Density Functional Investigation of Reactive Intermediates Derived from Alkyne – Co$_2$(CO)$_6$ Complexes

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Abstract: By applying the hybrid density functional method B3LYP and a flexible all-electron basis set, structures and energies of reactive intermediates derived from the 1-butyne complex of Co$_2$(CO)$_6$ (**1**) were calculated. In particular, the geometry, electronic distribution, and configurational stability of the cationic, radical, and anionic Co$_2$(CO)$_6$-complexed propargylic species were studied. The calculations revealed that the configurational barrier, that is, the racemization barrier for the antarafacial

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migration of the CHCH$_3$ group, is low (7.6 kcal mol^{-1}) for the radical and is similar to the experimental value for the corresponding cation (ca. 10 kcal mol^{-1}). However, a high racemization barrier (23.7 kcal mol^{-1}) for the anionic intermediate suggests the possibility of stereospecific reactions involving Co$_2$(CO)$_6$-complexed propargylic anions.

Introduction

Alkyne – Co$_2$(CO)$_6$ complexes have received much interest in recent years, particularly in the context of synthetic methodologies such as the Pauson – Khand reaction[1] and the Nicholas reaction.[2] In the latter, the Co$_2$(CO)$_6$ moiety stabilizes the positive charge in the propargylic position. Related effects are known for other transition metal π complexes, such as ferrocenes,[3] benzene – Cr(CO)$_3$ complexes,[4] and diene – Fe(CO)$_3$ complexes.[5] The last two can also stabilize negative charge or even radical centers adjacent to the complexed π system. While the ability of the cobalt moiety in alkyne – Co$_2$(CO)$_6$ complexes to stabilize cationic intermediates is well established as a key feature of Nicholas-type reactions,[2] it was demonstrated only recently that propargylic radicals are also stabilized by the Co$_2$(CO)$_6$ unit.[6] However, the corresponding anionic analogues have not yet been investigated.

We have exploited density functional methods as an accurate and effective tool for characterizing the structure and energy of reactive intermediates related to organometallic π complexes.[5, 7] Here we present the results of calculations on cationic, radical, and anionic reactive intermediates formally derived from neutral alkyne – Co$_2$(CO)$_6$ complexes of type **1** (see Scheme 1).

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Methods of Calculation

The calculations were performed with the hybrid density functional method B3LYP.[8] As in our previous calculations on transition metal tricarbonyl complexes we used an all electron basis set consisting of a basis set developed by Wachters[9] for the cobalt atom including f-functions, and the split valence basis set D95* by Dunning[10] for C, O, and H, as implemented in Gaussian 98.[11] The one-particle description for the cobalt atom is (14s11p6d3f) → (8s6p4d1f)/[62111111/331211/3111/3]. The stationary points on the potential energy surface were determined as minima (only positive frequencies) or maxima (one imaginary frequency; transition state) by analytical gradient techniques. Information on the density distribution in the complexes was obtained by the natural bond orbital (NBO) analysis developed by Weinhold et al.[12]

The program package Gaussian 98,[11] used throughout this study, was run on the multiprocessor SGI and Sun workstations of the Regionales Rechenzentrum der Universität zu Köln.

Results and Discussion

The neutral C$_4$H$_6$ – Co$_2$(CO)$_6$ complex: The 1-butyne – Co$_2$(CO)$_6$ complex **1** (Scheme 1) is the parent system for all reactive intermediates presented here. As expected for a neutral alkyne – Co$_2$(CO)$_6$ complex, the calculated structure has a tetrahedral core formed by the acetylene carbon atoms
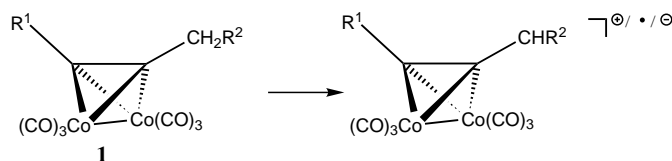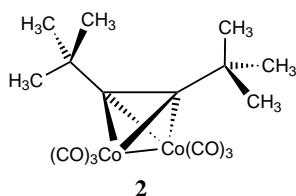

Scheme 1. The parent alkyne – Co$_2$(CO)$_6$ complex **1** (R^1 = H, R^2 = CH$_3$) and reactive intermediates derived therefrom.

and the two cobalt centers. Thus, the former triple bond is perpendicular to the Co–Co axis, and the substituents on the acetylene carbon atom are bent away from the metal atoms. The carbonyl groups on the two Co atoms are eclipsed with respect to the Co–Co axis (Figure 1).

To verify the accuracy of our theoretical approach, we compared the calculated bond lengths with those obtained by X-ray crystallography. A search in the Cambridge Structural Database revealed that no X-ray crystallographic data are available for complex **1**. Therefore, the di-*tert*-butylacetylene–$Co_2(CO)_6$ complex **2**, for which very accurate crystal structure data have been reported,

1

Figure 1. Two representations of the calculated structure of the neutral 1-butyne–$Co_2(CO)_6$ complex **1**. Partial charges and atom numbers (left) and bond lengths (right) are indicated.

2

was selected as a reference system.[13] The bond lengths for the calculated structures of **1** and **2** are listed in Table 1 together with the experimental data for **2**.

