis(carbonate) complex **4** (Scheme 1). As far as we are aware, this is the first example of insertion of CO<sub>2</sub> into a methylene diolate species.<sup>2,3</sup> Complexes **2**–**4** were stable under an inert atmosphere.

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**Scheme 2.** Formation and CO<sub>2</sub> Insertion Reactions of  $\mu_3$ -Oxo Yttrium Complexes (Ar = 1-Naphthyl)<sup>a</sup>



<sup>a</sup> C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub> ligands in the X-ray structures have been omitted for clarity.

To see how complex **1** would behave toward an isocyanate compound, a commonly accepted model of CO<sub>2</sub> with respect to reaction patterns,<sup>10</sup> reactions of **1** with some aryl isocyanates were carried out. The reaction of **1** with 2–2.5 equiv of 1-naphthyl isocyanate in benzene afforded the di- $\mu_3$ -oxo complex **5** (Y–O = 2.176(2)–2.187(2) Å) as red crystals in 68% yield, instead of a bis(methyleneolate/amido) analogue of **2** (Scheme 2). When 1 equiv of 1-naphthyl isocyanate was used, the mixed hydrido/oxo complex **7** (Y–O = 2.141(3)–2.229(3) Å; Y–H = 2.04(6)–2.36(6) Å) was obtained in 71% isolated yield. Addition of 1 equiv of 1-naphthyl isocyanate to **7** in C<sub>6</sub>D<sub>6</sub> yielded **5** instantly and quantitatively. In all these reactions, formation of *N*-naphthyl imine C<sub>10</sub>H<sub>7</sub>N=CH<sub>2</sub> as a coproduct was observed by <sup>1</sup>H NMR spectrum. A mono(methyleneolate/amido) species such as **6** could be an intermediate at the early stage of the reaction.<sup>11</sup> More remarkably, exposure of the di- $\mu_3$ -oxo complex **5** or the mixed hydrido/oxo complex **7** to an atmosphere of CO<sub>2</sub> at room temperature led to immediate formation of the bis(carbonate) complex **4** or the mixed methylene diolate/carbonate complex **3**, respectively (Scheme 2), demonstrating that the  $\mu_3$ -oxo units in **5** and **7** are even as active as a hydrido species toward CO<sub>2</sub>. Although formation of metal oxo complexes such as [Cp<sub>2</sub>ZrCl]<sub>2</sub>( $\mu$ -O),<sup>2a,3a,c,12</sup> [Cp<sub>2</sub>Zr( $\mu$ -O)]<sub>3</sub>,<sup>13</sup> and [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>U]<sub>2</sub>( $\mu$ -O)<sup>3b</sup> has been observed in various CO<sub>2</sub> reduction reactions, insertion of CO<sub>2</sub> into such a metal oxo species has not been reported previously. The present reactions of **5** and **7** with CO<sub>2</sub> may provide, at a molecular level, the first piece of evidence for interactions of CO<sub>2</sub> with metal oxides.<sup>2b,c,14</sup>

In summary, we have demonstrated that carbon dioxide can be easily reduced to structurally characterizable methylene diolate species (**2**) by a polyhydrido yttrium complex **1**, while similar reactions of an aryl isocyanate with **1** lead to formation of  $\mu_3$ -oxo complexes such as **5** and **7**. Both the methylene diolate and the oxo complexes can undergo CO<sub>2</sub> insertion reactions to give the corresponding carbonate complexes. These reactions not only afford a new series of polynuclear yttrium complexes having novel structures but also shed new light on the mechanistic aspects of the heterogeneous hydrogenation of CO<sub>2</sub>. The unusually high reactivity of the polynuclear  $\mu_3$ -oxo yttrium complexes **5** and **7**

could also make them novel molecular models for study of metal oxide-supported catalysts.<sup>14–16</sup>

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**Supporting Information Available:** Experimental details, ORTEP drawings, and tables of crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles for **2–5** and **7** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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