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Metal–Metal Bonding in Bis(alkylthio)hexacarbonyldicobalt Complexes: Open Structures vs. Butterfly and Tetrahedrane Structures

Menyhárt B. Sárosi,[a] Ioan Silaghi-Dumitrescu,[a][†] and R. Bruce King*[b]

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Density functional calculations on the $Co_2(CO)_6(SR)_2$ compounds (R = CH_3, CF_3) predict both open and butterfly structure types of similar energies. The open $Co_2(CO)_6(\mu\text{-}SR)_2$ structures have non-planar central Co_2S_2 units with two bridging RS groups and ca. 3.4 Å Co···Co distances indicating a lack of direct metal–metal bonding. The butterfly $Co_2(CO)_5(\mu\text{-}SR)(\mu\text{-}CO)(SR)$ structures have direct Co–Co bonds of lengths ca. 2.5 Å forming the "body" of the butterfly, one terminal RS group, one bridging RS group, and one bridging CO group. The lowest energy $Co_2(CO)_6(SCH_3)_2$ structure is an open isomer. However, this open isomer lies only 0.4 kcal/mol below the corresponding butterfly isomer. For the corresponding fluorinated derivative $Co_2(CO)_6(SCF_3)_2$ a butterfly structure with a direct Co–Co bond and a bridging CO group lies at a slightly lower energy than the lowest energy open structures. The relative energy difference between open and butterfly $Co_2(CO)_6(SCF_3)_2$ structures is more than five times higher than for the $Co_2(CO)_6(SCH_3)_2$ structures. The electronegativity of the RS group in the $Co_2(CO)_6(SR)_2$ structures has little effect on the geometric parameters but exerts a significant influence on the atomic charge distribution. The butterfly structures with a direct metal–metal bond are predicted to be nearly isoenergetic to open structures without a Co–Co bond. Unsuccessful attempts to optimize a previously proposed $Co_2(CO)_6(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2R_2)$ structure with a central Co_2S_2 tetrahedrane unit with one Co–Co bond, one S–S bond, and four Co–S bonds are consistent with the previous reformulation of the originally claimed Co_2S_2 tetrahedranes $Co_2(CO)_6[\mu\text{-}\eta^2{:}\eta^2\text{-}S_2(C_6X_5)_2]$ (X = F, Cl) as the trinuclear derivatives $Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8$.

1. Introduction

The chemistry of organosulfur metal carbonyl derivatives originated in 1937 with the discovery by Hieber and Spacu[1] of reactions between $Fe_3(CO)_{12}$ and various sulfides, mercaptans, and disulfides to give stable red $Fe_2(CO)_6(\mu\text{-}SR)_2$ compounds. At that time Hieber and Spacu also reported an analogous reaction of $Co_2(CO)_8$ with benzenethiol to give a product formulated as $Co_2(CO)_6(SC_6H_5)_2$.

Originally the nature of these compounds was rather obscure since the possibility of direct metal-metal bonds in molecular polynuclear transition metal derivatives had not yet been recognized at the time of their original discovery. Eventually, however, the possibility of an iron–iron bond in such compounds was recognized, suggesting structures formally described in Figure 1. Such structures can be considered to be butterfly structures with the iron-iron bond forming the "body" of the butterfly and the alkylthio groups the "wingtips" of the butterfly. In such butterfly structures each iron atom formally has the favored 18-electron configuration by receiving six electrons from the three

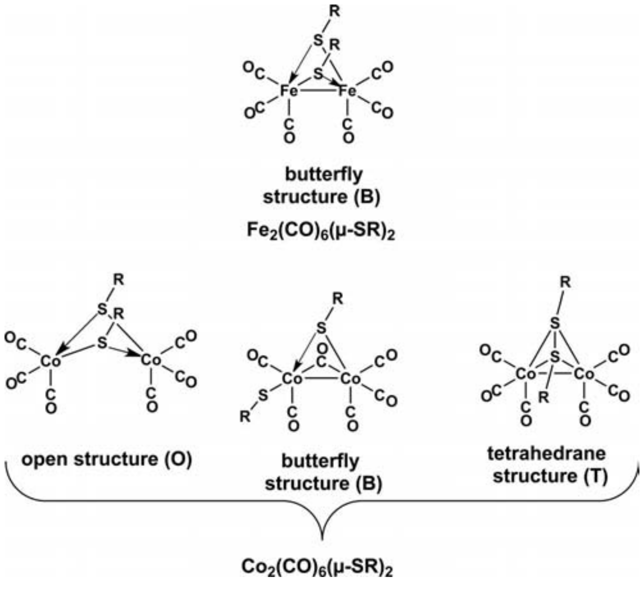

Figure 1. Structures of bis(alkylthio)dimetal hexacarbonyl complexes. Each sulfur atom in these structures has an additional lone pair (not shown for the sake of clarity).

