



Carbonyl versus butadiene dissociation in binuclear butadiene cobalt carbonyls

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ABSTRACT

Dicobalt octacarbonyl is known to react with diolefins to give substitution products of the types (diene)₂Co₂(CO)₆ and (diene)₂Co₂(CO)₄. The butadiene derivatives (C₄H₆)Co₂(CO)_n (*n* = 6, 5, 4, 3, 2) have been investigated by density functional theory using the B3LYP and BP86 methods. The lowest energy (C₄H₆)Co₂(CO)_n (*n* = 6, 5, 4) structures have bridging CO groups and terminal butadiene ligands. For the (C₄H₆)Co₂(CO)₆ and (C₄H₆)Co₂(CO)₅ structures the Co–Co distances of ~2.5 Å suggest formal single bonds. However, for the lowest energy (C₄H₆)Co₂(CO)₄ structure the significantly shorter Co≡Co distance of ~2.3 Å suggests the formal triple bond required to give the cobalt atom the favored 18-electron configuration. Bridging butadiene ligands are also found in (C₄H₆)Co₂(CO)_n structures including all of the lowest energy (C₄H₆)Co₂(CO)₃ and (C₄H₆)Co₂(CO)₂ structures. Both the B3LYP and BP86 methods predict butadiene dissociation from (C₄H₆)₂Co₂(CO)₄ to be energetically favored over CO dissociation by ~8 kcal/mol. For (C₄H₆)₂Co₂(CO)_n (*n* = 3, 2) the BP86 method predicts CO dissociation to be favored energetically over butadiene dissociation by ~8 kcal/mol. However, the B3LYP method predicts essentially equal CO and butadiene dissociation energies within ~1 kcal/mol from (C₄H₆)₂Co₂(CO)_n (*n* = 3, 2).

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1. Introduction

The chemistry of butadiene metal carbonyls is more than 80 years old. Thus the first description of a butadiene metal carbonyl was the 1930 report by Reihlen and coworkers [1] of the reaction of butadiene with Fe(CO)₅ at elevated temperatures in an autoclave to give butadiene-iron tricarbonyl as a stable distillable liquid freezing slightly below room temperature. The first binuclear butadiene metal carbonyl derivative was 1961 report of bis(butadiene)dicobalt tetracarbonyl by Fischer et al. [2] as a product from the photolysis of Co₂(CO)₈ with butadiene. The tetrahapto bonding of the butadiene ligands in these metal carbonyl complexes, anticipated from consideration of the 18-electron rule [3,4] (Fig. 1), was confirmed by X-ray crystallography in 1963 by Mills and Robinson [5] for (η⁴-C₄H₆)Fe(CO)₃ and in 1966 by Jones and Maslen [6] for (η⁴-C₄H₆)₂Co₂(CO)₄. Shortly after the discovery of (C₄H₆)₂Co₂(CO)₄ Winkhaus and Wilkinson [7] synthesized (diene)₂Co₂(CO)₄ and (diene)Co₂(CO)₆ derivatives from other diolefins such as norbornadiene, 1,3-cyclohexadiene, and 2,3-dimethylbutadiene by reactions of Co₂(CO)₈ with the corresponding dienes.

The (diene)₂Co₂(CO)₄ derivatives have two bridging CO groups. They may be regarded as substitution products of the doubly bridged Co₂(CO)₆(μ-CO)₂ structure of dicobalt octacarbonyl in which four terminal CO groups are replaced pairwise by the diolefin ligands. Winkhaus and Wilkinson [7] also prepared the first examples of (diene)Co₂(CO)₆ derivatives in which only one pair of terminal CO ligands in Co₂(CO)₆(μ-CO)₂ is replaced by the diolefin ligand.

The (diene)₂Co₂(CO)₂(μ-CO)₂ derivatives are significant in several ways. Thus they are the only examples of L₂M₂(CO)₄ derivatives containing acyclic hydrocarbon ligands that have been synthesized. In addition they contain two different ligands, namely CO and the diolefin, that are both stable in the free state and volatile. Both CO and the diene have π-acceptor properties. Thus CO is among the strongest π-acceptor ligands. The π-acceptor properties of butadiene are weaker than those of CO. Nevertheless the butadiene ligand can accept electron density from the metal atom to which it is bonded into its otherwise empty π* antibonding orbitals.