Agreement between the calculated and experimental values for **2** is good, with a maximum deviation of 0.02 Å and an average deviation of less than 0.01 Å. The perfect C_{2v} symmetry of the calculated structure of **2** is not found in any of the crystal structures, probably due to packing effects.

The cationic C_4H_5–$Co_2(CO)_6^{2+}$ complex: Having demonstrated the general reliability of the theoretical approach, we turned our attention to the reactive intermediates derived from **1**.

As mentioned above, the most important transformation exploiting cobalt-stabilized cationic intermediates **3** is the Nicholas reaction, in which a substituted product is formed by an S_N1-type process starting, for instance, from a $Co_2(CO)_6$-complexed propargylic alcohol (Scheme 2). The structural features of reactive intermediates of type **3** have been the subject of several investigations, but it proved difficult to determine the exact structure of such species experimentally (e.g., by X-ray crystallography). Only for a compound in which a carbenium center is stabilized by two alkyne–$Co_2(CO)_6$ fragments was an X-ray structure
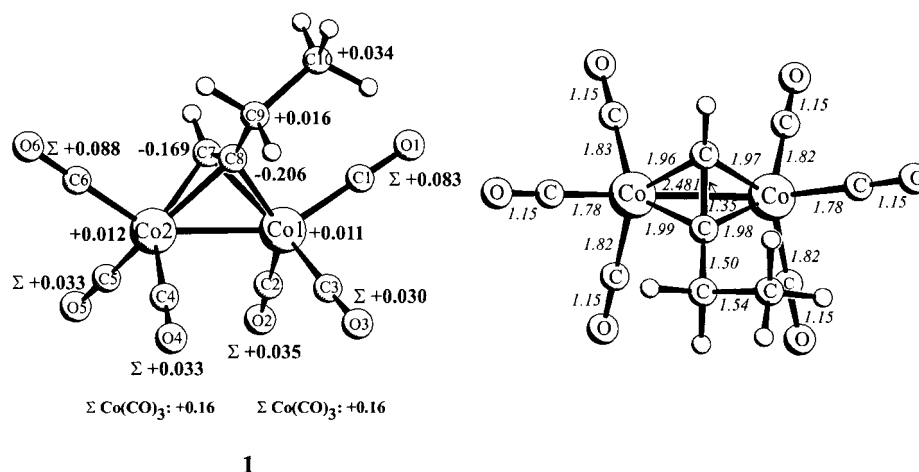
Table 1. Bond lengths of the calculated structures **1** and **2** in comparison with the experimental data for **2**.

Parameter	**1** (calcd)	**2** (calcd)	**2** (exptl)[13a]
Co1–Co2	2.480	2.461	2.462
Co1–C1	1.783	1.779	1.796
Co1–C2	1.822	1.816	1.819
Co1–C3	1.820	1.821	1.828
Co2–C4	1.817	1.816	1.819
Co2–C5	1.827	1.821	1.830
Co2–C6	1.783	1.779	1.791
Co1–C7	1.966	1.999	1.984
Co1–C8	1.982	2.002	1.988
Co2–C7	1.961	1.999	1.985
Co2–C8	1.985	2.002	1.983
C7–C8	1.345	1.343	1.349
C7–C9	–	1.522	1.519
C8–C13	1.499	1.522	1.516
C–O (av)	1.153	1.155	1.140
C_{tBu}–C_{tBu} (av)	–	1.546	1.539

reported.[14] The structure of this cationic species is not significantly distorted with respect to those of neutral alkyne–$Co_2(CO)_6$ complexes. However, NMR[15] spectroscopic investigations and theoretical studies[16] revealed a bent structure for cationic intermediates of type **3**, in which the carbenium center is bent towards one of the Co atoms. This was additionally supported by extended Hückel theory (EHT) calculations.[17]

As expected, the calculated structure of the cationic C_4H_5–$Co_2(CO)_6^+$ complex **3** (R = H, R′ = H, R″ = CH_3) (Figure 2) shows a distorted geometry, in which the cationic center C9 is bent towards one of the cobalt atoms, and the C9–Co1

3
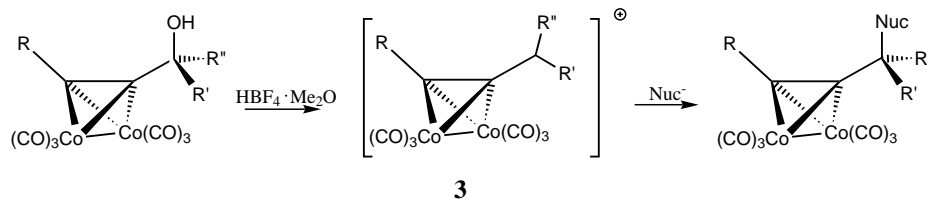
Scheme 2. Mechanism of the Nicholas reaction.

distance is shortened to 2.421 Å (3.225 Å in **1**). Furthermore, the C8–C9 bond length of 1.392 Å in **3** is significantly shorter than that of 1.51 Å in the neutral parent system **1**, and this indicates a significant double-bond character.

In the calculated structure of **3**, the formal propargylic center C9 carries a positive partial charge of $+0.086$ e, which is only slightly more positive than C9 in the parent system **1** ($+0.015$ e). Thus, the additional positive charge is almost completely delocalized over the metal carbonyl moieties. While each $Co(CO)_3$ group in **3** accepts about $+0.5$ e, the cobalt atoms themselves remain nearly neutral, as in **1**.