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[a] Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University,
Cluj-Napoca, Romania
[b] Department of Chemistry, University of Georgia,
Athens, Georgia 30602, USA

[†] Prof. Ioan Silaghi-Dumitrescu passed away on December 25, 2009

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carbonyl groups, one electron from the iron-iron bond, one electron from a two-electron two-center bond with the sulfur atom of one of the RS groups, and two electrons from a dative bond from the sulfur atom of the other RS group. The dative bonds are represented schematically by arrows in Figure 1. A structure of this type was confirmed by X-ray crystallography for the ethylthio derivative $Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2$.[2] In addition, two stereoisomers of the methylthio derivative $Fe_2(CO)_6(\mu\text{-}SCH_3)_2$ have been separated by chromatography.[3] These stereoisomers differ in the relative orientations of the alkyl groups in the central Fe_2S_2 network. Since their original discovery the $Fe_2(CO)_6(\mu\text{-}SR)_2$ derivatives and related compounds such as $Fe_2(CO)_6(\mu\text{-}S_2)$[4] have received considerable attention, particularly in recent years after their significance as a model for the [FeFe]-only hydrogenase from *C. pasteurianum* was recognized.[5]

The corresponding (alkylthio)cobalt carbonyl complexes $Co_2(CO)_6(\mu\text{-}SR)_2$ have received much less attention since the original report of $Co_2(CO)_6(\mu\text{-}SC_6H_5)_2$ by Hieber and Spacu.[1] Simple application of the 18-electron rule suggests an open structure without a Co–Co bond for the $Co_2(CO)_6(\mu\text{-}SR)_2$ derivatives (Figure 1). However, subsequent attempts to reproduce the original results of Hieber and Spacu were unsuccessful. Thus reactions of $Co_2(CO)_8$ with thiols and disulfides were found to give complicated mixtures of carbonylcobalt clusters with three to six cobalt atoms containing both Co–Co bonds and doubly and triply bridging RS groups.[6] However, in 1971 Bor and Natile[7] claimed that the reactions of the pentahaloaryl disulfides $C_6X_5SSC_6X_5$ (X = F, Cl) with $Co_2(CO)_8$ gave the simple binuclear derivatives $Co_2(CO)_6(\mu\text{-}SC_6X_5)_2$. The infrared ν(CO) frequencies of this product suggested that all of the carbonyl groups are terminal carbonyl groups. Furthermore, the similarity of the ν(CO) spectrum of the supposed $Co_2(CO)_6(\mu\text{-}SC_6F_5)_2$ to the ν(CO) spectra of the alkyne-hexacarbonyldicobalt complexes[8] $Co_2(CO)_6C_2R_2$ containing a central Co_2C_2 tetrahedrane unit led Bor and Natile[7] to propose for their product an analogous $Co_2(CO)_6S_2(C_6F_5)_2$ structure containing an analogous central Co_2S_2 tetrahedrane unit (Figure 1). This proposed $Co_2(CO)_6S_2(C_6F_5)_2$ tetrahedrane structure is distinctive in containing two tetracoordinate hypervalent sulfur atoms with a stereoactive lone pair.

Subsequent attempts by Bor and collaborators[9] to confirm the Co_2S_2 tetrahedrane structure by X-ray diffraction indicated that this cobalt complex was not the previously suggested[7] binuclear complex $Co_2(CO)_6S_2(C_6F_5)_2$ but instead a trinuclear compound with the rather different stoichiometry $Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8$. This trinuclear complex has a tetrahedrane structure but with a central Co_3S unit rather than the Co_2S_2 unit of the originally suggested $Co_2(CO)_6S_2(C_6F_5)_2$ structure. This reaction is interesting since the C_6F_5S ligand has split into a C_6F_5 group σ-bonded to a cobalt atom and an isolated sulfur atom bridging all three cobalt atoms. Thus no genuine $Co_2(CO)_6(SR)_2$ derivative of any type has yet been synthesized and definitively characterized.

