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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 [μ_2-{ethoxycarbonyl(methylene)}-μ_2-(carbonyl)- bis(tricarbonyl-cobalt) (Co–Co)] $Co_2(CO)_7(CHCO_2Et)$ (**1**) and [di-μ_2-{ethoxycarbonyl(methylene)}-bis(tricarbonyl-cobalt) (Co–Co)] $Co_2(CO)_6(CHCO_2Et)_2$ (**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 $Co_2(CO)_6(CHCO_2Et)$ 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 $Co_2(CO)_6(CHCO_2Et)$ and $Co_2(CO)_5(CHCO_2Et)_2$ the CO ligands show also many variations of internal rearrangements. In complex **1** the effect of the rotation of the $C_{carbene}$–$C_{carbonyl}$ bond on the energy of the rotamers was also examined.
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1. Introduction

The isolable and spectroscopically characterized ethoxycarbonylcarbene-bridged dicobalt complexes $Co_2(CO)_7$-$(CHCO_2Et)$ (**1**) and $Co_2(CO)_6(CHCO_2Et)_2$ (**2**) (Scheme 1) were found to be intermediates in the $Co_2(CO)_8$-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 (μ-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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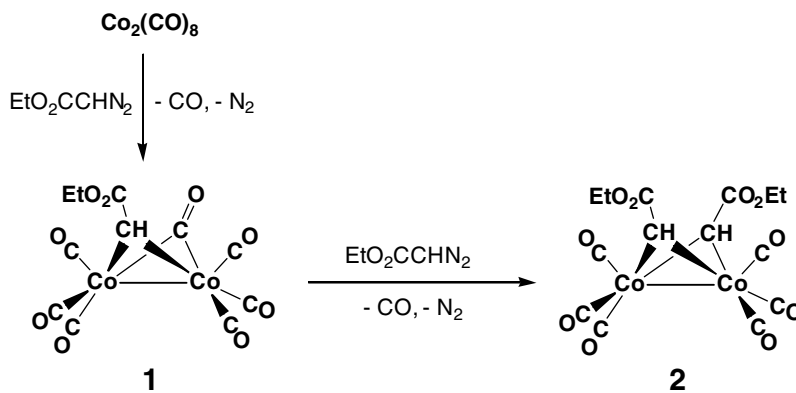
Scheme 1.

'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.
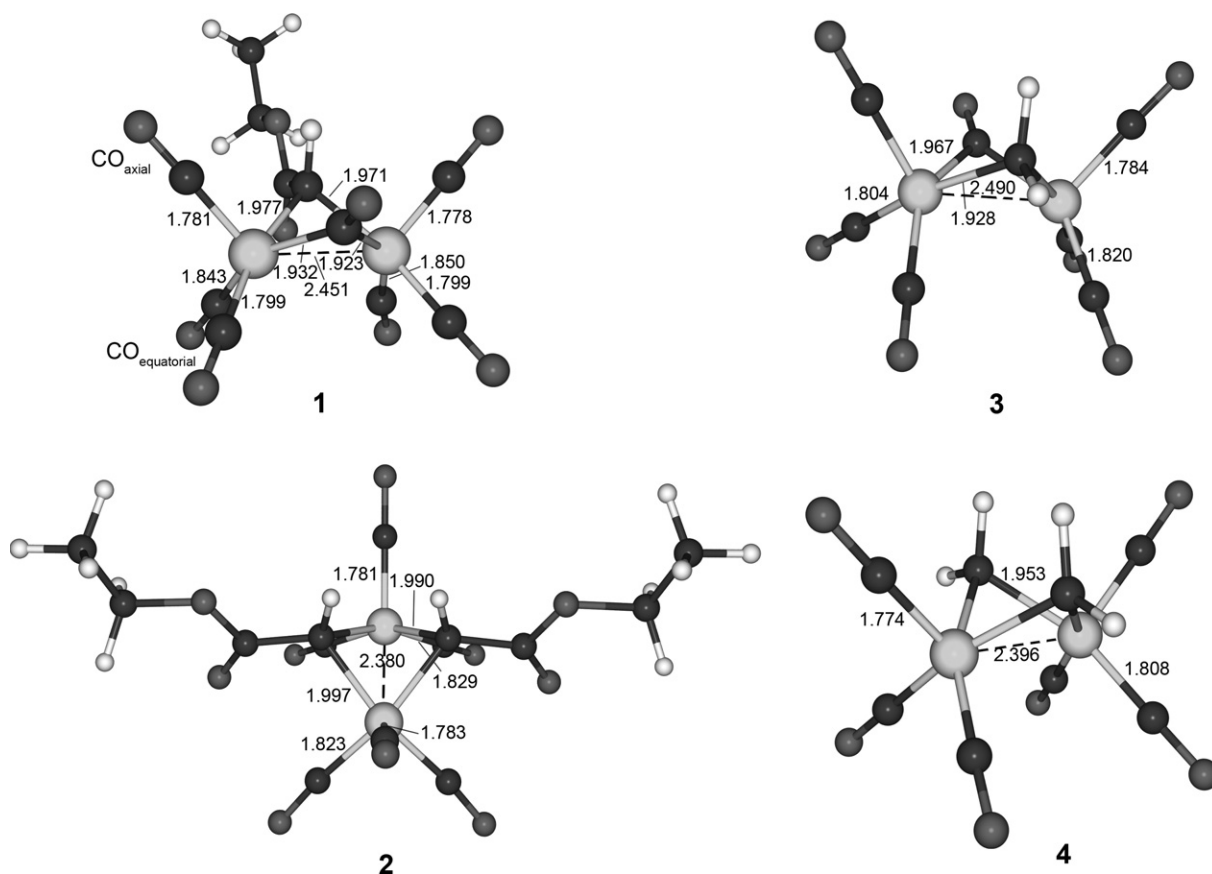

Fig. 1. Optimized geometries of the carbene–cobalt complexes $Co_2(CO)_7(CHCO_2Et)$ (**1**), $Co_2(CO)_6(CHCO_2Et)_2$ (**2**), $Co_2(CO)_7(CH_2)$ (**3**), and $Co_2(CO)_6(CH_2)_2$ (**4**).