Studies on the fluxional behavior of related cationic complexes by NMR spectroscopy[15] revealed that the CR^1R^2 group easily migrates from one cobalt tricarbonyl moiety to the other. Two pathways were postulated for this process: 1) an antarafacial migration resulting in enantiomerization and 2) a suprafacial migration of the CR^1R^2 group without rotation around the formal C_{alkyne}–C9 double bond with retention of the stereochemistry at the propargylic center (Scheme 3).

In accordance with the NMR studies,[15] two processes, involving the transition states **4** (Figure 3) and **5** (Figure 4), were identified by the calculations, which thus reflect the proposed dynamic behavior of cationic alkyne – $Co_2(CO)_6$ complexes. Thus, the theoretical findings fully support the picture drawn by Schreiber et al. (Scheme 3).[15a]

Transition state **4**, depicted in Figure 3, has C_s symmetry with C7 – C10 in the mirror plane. While C9 ($+0.291$ e) and C10 ($+0.115$ e) have an enhanced positive partial charge, the majority of the charge is delocalized over the $Co_2(CO)_6$ fragment, as in **3**.

That **4** is indeed the transition state corresponding to antarafacial migration of the alkylidene group (resulting in

racemization) is indicated by a negative mode of 115 cm⁻¹ associated with the rotation around the C8–C9 bond. The calculated energy barrier for this rotation is 9.5 kcal mol⁻¹.[19] This result is in line with the above-mentioned NMR spectroscopic investigation, which gave an energy barrier of 10.5 kcal mol⁻¹ for a related system.
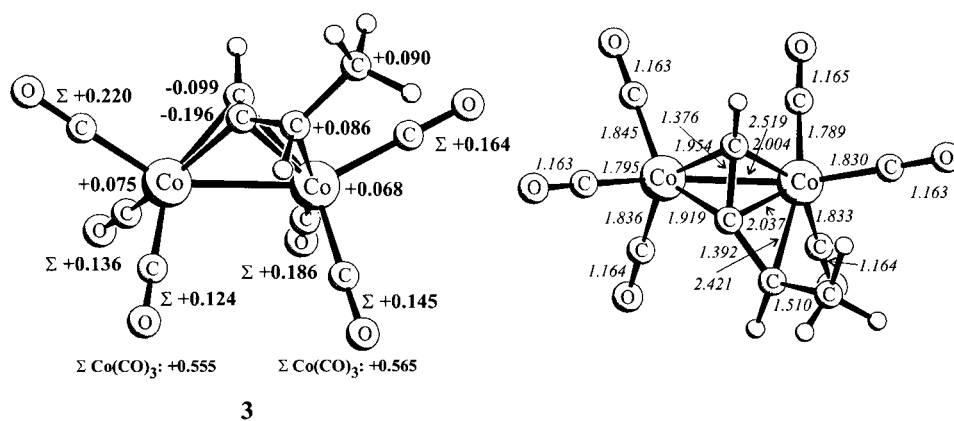

Figure 2. Two representations of the calculated minimum-energy structure of the cationic intermediate **3**. Partial charges (left) and bond lengths (right) are indicated.
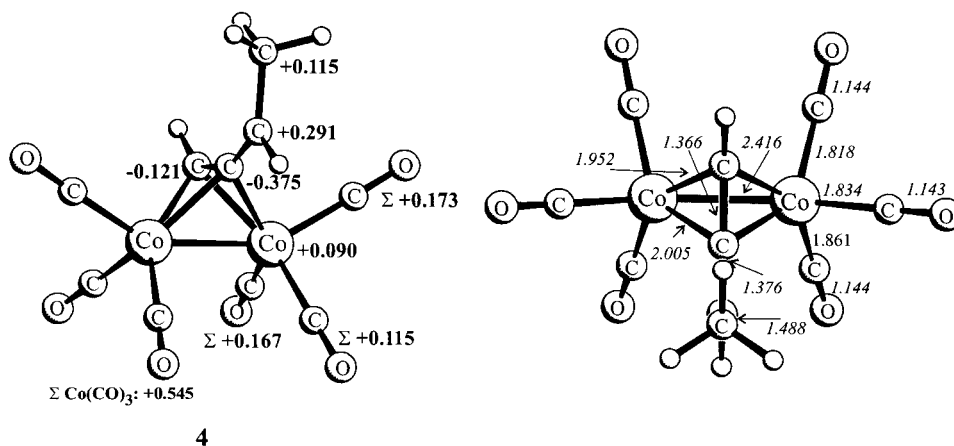

