



# Mechanistic aspects of CO<sub>2</sub> activation mediated by phenyl yttrium cation: A combined experimental/theoretical study



Marjan Firouzbakht, Maria Schlangen, Martin Kaupp, Helmut Schwarz\*

Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

## ARTICLE INFO

### Article history:

Received 14 August 2015

Revised 10 September 2015

Accepted 16 September 2015

Available online 17 October 2015

### Keywords:

Bond activation

Carbon dioxide

Yttrium phenyl cation

C–C bond formation

Decarbonylation

ESI-MS

## ABSTRACT

The thermal reactions of the per-deuterated yttrium phenyl cation with carbon dioxide have been investigated experimentally by using electrospray-ionization mass spectrometry and computationally by means of density functional theory. The process proceeds by migratory insertion under C–C bond formation followed, to some extent, by decarbonylation. Labeling experiments with C<sup>18</sup>O<sub>2</sub> confirm the origin of the oxygen incorporated in both productions. With regard to the mechanisms, the calculations reveal that the benzoate salt of yttrium corresponds to the most stable isomer. While extrusion of CO starting from this ion, or from two isomeric encounter complexes, is hampered by kinetic barriers, decarbonylation is accessible under thermal conditions from other intermediates which are generated after insertion of CO<sub>2</sub> into the Y–C bond of [YC<sub>6</sub>D<sub>5</sub>]<sup>+</sup>.

© 2015 Elsevier Inc. All rights reserved.

## 1. Introduction

Owing to human activities, the anthropogenic component in atmospheric CO<sub>2</sub> is steadily increasing. One way to make sensible use of the CO<sub>2</sub> emissions is to explore and employ efficient methods by which CO<sub>2</sub> is converted into more valuable chemicals [1–3]. Not surprisingly, carbon dioxide is rightly viewed as an optimal C1 source in organic synthesis due to its abundance, low cost, and nontoxicity [4,5], in contrast to other C1 carbon sources such as phosgene or carbon monoxide [6]. Although carbon dioxide is thermodynamically very stable and kinetically rather inert, CO<sub>2</sub> activation with suitably reactive reagents is feasible [3], and there exist quite a few methodologies to activate and transform CO<sub>2</sub> into value-added chemicals. One of them employs high-energy starting materials such as organometallics or highly-strained ring compounds [6,7]. Also, transition-metal complexes have served as appropriate candidates for the activation of CO<sub>2</sub> [8–10] on the ground that some of these metals are capable to change easily their valence state and mode of coordination and are thus capable to initiate insertion reactions [11]. With regard to the elucidation of strictly molecular-level based reaction mechanisms, gas-phase experiments proved useful as they are not obscured by ill-defined effects such as the role of solvents, aggregation phenomena, or counter-ion effects. In recent years, both bare and

ligated-metal ions have been investigated and probed with respect to the activation of CO<sub>2</sub>. For instance, oxygen-atom transfer from CO<sub>2</sub> to bare, early transition-metal cations has been observed in the gas phase reflecting the high oxophilicity of these species [12,13]; for the same reason, a favorable interaction of CO<sub>2</sub> with heteronuclear oxide clusters [MMgO]<sup>+0/-</sup> (M = Sc–Zn) possessing early transition metals has been predicted in a recent theoretical study [14]. Further, the ligand-controlled CO<sub>2</sub> activation by [LTiH]<sup>+</sup> (L = Cp<sub>2</sub>, O) proceeds via CO<sub>2</sub> insertion and, in the case of [OTiH]<sup>+</sup>, subsequent CO extrusion occurs [15]. Likewise, the carbene complex [Ta(CH<sub>2</sub>)]<sup>+</sup> in its reaction with carbon dioxide forms the acetic acid equivalent CH<sub>2</sub>CO, thus providing a rare example for the stoichiometric coupling of methane and carbon dioxide [16].

A prominent strategy for CO<sub>2</sub> activation involves the insertion of CO<sub>2</sub> into a metal–hydrogen or metal–carbon bond [15,17–25], and the greater oxophilicity of early transition metals can accelerate this reaction by providing a stronger M–OCO interaction [23]. Here, we describe the reactivity of the cationic yttrium phenyl complex toward carbon dioxide in the gas phase as investigated by using electrospray ionization mass spectrometry (ESI-MS) in conjunction with density functional theory (DFT); we aim at understanding mechanistic aspects of the CO<sub>2</sub> activation promoted by an insertion process of an early transition-metal complex at a strictly molecular level. Although yttrium exists mainly in the +3 oxidation state, also Y<sup>2+</sup> complexes have been isolated [26]; these complexes are supposed to be highly reactive. Ligated group 3 transition-metal ions LM<sup>+</sup>, with L corresponding to an anionic

\* Corresponding author.