Most metal carbonyl complexes containing other ligands undergo preferential loss of CO rather than other ligands upon heating, photolysis, or reactions with nucleophiles. However, butadiene metal carbonyl derivatives can, in principle, undergo dissociation of either their CO or butadiene ligands under such conditions, since butadiene, like CO, is a volatile stable compound and hence a good leaving group. The binuclear butadiene cobalt carbonyls are good model systems to investigate the relative energetics of CO versus butadiene elimination. In a previous paper [8] we have used density

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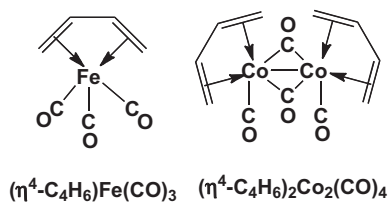
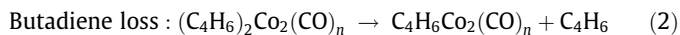
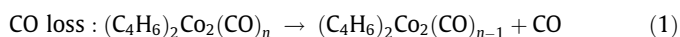


Fig. 1. The tetrahapto butadiene derivatives of iron and cobalt carbonyls.

functional theory to determine the structures and energetics of binuclear butadiene cobalt carbonyls having two butadiene ligands per Co_2 unit, namely $(\text{C}_4\text{H}_6)_2\text{Co}_2(\text{CO})_n$ derivatives. In order to have data to compare the energies of butadiene and CO losses from such binuclear $(\text{C}_4\text{H}_6)_2\text{Co}_2(\text{CO})_n$ derivatives, similar information on the structure and energetics of binuclear butadiene cobalt carbonyls having only one butadiene ligand per Co_2 unit, namely $\text{C}_4\text{H}_6\text{Co}_2(\text{CO})_n$, is required. The relative energies required for CO and butadiene loss can then be determined from the energies of reactions of the following types:



This paper presents a density functional theory study of the $\text{C}_4\text{H}_6\text{Co}_2(\text{CO})_6$ derivatives produced by butadiene loss from $(\text{C}_4\text{H}_6)_2\text{Co}_2(\text{CO})_n$ as well as a summary of the thermochemistry for reactions represented by the above Eqs. (1) and (2).

2. Theoretical methods

Double- ζ plus polarization (DZP) basis sets were used in this work. For carbon and oxygen, one set of pure spherical harmonic d functions is added with orbital exponents $\alpha_d(\text{C})=0.75$ and $\alpha_d(\text{O})=0.85$ to the Huzinaga–Dunning standard contracted DZ sets, and they are designated (9s5p1d/4s2p1d) [9,10]. For hydrogen, a set of p polarization functions, $\alpha_p(\text{H})=0.75$, is added to the Huzinaga–Dunning DZ sets. For cobalt, in our loosely contracted DZP basis set, the Wachters' primitive set is used but augmented by two sets of p functions and one set of d functions, contracted following Hood et al., and designated (14s11p6d/10s8p3d) [11,12].

Electron correlation effects have been included by employing density functional theory (DFT) methods, which have been suggested as a practical and effective computation tool, especially for organometallic compounds [13–19]. Two DFT methods were used in our present study. The first method is the hybrid B3LYP method, which combines Becke's three parameter functional (B3) with the Lee, Yang, and Parr (LYP) correlation functional [20,21]. The second method is the BP86 method, which marries Becke's 1988 exchange functional (B) with Perdew's 1986 correlation functional [22,23]. Since the B3LYP and the BP86 methods are constructed in very different ways, confident predictions can be made when these two very different DFT methods agree. For most of the properties investigated in this work, both methods agree quite well. However, in the present paper, the B3LYP and the BP86 methods predict different relative energies for different spin states. This is not surprising, since Reiher and co-workers [24] have found that B3LYP always favors the high-spin state and BP86 favors the low-spin state for a series of Fe(II) complexes. The real relative energies should lie between the B3LYP and BP86 predictions.

The geometries of all structures were fully optimized using both the B3LYP/DZP and BP86/DZP methods. The harmonic vibrational frequencies were determined at the same levels by evaluating

analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All computations were carried out using the Gaussian 09 program [25], in which the fine grid (75, 302) is the default for evaluating integrals numerically, and the tight designation is the default for the energy convergence.