3. Results and discussion

3.1. Structural and electronical properties of mono- and biscarbene complexes

The B3LYP-optimized structure of **1** and **2** as well as $Co_2(CO)_7(\mu\text{-}CH_2)$ (**3**) and $Co_2(CO)_6(\mu\text{-}CH_2)_2$ (**4**) are depicted in Fig. 1. The symmetry point group is C_s for **3** and C_{2v} for **4**. Although the arrangement of the ethoxycarbonyl group would also suggest a symmetry close to C_s for **1**, and C_{2v} for **2**, the Co–C bond lengths of the terminal carbonyl groups and the bridging groups are different. Compared to $Co_2(CO)_8$ the bond lengths between cobalt and carbons belonging to the terminal carbonyl groups in equatorial position differ appreciably. (1.816 Å in $Co_2(CO)_8$ at the same level of theory and 1.843 and 1.799 Å in **1**, in *cis* or *trans* position to the bridging carbene group, respectively.) The difference caused by different bridging groups is much less in **3** (1.820 Å, 1.804 Å) thus it may primarily be attributed to the electron withdrawing properties of the ethoxycarbonyl group. Possibly the electron withdrawing character is responsible for the larger bond lengths between cobalt and carbons belonging to the equatorial terminal carbonyl groups in **2** compared to **4**. The Wiberg bond indices are in strong correlation with the bond lengths as seen in Table 1.

The fluxional behavior of $Co_2(CO)_8$ is generally explained with the very facile interconversion between the double-bridged C_{2v} and the unbridged D_{2d} and D_{3d} structures [10]. However in metal carbonyl clusters the so-called tripodal rotation of the $M(CO)_3$ moiety is a commonly observed exchange process as well [11]. It is known that the interconversion processes take place with rather small activation energies, namely 3 and 8.4 kcal/mol at B3LYP/LANL2DZ level [12], which are smaller than the 11.7 ± 0.6 value measured by solid-state ^{13}C NMR spectroscopy [13].

In order to see whether the intramolecular ethoxycarbonyl–carbene scrambling between a bridging and a terminal position is possible, local minima for cobalt carbonyl carbenes and biscarbenes having terminal carbene ligand(s) were evaluated. As seen in Scheme 2, the double-bridged and the unbridged monocarbene complexes are at significantly higher energy compared to **1**. The energy difference is even greater in case of the unbridged biscarbene complex ($\Delta E = 57.2$ kcal/mol). The energy of the 'mixed' biscarbene possessing one bridging and one terminal ethoxycarbonyl-carbene group is still at 31.3 kcal/mol above **2**.

Therefore it is unlikely that the fluxionality involves those high-energy species. So we examined other intramolecular exchange processes such as the tripodal rotation.

3.2. Fluxionality of coordinative saturated cobaltcarbonylcarbene complexes

We first investigated the tripodal rotation of C_{2v} $Co_2(CO)_8$ and located the corresponding transition state

Table 1
Wiberg bond indices of $Co_2(CO)_8$ and complexes **1**–**4**

Complex	Co–CO_{cis}[a]	Co–CO_{trans}[a]
$Co_2(CO)_8$	0.701	–
1	0.634, 0.619	0.748, 0.744
2	0.683, 0.668	–
3	0.674	0.743
4	0.704	–

[a] Terminal CO *cis* or *trans* to the bridging carbene.
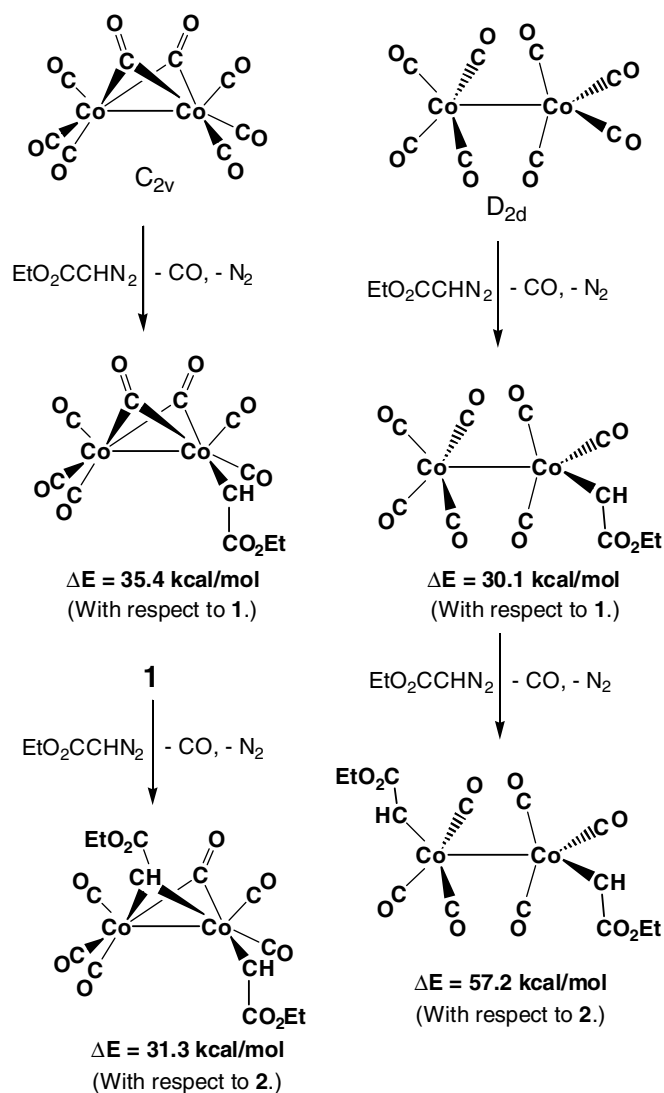
Scheme 2.

