

Internal carbon monoxide exchange and CO dissociation in cobalt carbonyl carbene complexes. A density functional study

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Dedicated to Professor Gyula Pályi on the occasion of his 70th birthday.

Abstract

Structures, intramolecular CO-exchanges, and CO-dissociation of ethoxycarbonylcarbene-bridged dicobalt carbonyl complexes $[\mu_2\text{-}\{\text{ethoxycarbonyl(methylene)}\}\text{-}\mu_2\text{-(carbonyl)-bis(tricarbonyl-cobalt) (Co-Co)}]\text{Co}_2(\text{CO})_7(\text{CHCO}_2\text{Et})$ (**1**) and $[\text{di-}\mu_2\text{-}\{\text{ethoxycarbonyl(methylene)}\}\text{-bis(tricarbonyl-cobalt) (Co-Co)}]\text{Co}_2(\text{CO})_6(\text{CHCO}_2\text{Et})_2$ (**2**) were investigated by utilizing the density functional theory at the B3LYP/6-31G(d) level. In the lowest energy isomer of **1** the equatorial carbonyl group *cis* to the bridging ethoxycarbonylcarbene is prone to dissociate resulting in a coordinative unsaturated $\text{Co}_2(\text{CO})_6(\text{CHCO}_2\text{Et})$ complex stabilized by an intramolecular cobalt–oxygen orbital interaction. Several mechanisms describing the fluxional behavior of **1** and **2** were found. It was found that the internal transformation designated as ‘tripodal rotation’ is responsible for the temperature-dependent broadening of the ^{13}C NMR signals for compound **2**. For **1** the tripodal rotation needs to be taken into account as well, however an even faster internal CO-exchange allows for the carbonyls to switch between the terminal and bridging positions. In the coordinative unsaturated complexes $\text{Co}_2(\text{CO})_6(\text{CHCO}_2\text{Et})$ and $\text{Co}_2(\text{CO})_5(\text{CHCO}_2\text{Et})_2$ the CO ligands show also many variations of internal rearrangements. In complex **1** the effect of the rotation of the $\text{C}_{\text{carbene}}\text{--C}_{\text{carbonyl}}$ bond on the energy of the rotamers was also examined.

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Keywords: Cobalt; Carbene; Carbon-monoxide; Fluxionality; Density functional theory

1. Introduction

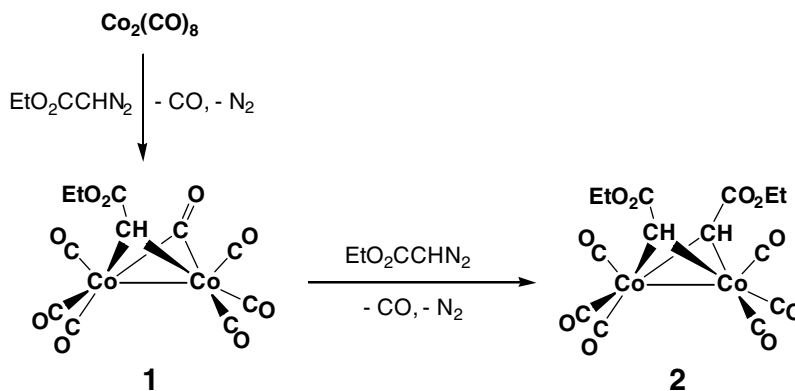
The isolable and spectroscopically characterized ethoxycarbonylcarbene-bridged dicobalt complexes $\text{Co}_2(\text{CO})_7(\text{CHCO}_2\text{Et})$ (**1**) and $\text{Co}_2(\text{CO})_6(\text{CHCO}_2\text{Et})_2$ (**2**) (Scheme 1) were found to be intermediates in the $\text{Co}_2(\text{CO})_8$ -catalyzed carbonylation of ethyl diazoacetate to malonic acid derivatives [1]. Both complexes show fluxional behavior deduced from their temperature-dependent ^{13}C NMR spectra. Under an atmosphere of ^{13}CO , the bridging and terminal CO ligands of **1** exchange with ^{13}CO at the same rate. As a contrast, complex **2** does not exchange its CO ligands

for ^{13}CO at all [2]. In order to understand the different chemical behavior of complexes **1** and **2** we investigated their geometries, the bond strength of the ligands, and the energy of the various structural isomerizations by computational methods. For comparison the $(\mu\text{-CH}_2)$ analogues of **1** and **2** were also considered.

2. Computational details

All the geometries were calculated without any symmetry constraints using the B3LYP hybrid density functional method [3] with the 6-31G* basis set [4] augmented with an f-type polarization function on cobalt ($\zeta_f = 0.8$). The initial structures for geometry optimizations were obtained by Monte Carlo conformational analyses using the Spartan

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Scheme 1.