Figure 3. Two representations of the C_s-symmetric transition structure **4** of the cationic C_4H_5 – $Co_2(CO)_6$ complex. Partial charges (left) and bond lengths (right) are indicated.
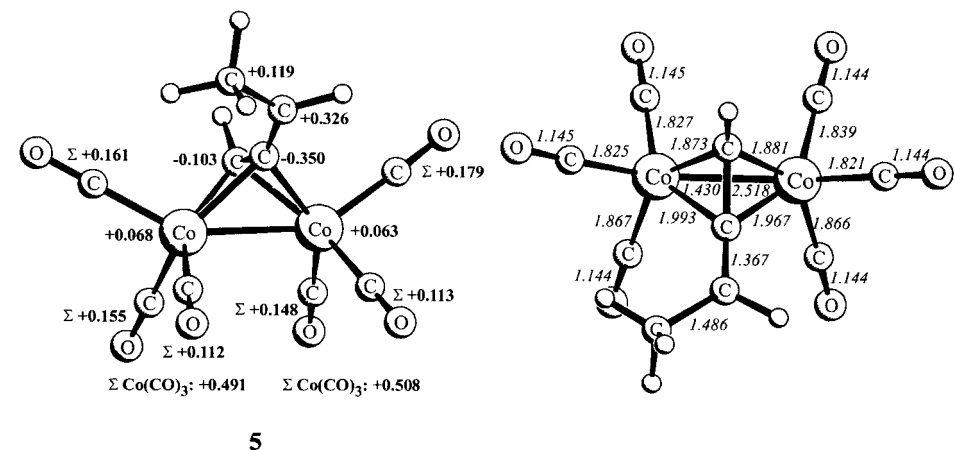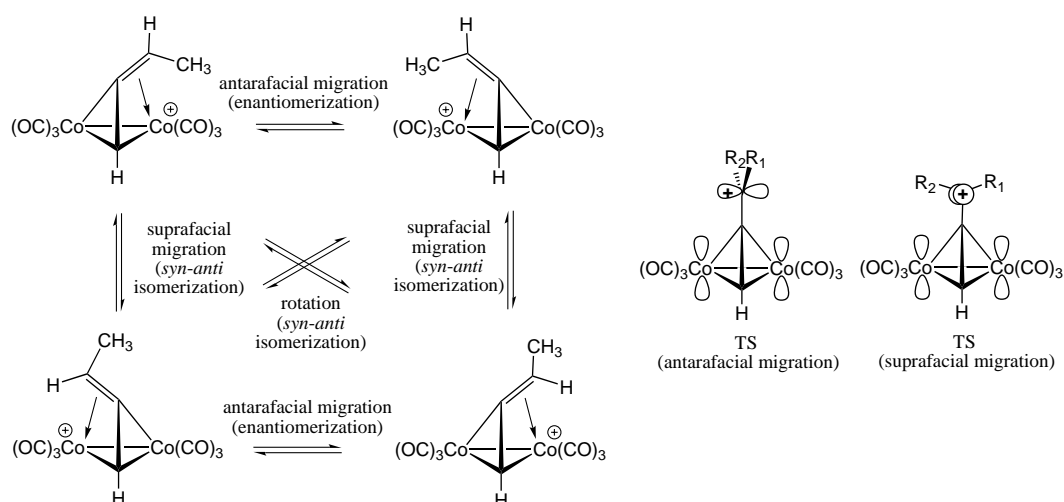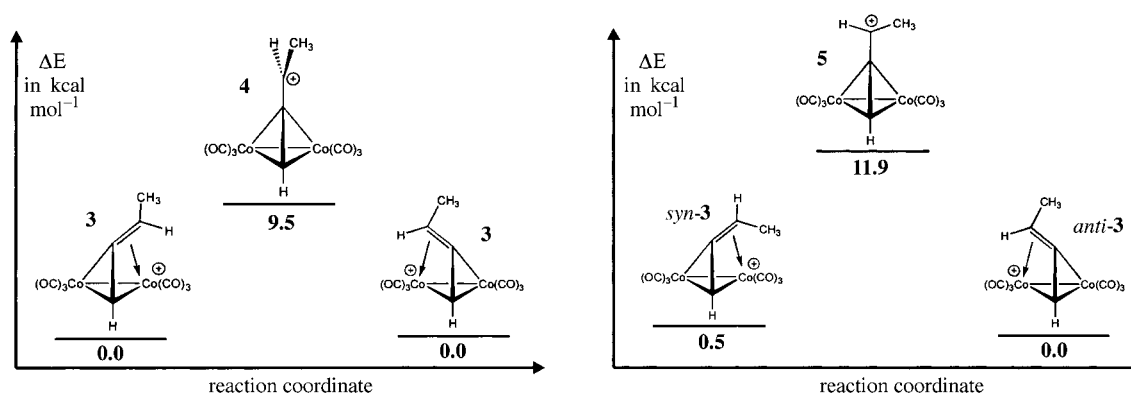

Figure 4. Two representations of the calculated structure of the transition state **5** for suprafacial migration of the $CHCH_3$ group from one Co center to the other (*syn/anti* isomerization). Partial charges (left) and bond lengths (right) are indicated.

Scheme 3. Schematic representation of the possible fluxional processes in cationic complexes of type **3**.[18]

Figure 5. Energy profiles for antarafacial (left) and suprafacial (right) migration of the alkylidene group in **3**.

The transition state **5** (Figure 4) for suprafacial migration of the CHCH$_3$ group in **3** is energetically disfavored by 2.5 kcal mol^{-1} relative to **4**; this corresponds to a rotational barrier of 13 kcal mol^{-1}. The calculations furthermore revealed a transition mode with an imaginary frequency of 208 cm^{-1}, which is indicative of the suprafacial interconversion of the *syn* and *anti* diastereomers. Because the two substituents at C9 (Me, H) are different, the symmetry of the transition state **5** is C_1. However, the acetylene–Co$_2$(CO)$_6$ substructure is almost symmetrical with respect to the plane defined by C7–C9. The energy profiles for both migration processes, as well as the relative energies of the *syn* and *anti* conformers are shown in Figure 5.