with a 11.3 kcal/mol free energy of activation which is in very good agreement with the experimental energy given by Hanson et al. [13]. The IRC reaction path, as seen in Fig. 2, shows a complex motion with the $Co(CO)_3$ moiety rotating around the axis determined by the two cobalt atoms and with the $Co(CO)_5$ moiety containing the two bridging carbonyls moving in the opposite direction

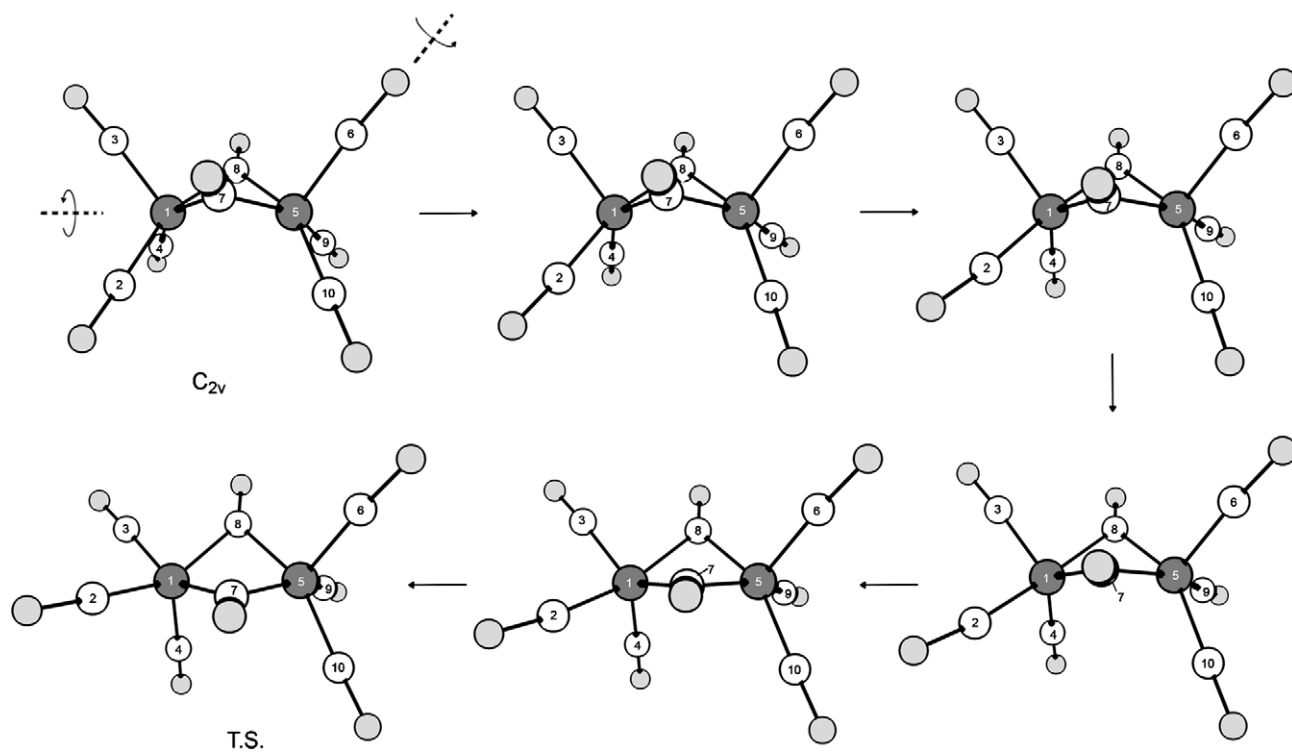Fig. 2. Half-IRC path of internal ligand position exchange in $Co_2(CO)_8$.
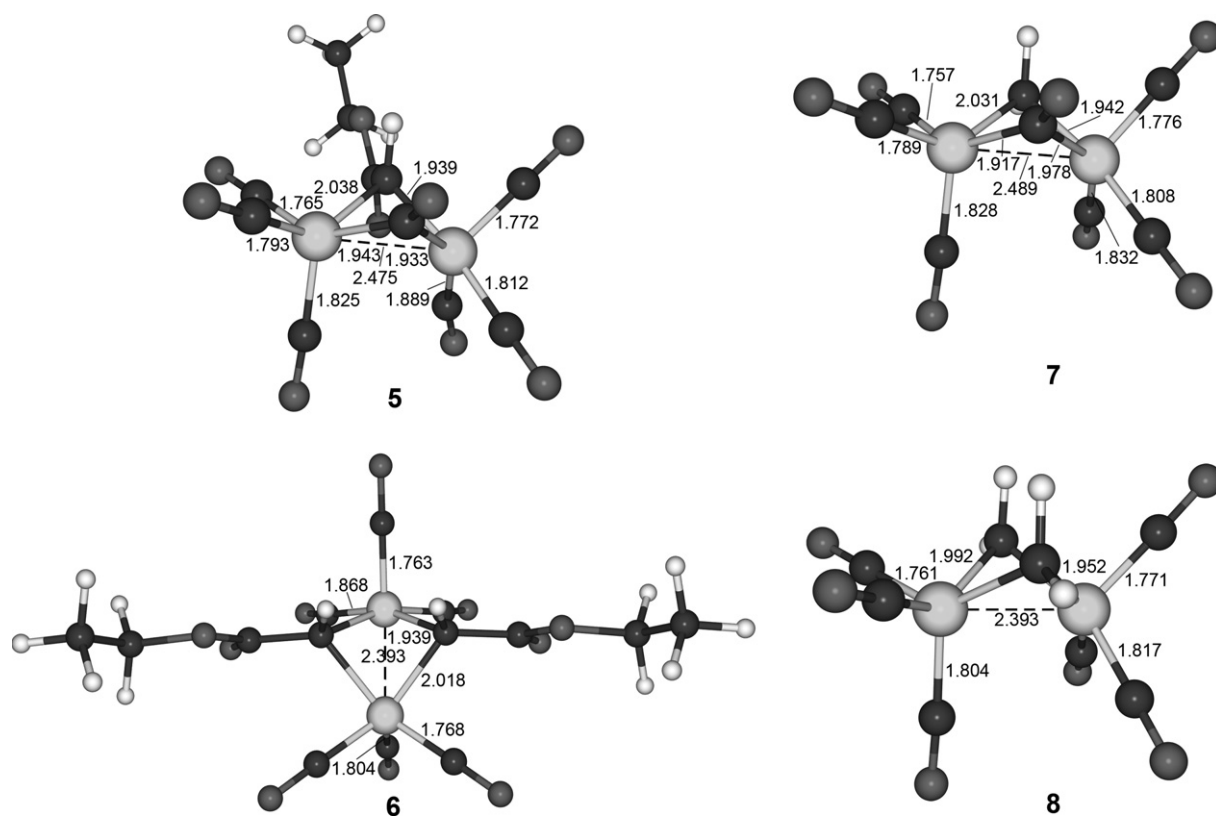