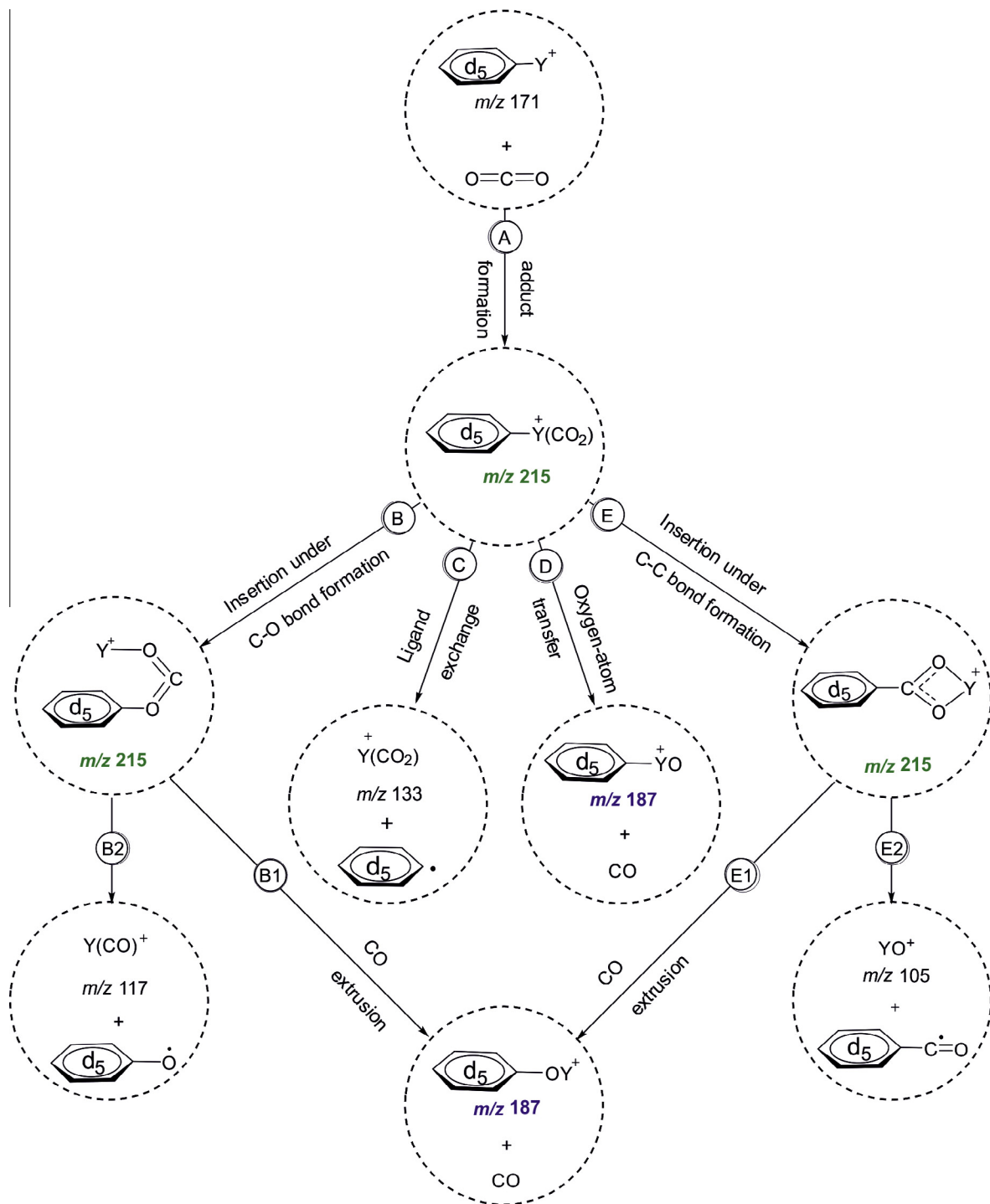
E-mail addresses: [Martin.Kaupp@tu-berlin.de](mailto:Martin.Kaupp@tu-berlin.de) (M. Kaupp), [Helmut.Schwarz@tu-berlin.de](mailto:Helmut.Schwarz@tu-berlin.de) (H. Schwarz).

ligand, possess only one unpaired valence electron at the metal center; thus, the traditional oxidative addition pathway will be disfavored as compared with, e.g., migratory insertion processes [27–29].

## 2. Experimental section and computational details

The experiments were performed using a VG Bio-Q mass spectrometer of QHQ configuration (Q: quadrupole; H: hexapole) equipped with an electrospray-ionization (ESI) source, as described

in detail previously [30]. To avoid the mass overlap between the yttrium phenyl cation  $[Y(C_6H_5)]^+$  and the isobaric  $^{13}C$  signal of the yttrium benzyne cation  $[Y(C_6H_4)]^+$ , deuterated  $[Y(C_6D_5)]^+$  has been utilized instead of  $[Y(C_6H_5)]^+$ . To generate  $[Y(C_6D_5)]^+$ , a millimolar solution of yttrium(III) acetate hydrate and perdeuterated benzoic acid in a methanol/water mixture was used for ESI; the precursor ion is formed presumably by endothermic decarboxylation in the ion source. Methanol, water, deuterated benzoic acid, yttrium(III) acetate hydrate,  $CO_2$ , and  $C^{18}O_2$  were obtained from Sigma–Aldrich and utilized without further purification. The solution has been introduced into the mass spectrometer



**Scheme 1.** Possible routes for the reaction of  $[Y(C_6D_5)]^+$  with carbon dioxide.

Download English Version:

<https://daneshyari.com/en/article/6455951>

Download Persian Version:

<https://daneshyari.com/article/6455951>

[Daneshyari.com](https://daneshyari.com)