The calculations on the parent dicationic system **6** revealed two minima: a *cisoid* structure in which both methylene groups are bent towards the same cobalt atom (**6a**), and a *transoid* structure in which each methylene group is bent towards one of the Co atoms (**6b**). The *transoid* structure **6a** is energetically favored by 9.5 kcal mol^{-1} relative to **6b**.

Interestingly, the Co$_2$(CO)$_6$ moiety can compensate both cationic charges, as indicated by the NBO analysis. In both structures (Figure 6) the Co$_2$(CO)$_6$ group carries a charge of

6 (L=CO)
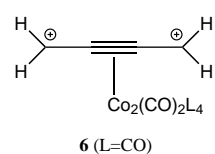
about +2.0 e. Nevertheless, C9 still carries a small partial charge of +0.2 e, in contrast to the monocationic complex **3**, in which C9 is nearly neutral.

The radical complex C$_4$H$_5$–Co$_2$(CO)$_6$·: Recent experimental work suggests[6] that the dicobalt hexacarbonyl fragment can stabilize not only cations but also radicals in the propargylic position of alkyne–Co$_2$(CO)$_6$ complexes. An example of a reaction involving such radical intermediates is outlined in Scheme 4. In contrast to the cationic intermediates discussed above, almost nothing is known about the structure, energy, and electron distribution of the corresponding radical inter-
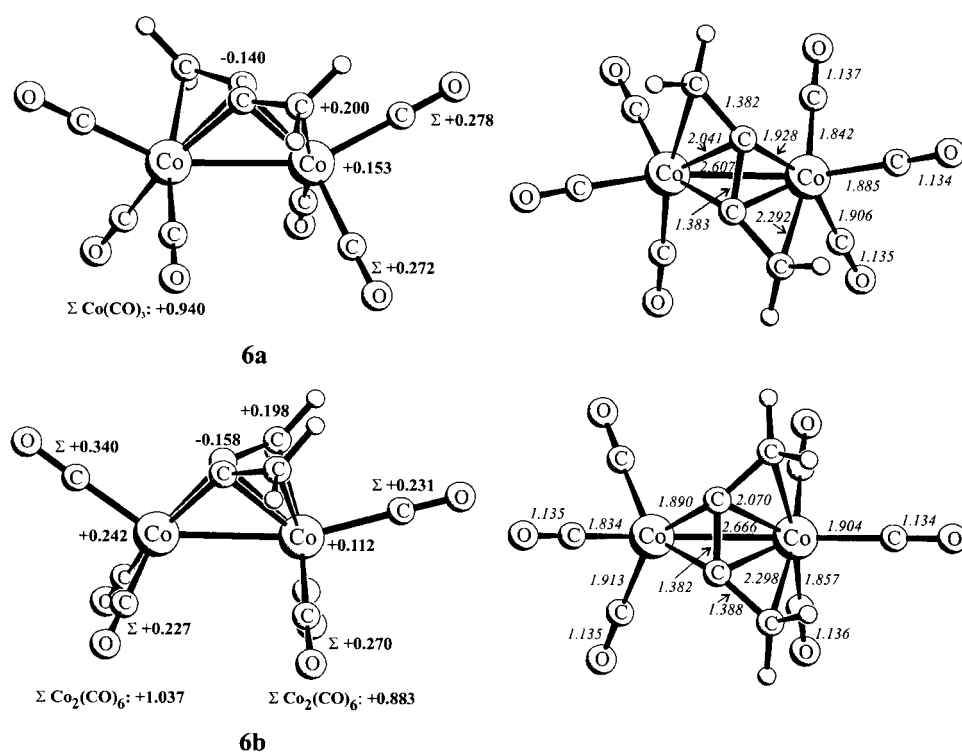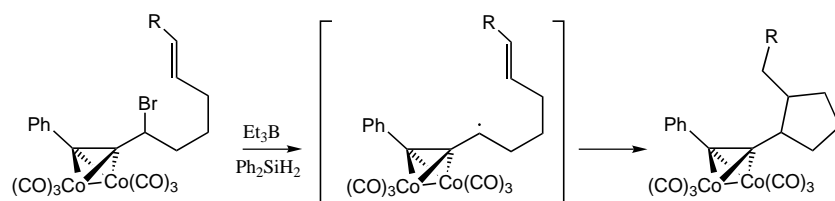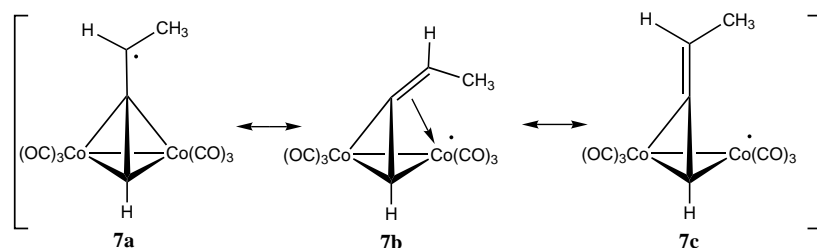