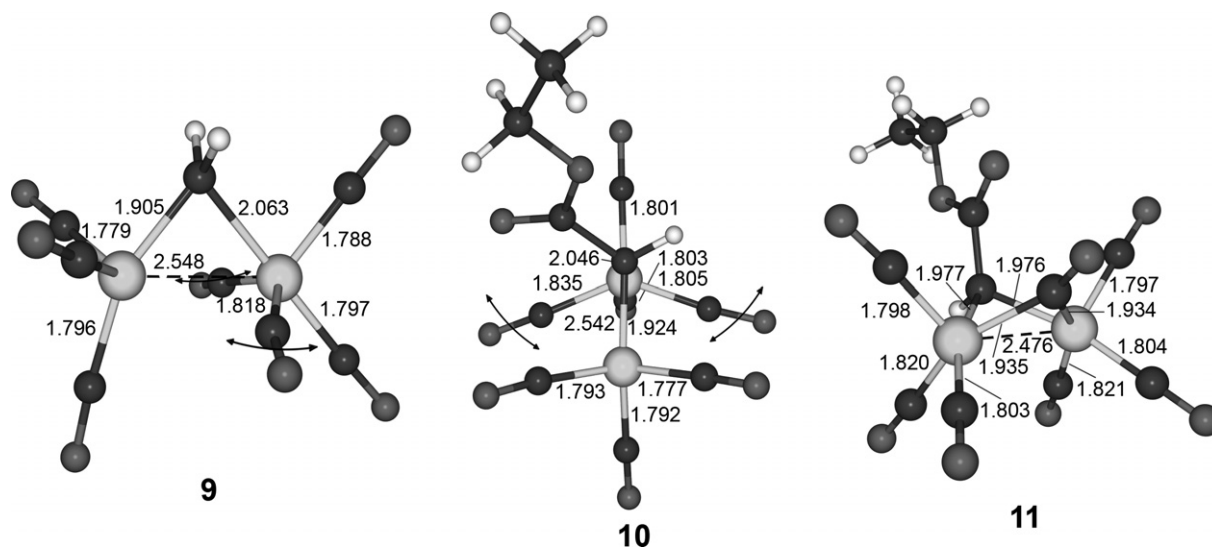Fig. 3. Transition states for tripodal rotation of **1–4**.

Fig. 4. Transition states for the CO exchange between terminal and bridging positions (**9,10**) and the isomer of **1** formed after the CO exchange (**11**).

around the axis determined by the cobalt-axial CO bond. Thus the internal rearrangement is more complex, than it was assumed before, but the term 'tripodal rotation' will be kept for simplicity throughout this study.

Fig. 3 shows the tripodal transition state of complexes **1**–**4**. As the Co–Co–CO$_{axial}$ angle in **5** reaches its minimum namely 86.4°, the Co–Co bond slightly elongates while the Co–CO$_{axial}$ and both of the Co–CO$_{equatorial}$ bonds become shorter. According to NBO studies, both cobalt atoms become somewhat cationic and at the same time the carbon atom of the axial CO becomes less positively charged ($+0.3 \rightarrow +0.24$). The Gibbs free energy of activation was calculated to be 12.5 kcal/mol.

The electron-rich carbon (-0.82) belonging to the second bridging carbene group in case of **6** takes away more electron density from cobalt atoms ($+0.90$), however neither the charge distribution nor the bond distances of the carbonyl ligands change significantly compared to **5**. The Co–Co bond in **2** and in the tripodal transition state (**6**) becomes shorter compared to that found for **1** and **5**, 2.380 Å and 2.393 Å, respectively. The free energy of activation is lower than in tripodal rotation of **1** (through transition state **5**) by 2.2 kcal/mol.