In the search for minima using the DFT methods, low-magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations. For this reason, imaginary vibrational frequencies with a magnitude of less than $50i \text{ cm}^{-1}$ are considered questionable and are given less weight in the analysis [26,27]. Therefore, we do not always follow such low imaginary vibrational frequencies.

The $(\text{C}_4\text{H}_6)\text{Co}_2(\text{CO})_n$ structures are shown in Figs. 2–6, and designated as **aX – b** where **a** is the number of CO groups, **X** relates to the spin state (**S** = singlet and **T** = triplet), and **b** orders the structures according to their BP86 relative energies. Thus the energetically lowest singlet structure of $(\text{C}_4\text{H}_6)\text{Co}_2(\text{CO})_6$ predicted by BP86 is designated **6S-1**.

3. Results and discussion

3.1. $(\text{C}_4\text{H}_6)\text{Co}_2(\text{CO})_6$ structures

Four structures are found for $(\text{C}_4\text{H}_6)\text{Co}_2(\text{CO})_6$ (Fig. 2). Three of these four structures (**6S-1** through **6S-3**) are doubly bridged $(\text{C}_4\text{H}_6)\text{Co}_2(\text{CO})_4(\mu\text{-CO})_2$ structures having Co–Co distances in the range of 2.52–2.64 Å, which are close to the experimental Co–Co distance of 2.528 Å for the doubly bridged $\text{Co}_2(\text{CO})_8$ structure, determined by X-ray crystallography [28]. In addition a related (norbornadiene) $\text{Co}_2(\text{CO})_6$ structure has been shown by X-ray crystallography to have a doubly bridged structure analogous to **6S-1** with an experimental Co–Co distance of 2.531 Å [29]. The C_s structure **6S-1** with a terminal $\eta^4\text{-C}_4\text{H}_6$ ligand is the global minimum. The coordination geometry of each cobalt atom in **6S-1** can be considered to be distorted trigonal bipyramidal with a bridging CO group in an axial position. The C_s structure **6S-2** is similar to **6S-1** in geometry except for the different orientation of the butadiene ligand, and lies 5.5 kcal/mol (B3LYP) or 5.0 kcal/mol (BP86) above **6S-1**. Structure **6S-3** lying 10.0 kcal/mol (B3LYP) or 7.8 kcal/mol (BP86) above **6S-1**, has a bridging $\eta^2, \eta^2\text{-C}_4\text{H}_6$ butadiene ligand with each Co atom bonded to two butadiene carbon atoms.

One unbridged $(\text{C}_4\text{H}_6)\text{Co}_2(\text{CO})_6$ structure was found by the B3LYP method, namely the C_1 structure **6S-4**, lying 4.9 kcal/mol (B3LYP) above the global minimum **6S-1** (Fig. 2). However, attempted optimization of the unbridged structure **6S-4** by the BP86 method led to the global minimum **6S-1**. In structure **6S-4**, one cobalt atom is bonded to two terminal carbonyl groups and the tetrahapto butadiene ligand, whereas the other cobalt is bonded to four terminal carbonyl groups. The unbridged Co–Co single bond distance of 2.777 Å (B3LYP) is ~ 0.2 Å longer than the doubly bridged Co–Co bond distance in other $(\eta^4\text{-C}_4\text{H}_6)\text{Co}_2(\text{CO})_4(\mu\text{-CO})_2$ structures. The longer Co–Co single bond distance in the unbridged structure **6S-4** relative to the Co–Co single bond distances in the doubly bridged structures **6S-1**, **6S-2**, and **6S-3** is a consequence of the bridging groups in the latter three structures as compared with the lack of bridging groups in **6S-4**.

3.2. $(\text{C}_4\text{H}_6)\text{Co}_2(\text{CO})_5$ structures

Five $(\text{C}_4\text{H}_6)\text{Co}_2(\text{CO})_5$ structures (three singlets and two triplets) were optimized (Fig. 3). The C_1 structure **5S-1** with two bridging CO groups is the global minimum predicted by the BP86 method. One cobalt atom in **5S-1** has a terminal CO group and a $\eta^4\text{-C}_4\text{H}_6$

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