6a   **6b**
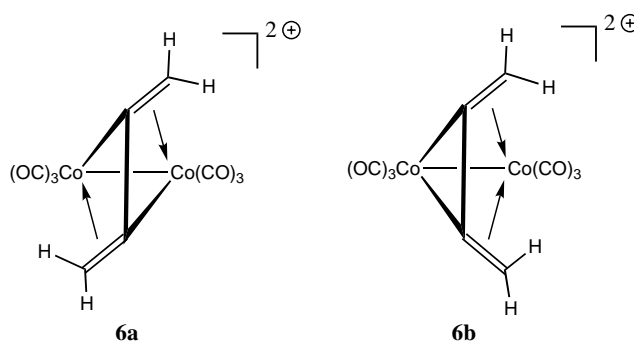
Figure 6. Two representations of the calculated geometry and partial charges of the dicationic complexes **6a** and **6b**. Partial charges (left) and bond lengths (right) are indicated.

Scheme 4. Cyclization reaction via a Co$_2$(CO)$_6$-stabilized radical intermediate.

Scheme 5. Possible mesomeric structures for the radical intermediate **7**.

mediates. Especially the configurational stability of such radicals has yet to be studied.

Formally, the radical can be located (Scheme 5) at the propargylic center (**7a**) or at one of the cobalt atoms (**7b**, **7c**). In the latter cases, the propargylic center would be part of a double bond which could be coordinated (**7b**) to the radical-bearing cobalt atom or not (**7c**).

The calculated minimum-energy structure of **7** is depicted in Figure 7. One Co atom is no longer bound to C8 (one of the former acetylene centers), and all of the spin density is located at this cobalt atom (NBO analysis). In addition, the C8–C9

bond length is only 1.335 Å, which indicates a double bond. Thus, this radical is best represented by mesomer **7c**. In contrast to the eclipsed arrangements of neutral complex **1** and the cationic species **3**, the carbonyl groups in **7** are arranged in a staggered fashion along the Co–Co axis.

As in the case of the cation **3**, four stereoisomers (two pairs of enantiomers) are possible for radical **7**, and they may be interconvertable in a related dynamic system (cf. Scheme 3). According to the calculations, there are again two transition states, corresponding to antara- and suprafacial migration of the alkylidene group from one cobalt atom to the other.

The C_s-symmetric transition state **8** (Figure 8) for the antarafacial process has a very similar geometry to **4**: the CHCH$_3$ group stands upright in the middle between the two Co-(CO)$_3$ fragments. The NBO analysis shows that about half of the spin density is still delocalized over the cobalt atoms, while the other half is located at C9. This indicates that only in the distorted structure **7** is the cobalt moiety able to fully accommodate the unpaired electron. Interestingly, in the transition state **8** the carbonyl groups are eclipsed with respect to the cobalt–cobalt axis, in contrast to the minimum-energy structure **7**, in which the carbonyl groups are staggered.

Although the participation of the cobalt atoms in the delocalization of the spin density is much lower in **8** than in **7**, the energy barrier for the antarafacial migration is quite low and amounts to only 7.6 kcal mol^{-1}. Therefore, racemization of such radicals is expected to occur even more rapidly than in the corresponding cationic species (see above). This means that reactions via cobalt-stabilized propargylic radicals would not proceed in a stereospecific manner, in contrast to reactions involving Cr(CO)$_3$-complexed benzylic radicals.[21]