The bridging bond length and the cobalt–carbonyl distances in the tripodal transition states are closer to their ethoxycarbonyl-substituted counterparts than in the local minima i.e. in spite of the electron withdrawing group the geometry of **7** and **8** are fairly close to **5** and **6**, respectively. Especially the geometry of the Co(CO)$_3$ moiety shows hardly any difference in ethoxycarbonylmethylene and the unsubstituted methylene complexes. However the free energies of activation is larger for the tripodal rotation of **4** than for **2** by 0.6 kcal/mol, while comparing the monocarbene complexes the free energy of activation is smaller by 0.8 kcal/mol in case of **3**.

3.3. CO site-exchange in Co$_2$(CO)$_7$(μ-CHCO$_2$Et)

IR studies of complex **1** under a ^{13}CO enriched CO-atmosphere revealed an indiscriminate fast ^{13}CO exchange process for both terminal and bridging carbonyl ligands [2] suggesting an even faster exchange of the terminal and bridging positions.

Fig. 4 shows the transition state **9** of such a process starting from **3**. This TS shows a C$_s$ symmetry leading to **3** at both sides of the intrinsic reaction path; the carbonyl groups at both sides of the symmetry plane make an anti-parallel movement between the terminal and bridging positions. During this process the axial and equatorial terminal carbonyl groups change positions as well.

In complex **1** a very similar transformation may occur, however the ethoxycarbonyl group breaks the symmetry, thus the transition state **10** interconnects **1** and its isomer **11**. The free energy of activation is 7.4 kcal/mol (8.5 kcal/mol for the methylenecarbene complex) indicating the process as a very fast one.

Table 2
Activation energies and Gibbs free energies (in kcal/mol) of tripodal rotation and terminal-bridging carbonyl exchange

Process	ΔE	ΔG	Imaginary frequency (cm^{-1})
Tripodal rotation			
Co$_2$(CO)$_8$	10.0	11.3	66.1i
$1 \rightarrow 5 \rightarrow 1$	11.1	12.5	56.5i
$2 \rightarrow 6 \rightarrow 2$	9.5	10.3	49.8i
$3 \rightarrow 7 \rightarrow 3$	9.7	11.7	70.8i
$4 \rightarrow 8 \rightarrow 4$	9.3	10.9	87.7i
Terminal CO exchange			
$3 \rightarrow 9 \rightarrow 3$	7.4	8.5	84.9i
$1 \rightarrow 10 \rightarrow 11$	6.8	7.4	68.8i

It is worth comparing the geometry of the product of the internal CO exchange (**11**) with the starting complex (**1**). In **11** the difference between the Co–CO$_{cis}$ and Co–CO$_{trans}$ bond lengths is smaller than in **1**, but it is very close to them in the methylenecarbene analogue **3**, however the Co–CO$_{axial}$ distance is by ca. 0.02 Å larger. Thus the weakening of the

Co–C bonds caused by the electron withdrawing effect of the ethoxycarbonyl group acts on the axial terminal carbonyl groups rather than on the equatorial ones.

The activation energies and Gibbs free energies of tripodal rotation and of the internal terminal-bridging CO exchange are summarized in Table 2.
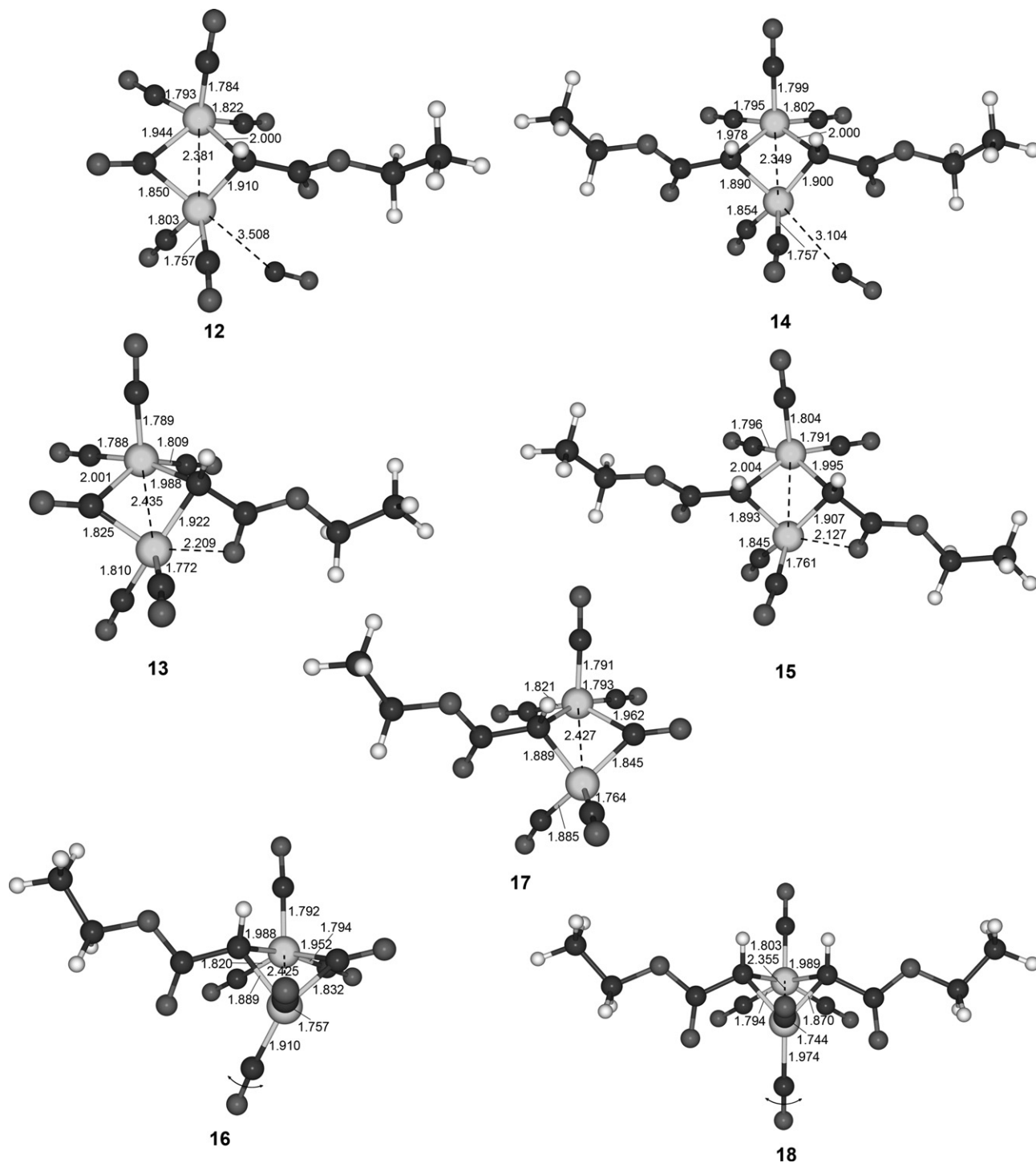