'04 program package [5] with the MMFF force field and the PM3(tm) parameter set. Full geometry optimizations at DFT level were taken on the lowest energy conformers and the most stable ones were considered throughout this study.

For all stationary points the Hessian was evaluated in order to characterize the genuine minima (no imaginary frequency) and the transition states (1 imaginary frequency). Zero-point vibrational energy and thermal correction for the Gibbs free energy (at 298 K) have been

estimated on the basis of the frequency calculations at the optimization level. Intrinsic reaction coordinate (IRC) analyses [6] were carried out throughout the reaction pathways to confirm that the stationary points are smoothly connected to each other. Natural population analyses and natural bond orbital (NBO) analyses [7] were performed at the same level of theory as the one used for geometry optimization. For the calculations the PC GAMESS 7.0 [8] software, a modified version of the GAMESS-US [9] program was used.

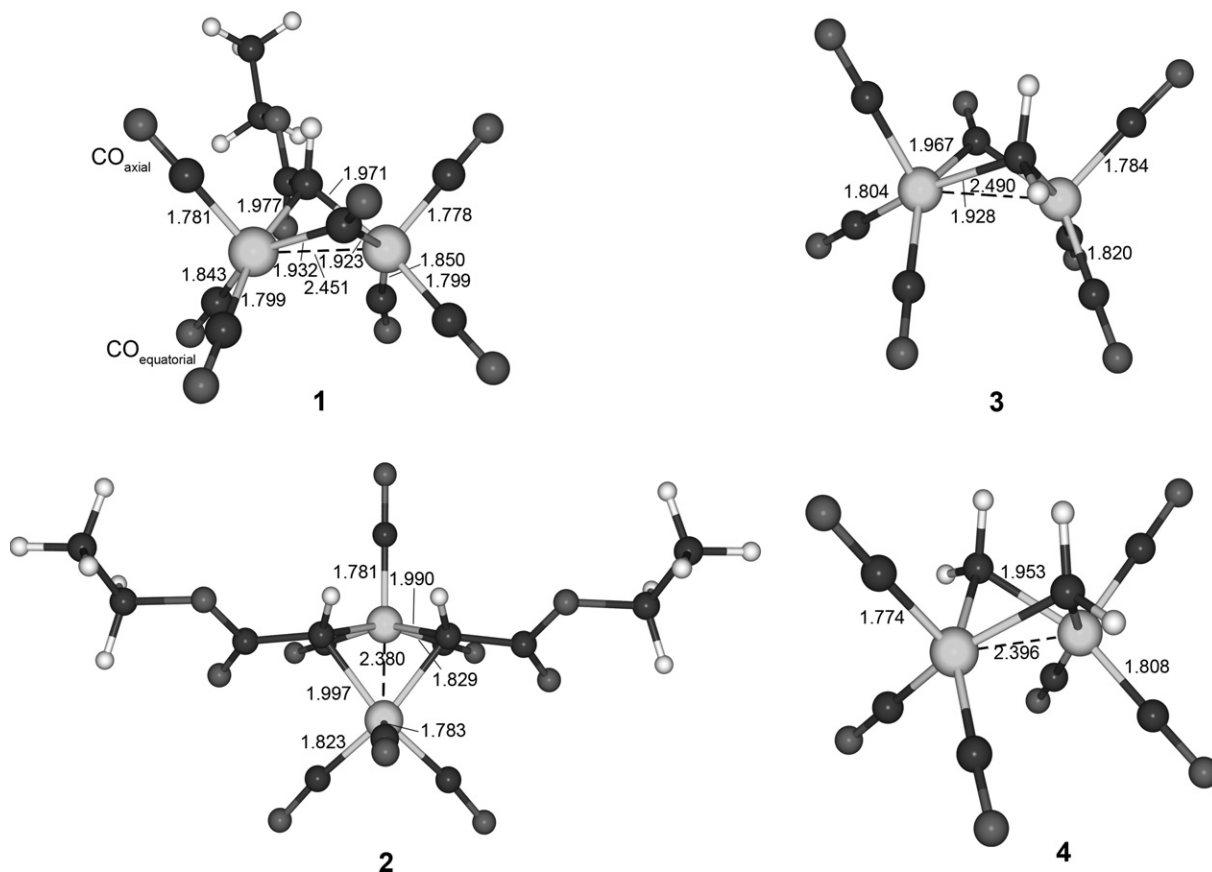


Fig. 1. Optimized geometries of the carbene–cobalt complexes $\text{Co}_2(\text{CO})_7(\text{CHCO}_2\text{Et})$ (**1**), $\text{Co}_2(\text{CO})_6(\text{CHCO}_2\text{Et})_2$ (**2**), $\text{Co}_2(\text{CO})_7(\text{CH}_2)$ (**3**), and $\text{Co}_2(\text{CO})_6(\text{CH}_2)_2$ (**4**).

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