The transition state **9** for suprafacial isomerization (Figure 9) has C_1 symmetry and lies 7.4 kcal mol^{-1} above **8**, which corresponds to a barrier of 15 kcal mol^{-1}. Its structure is best
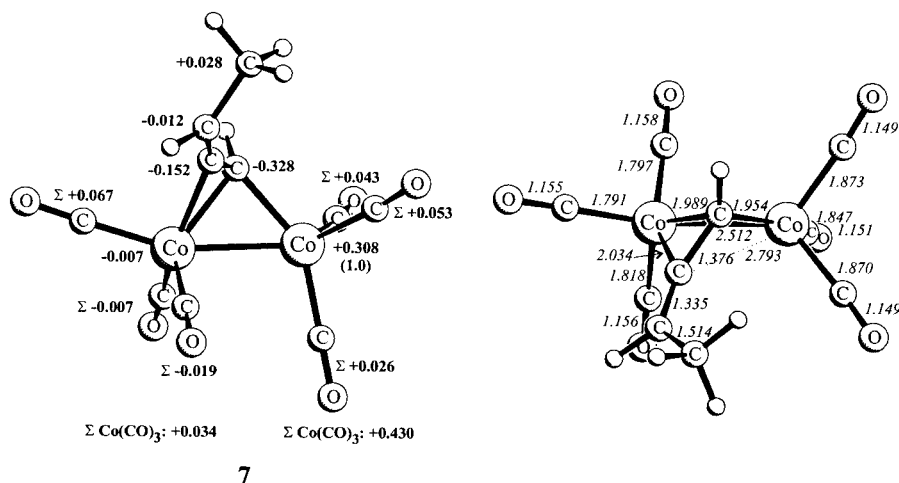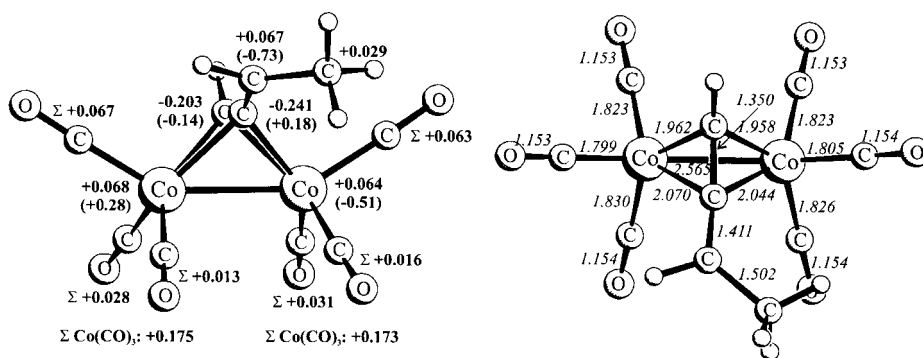
Figure 7. Two representations of the calculated structure of the radical intermediate **7**. Partial charges (left) and bond lengths (right) are indicated.
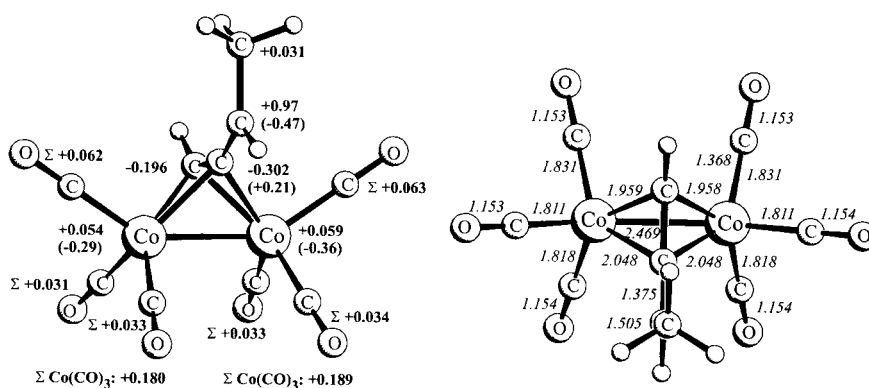
Figure 8. Two representations of the transition state for the antarafacial migration of the CHCH$_3$ group in the radical complex **7**. Partial charges (left) and bond lengths (right) are indicated.

Figure 9. Two representations of the transition state **9** for the suprafacial migration of the CHCH$_3$ group in the radical complex. Partial charges (left) and bond lengths (right) are indicated.

described by resonance formula **7a**, because the majority of the spin density is now located at C9, and the C8–C9 bond length of 1.411 Å is indicative of a less pronounced double-bond character (cf. 1.375 Å in **8**). The less pronounced delocalization of the spin density over the cobalt moieties may explain the higher energy of this transition state.

The anionic complex C$_4$H$_5$–Co$_2$(CO)$_6^-$: To the best of our knowledge, no experiments involving anionic cobalt complexed intermediates have been reported. Therefore, a theoretical investigation might give some ideas for such chemistry.

Figure 10 shows the calculated structure of the anionic C$_4$H$_5$–Co$_2$(CO)$_6^-$ complex **10**, formally derived by abstraction of a propargylic proton from **1**. The geometry of **10** has much in common with that of the radical complex **9**. The tetrahedral core is distorted in that the bond between Co1 and the substituted acetylene carbon atom C8 is elongated to 2.868 Å (Co1–C8 in **1**: 1.988 Å). The C8–C9 bond has again changed from a single bond in **1** to a double bond (1.336 Å).

Whereas the positive charge in **3** and the spin density in **7** are more or less completely delocalized over the Co$_2$(CO)$_6$ fragment, in **10** less than half of the negative charge is delocalized over the cobalt moieties. The remainder of the charge is partitioned mainly over the acetylenic carbon atoms; the propargylic center C9 carries only a small partial charge of -0.076 e.

The calculations further revealed an unexpectedly high energy barrier (23.7 kcal mol^{-1}) for the antarafacial migration of the ethyl group from one cobalt atom to the other via the C_s-symmetric transition state **11** (Figure 11) resulting in enantiomerization. Therefore, it is possible that stereospecific transformations involving such anionic intermediates could be realized.