Fig. 5. Transition states for CO-dissociation of **1** and **2** (**12**,**14**) leading to the coordinative unsaturated **13** and **15** and transition states of the equatorial terminal CO-movement (**16**,**18**) and the local minimum in case of **13** (**17**).

3.4. CO-dissociation in $Co_2(CO)_7(CHCO_2Et)$ and in $Co_2(CO)_6(CHCO_2Et)_2$

The ^{13}CO exchange is assumed to take place through a dissociative mechanism. Thus, the dissociation of one of the terminal carbonyl ligands must be considered.

Because of the shorter length and hence the stronger Co–C bond the dissociation of the axial carbonyl groups in **1** and **2** were omitted from this study; only the dissociation of the two equatorial carbonyl groups were investigated.

As we have shown in Section 3.1, the CO *cis* to the bridging carbene group is more easy to remove. The net bond dissociation energy was found to be 17.1 kcal/mol. However, the cleavage of the Co–C bond takes place through the corresponding transition state **12** with an energy barrier of 18.3 kcal/mol ($\Delta G = 15.7$ kcal/mol, which is somewhat lower because of larger reaction entropy) resulting in the coordinative unsaturated **13** (Fig. 5). The stabilization of **13** is due to the electron delocalization between the lone pair of the ester carbonyl–oxygen and non-bonding d-electrons of cobalt. Similar
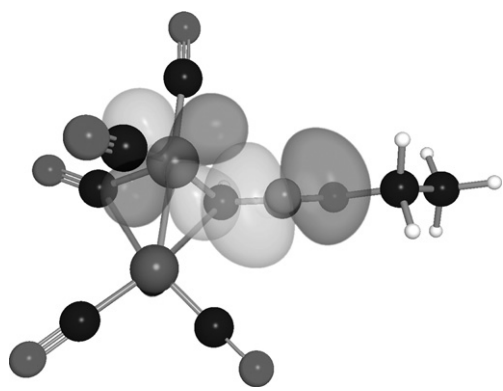
interaction between the polar groups in an organic ligand and the cobalt has been reported earlier [14]. Natural bond orbital (NBO) analysis revealed that a natural bond orbital of lone pair character is formed from the d_{xy}, d_{yz}, and $d_{x^2-y^2}$ orbitals of cobalt and can readily overlap with one of the lone pairs formed almost entirely from the $2p_x$ orbital of the ester carbonyl–oxygen. The orbital interaction diagram is depicted in Fig. 6.

The dissociation of one of the equatorial-terminal carbonyl groups from **2** takes place in a similar manner.

Fig. 6. Natural bond orbital interaction in **13**.

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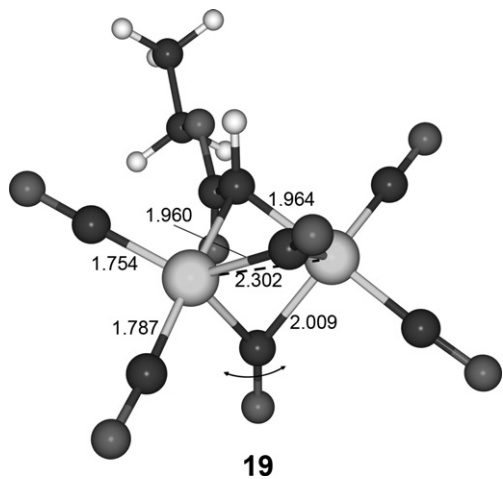
Fig. 7. Transition state for the CO-exchange between cobalt atoms of **13**.

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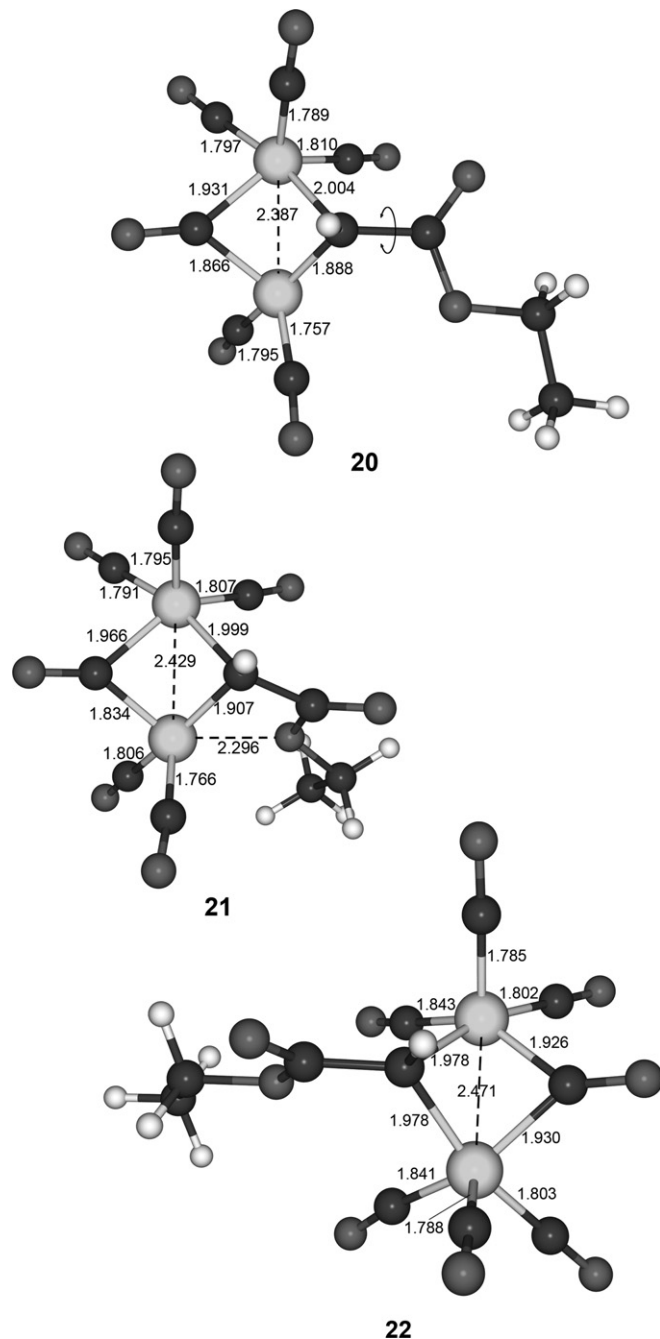
Fig. 8. Transition state (**20**) and the local minimum (**21**) of $C_{carbene}$–$C_{carbonyl}$ bond rotation and structure of **22** originated from **1** by the rotation of $C_{carbene}$–$C_{carbonyl}$ bond.

Table 3
Relative energies and Gibbs free energies (in kcal/mol) of species originating from **1** and **2**

Complex	ΔE	ΔG
1	0	0
11	1.1	2.2
12	18.3	15.7
13 (+CO)	17.1	6.9
16 (+CO)	36.2	25.6
17 (+CO)	36.1	25.5
19 (+CO)	24.7	14.7
20 (+CO)	24.6	15.1
21 (+CO)	20.0	9.8
22	2.1	2.2
2	0	0
14	24.3	23.4
15 (+CO)	18.7	9.4
18 (+CO)	33.1	23.3

Table 4
Activation energies and Gibbs free energies (in kcal/mol) of selected transformations related to the coordinative unsaturated carbene complexes

Process	ΔE	ΔG	Imaginary frequency
1 → 12 → 13	18.3	15.7	29.7i
13 → 16 → 17	19.1	18.7	114.6i
13 → 19 → 13	7.6	7.8	98.8i
13 → 20 → 21	7.5	8.2	31.9i
2 → 14 → 15	24.3	23.4	82.7i
15 → 18 → 15	14.4	13.9	261.1i

However the distance between cobalt and the leaving carbonyl group in the transition state **14** is significantly larger than that in **12** in accordance with the stronger Co–C bond in **2**. The free energy barrier of dissociation is 23.4 kcal/mol, which is much higher than the free energy of activation of the carbene–carbon monoxide coupling to the corresponding ketene in complex **2**. This explains the lack of ^{13}CO incorporation when **2** is treated under a ^{13}CO atmosphere [2].

According to the shorter bond length and the larger WBI in **1**, the bond dissociation energy of the terminal carbonyl group *trans* to the bridging carbene group was expected to be higher. For the bond dissociation energy of the CO group 36.1 kcal/mol was calculated. As the result of the dissociation, the coordinative unsaturated **17** is formed which can isomerize to **13** through the transition state **16** in an almost barrierless manner.

The equatorial-terminal CO on the coordinative unsaturated side of the biscarbene complex **15** can change its position with the cleavage of the interaction of cobalt with the carbonyl oxygen of one of the ethoxycarbonyl groups and forming the same interaction on the other side through the transition state **16**. The free energy barrier for the CO tilting is 13.9 kcal/mol. The geometry of **17** and the transition states **16** and **18** are depicted in Fig. 7.