The other transition state **12** (Figure 11) is energetically disfavored by 19.3 kcal mol^{-1} relative to the anionic minimum-energy structure **10**. Thus, in the anionic intermediate the transition state for antarafacial migration is higher in energy than that for suprafacial migration, opposite to the situation in the cationic and radical complexes. The NBO analysis for **12** showed that the Co$_2$(CO)$_6$ fragment adopts a partial charge of -0.5 e, as in **10** and **11**. Compared to **11**, the propargylic position in **12** has a slightly higher negative charge (-0.134 e).
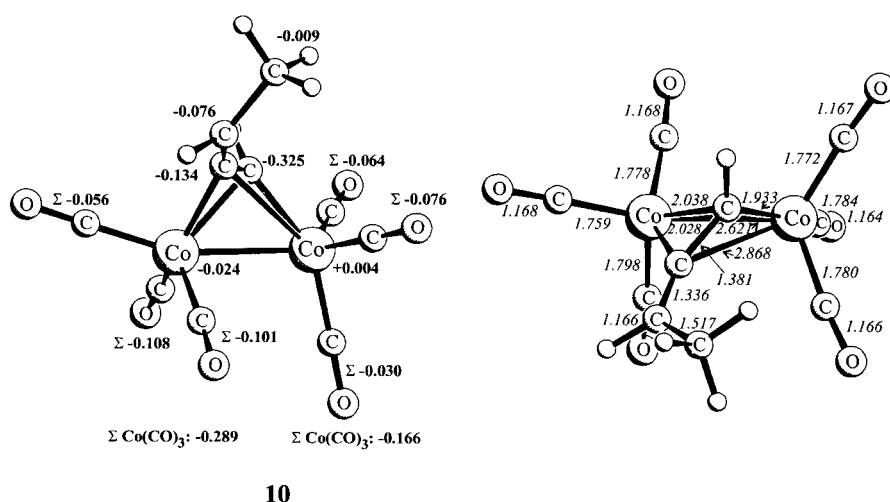
10

Figure 10. Two representations of the minimum-energy structure of the anionic intermediate **10**. Partial charges (left) and bond lengths (right) are indicated.
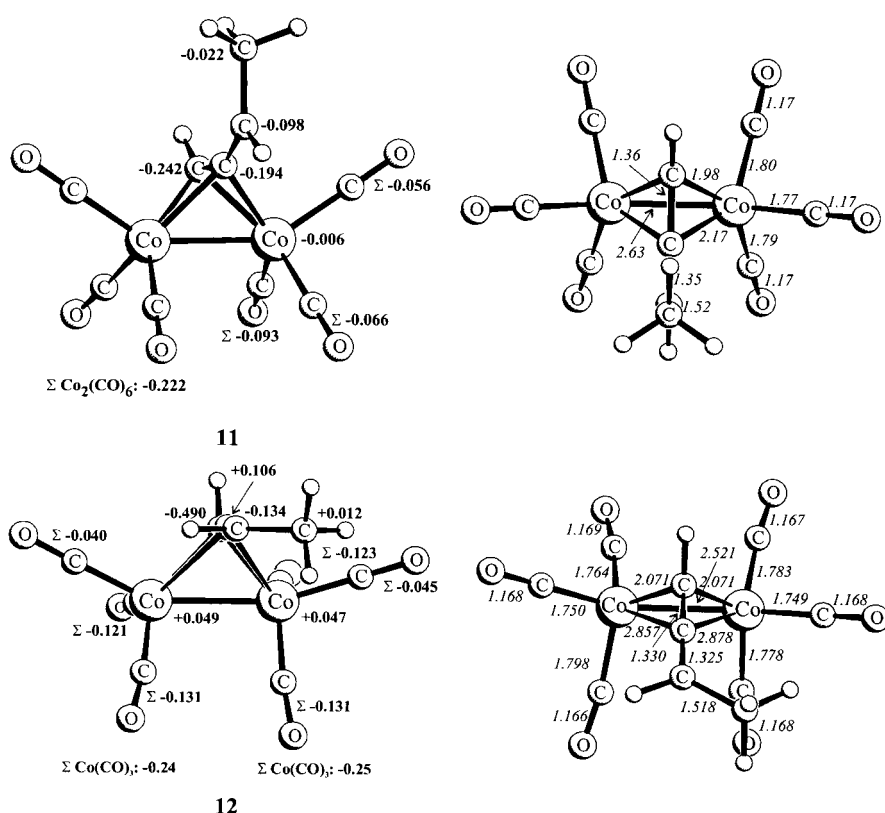

11

12

Figure 11. Two representations of the transition states for antarafacial (**11**) and suprafacial (**12**) migration of the -CHCH$_3$ group in the anionic intermediate. Partial charges (left) and bond lengths (right) are indicated.

Conclusion

The density functional study reported here provides a clear picture of the geometry, electronic structure, and configurational stability of the cationic, radical, and anionic propargylic intermediates derived from 1-butyne – Co$_2$(CO)$_6$ (**1**). Besides the accuracy of the theoretical approach, the radical and the anionic intermediates were studied for the first time.

In all cases, two transition states could be identified for isomerization of the reactive intermediates. The barrier for the antarafacial migration of the propargylic center from one Co atom to the other with enantiomerization of the complex is decisive for the feasibility of stereospecific reactions. This barrier is rather low for the cationic (9.5 kcal mol^{-1}) and the radical (7.6 kcal mol^{-1}) intermediates (see Table 2), but is rather high for the anionic intermediate (23.7 kcal mol^{-1}). We are confident that the results of this study will be of value for experimental chemists by assisting them in evaluating potential applications in stereoselective synthesis.

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Table 2. Energy barriers of the two isomerization processes and resonance structures for the reactive intermediates **3**, **7**, and **10**.

Reactive intermediate	Resonance structures antarafacial isomerization	Energy barrier for suprafacial isomerization (enantiomerization)	Energy barrier for (syn/anti isomerization)
3		9.5 kcal mol^{-1}	11.9 kcal mol^{-1}
7		7.6 kcal mol^{-1}	15.0 kcal mol^{-1}
10		23.7 kcal mol^{-1}	19.3 kcal mol^{-1}

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