3.5. Other internal rearrangements related to $Co_2(CO)_6(\mu$-$CHCO_2Et)$

On the $Co_2(CO)_6(\mu$-$CHCO_2Et)$ potential energy surface a tribridged structure with C_s symmetry was also located (**19**) which was identified as a transition state describing the migration of one of the terminal CO ligands *cis* to the carbene group from one cobalt to the other. This transformation was found to be a fast reaction (assuming gas phase conditions and a typical preexponential kinetic factor for unimolecular processes) with a free energy of activation of 7.8 kcal/mol (Fig. 7).
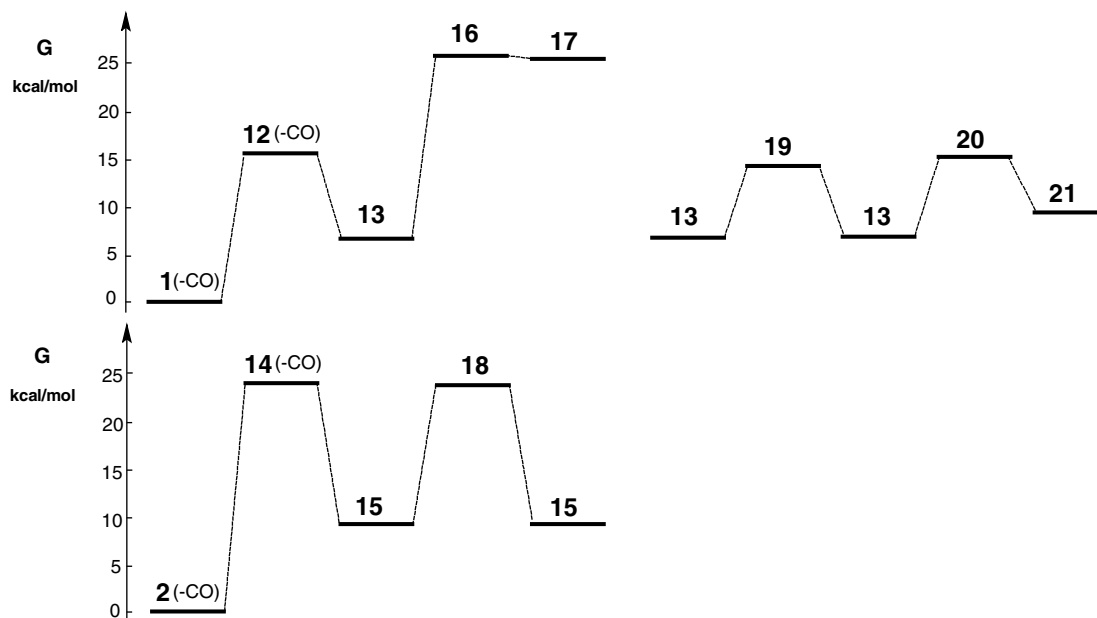

Fig. 9. Free energy diagram of selected transformations related to the coordinative unsaturated carbene complexes.

Among the conformational changes of the ethoxycarbonyl group only the rotation of the $C_{carbene}$–$C_{carbonyl}$ bond was examined in this study. The conformational transition state (**20**) was located after a 112° of rotation of the ethoxycarbonyl group with a rotational free energy barrier of 8.2 kcal/mol. The cobalt–carbonyl oxygen interaction is broken, however a new, weaker interaction between cobalt and the sp^3 oxygen of the ethoxy group is formed resulting in compound **21**.

After a CO-uptake **21** can turn into the coordinative saturated **22** which can also be originated from **1** after a $C_{carbene}$–$C_{carbonyl}$ bond rotation. **22** is higher in energy by 2.1 kcal/mol than **1**, thus it may also appear during experimental infrared studies. The net Co–CO dissociation energy is 17.9, slightly lower than in case of **1**. It is assumed that the dissociation occurs with a small barrier due to the simultaneous Co–CO cleavage and the weak interaction between Co and the ethoxy oxygen, however this mechanism was not investigated in this particular case. **22** (depicted in Fig. 8) can also be originated from **1** by the rotation of $C_{carbene}$–$C_{carbonyl}$ bond with a free energy barrier of 2.9 kcal/mol.

All the relative energies of species related to **1** or **2** are summarized in Table 3. The activation energies and Gibbs free energies of the coordinative unsaturated carbene complexes are shown in Table 4 and depicted in Fig. 9.

4. Conclusions

The calculated reaction profiles and structural properties support our earlier experimental work and offer detailed explanations concerning the reaction of $Co_2(CO)_7(CHCO_2Et)$ and $Co_2(CO)_6(CHCO_2Et)_2$ with CO.

In term of the equatorial terminal carbonyl ligands the difference in Co–CO_{cis} and Co–CO_{trans} bond lengths in $Co_2(CO)_7(CHCO_2Et)$ complexes is greatest in case of **1**, which is the lowest energy isomer, hence the dissociation of the CO group *cis* to the bridging carbene ligand occurs most readily in this case resulting in the coordinative unsaturated **13**. However the relative energy difference between **1**, **11**, and **22** is rather low, which may give an explanation for the three bridging carbonyl signs in the IR spectrum of $Co_2(CO)_7(CHCO_2Et)$ measured in hexane [1].

The low free energy barrier of CO dissociation in **1** is in good agreement with the facile ^{13}CO exchange measured by infrared spectroscopy [2]. Furthermore the significantly higher free energy of activation, coupled with the experimentally found faster ketene formation, explains why **2** does not exchange its CO ligands for ^{13}CO at all at room temperature.

The fluxional behavior suggested on the basis of ^{13}C NMR spectra of **1** and **2** [2] can be originated to (i) fast exchange of terminal and bridging positions of CO ligands in **1**, (ii) tripodal rotation of a CoL_3 moiety with terminal ligands (simultaneously with the rotation of the remaining CoL_5 moiety containing two bridging ligands) in case of **1** or **2** or their methylenecarbene containing analogues **3** or **4**, which were not examined experimentally yet (L is carbonyl or bridging carbene).

The coordinative unsaturated cobalt carbonyl carbene complexes also show fluxional behavior according to this theoretical study. The equatorial-terminal CO can change its relative position to the neighboring bridging carbene ligands and can leap from one cobalt to the other in an even faster reaction.

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