There are three possible structure types for $Co_2(CO)_6(SR)_2$ derivatives (Figure 1). The originally suggested open structure (**O**) contains four Co–S bonds but no direct Co–Co or S–S bonds in the central Co_2S_2 unit. Both RS groups bridge the pair of cobalt atoms. A second $Co_2(CO)_6(SR)_2$ structure type is the butterfly structure (**B**) in which the central Co_2S_2 unit has four Co–S bonds, a Co–Co bond, but no S–S bond. The Co–Co bond forms the "body" of the butterfly. In this structure one of the RS groups is a terminal RS group and the other RS group is a bridging RS group. Also one of the carbonyl groups is a bridging carbonyl group. These bonding modes give each cobalt atom in the butterfly $Co_2(CO)_6(SR)_2$ structure the favored 18-electron configuration. The third possible $Co_2(CO)_6(SR)_2$ structure is the tetrahedrane structure (**T**) originally suggested by Bor and Natile[7] for the supposed $Co_2(CO)_6(SC_6F_5)_2$ that later was shown to be $Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8$ (Figure 2). In the tetrahedrane $Co_2(CO)_6(SR)_2$ structure the central tetrahedrane Co_2S_2 unit contains not only four Co–S bonds but also a direct Co–Co bond and a direct S–S bond leading to four-coordinate hypervalent sulfur atoms.

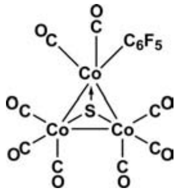

Figure 2. The structure of $Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8$ determined by X-ray diffraction. This substance was originally believed to be $Co_2(CO)_6(SC_6F_5)_2$.

This paper reports density functional theory (DFT) studies on $Co_2(CO)_6(SR)_2$ complexes in order to assess the relative stabilities of these three structure types. Both alkylthio and perfluoroalkylthio RS groups were chosen for this study in order to assess the effect of substituting hydrogen atoms with the more electronegative fluorine atoms. The simplest examples of alkyl and perfluoroalkyl groups were chosen for this study, namely methyl and trifluoromethyl, respectively.

2. Theoretical Methods

Electron correlation effects were considered using a pure density functional theory (DFT) method. The BP86 functional combines Becke's 1988 exchange functional (B)[10] with Perdew's 1986 gradient correlation functional (P86).[11] This pure density functional has the best computational cost/performance ratio for 3d transition metal chemistry[12] and generally predicts the vibrational frequencies of transition metal carbonyl complexes within less than 1% of the experimental values.[13]

The calculations were performed using two different basis sets. The first series of calculations was carried out using the standard all-electron 6-31G(d) basis set[14] for all atoms. The second series of calculations used the Wachters primitive set,[15] with the *f* function exponents of Bauschlicher et al.[16] for Co, obtained from the EMSL Basis Set Library,[17] and the Dunning-Huzinaga full double zeta basis set[18] augmented with a *d* polarization function for all other atoms. Only the results obtained with the latter basis set are reported in the text. The results obtained with the 6-31G(d) basis can be found in the Supporting Information.

Initially, all geometries were fully optimized for their closed-shell singlet states. Then, based on the optimized singlet geometries, further calculations were carried out for the triplet states. However, all of the optimized triplet structures are predicted to have higher energies than the corresponding singlet structures. The energy gaps between the singlet and triplet states of the alkylthio substituted structures (>14 kcal/mol) are somewhat smaller than for the compounds with perfluoroalkyl RS groups (>19 kcal/mol). However, because of their significantly higher energies none of the optimized triplet structures were considered further.

All of the optimizations were carried out in the gas phase using the Gaussian 09 programs[19] with the fine grid (75,302) for evaluating integrals numerically and the tight (10^{-8} hartree) designation for the SCF convergence.

3. Results and Discussion

Although the central Co_2S_2 unit in the open $Co_2(CO)_6(\mu\text{-SR})_2$ structures (**O**) is non-planar, these geometries are not of the butterfly type because there is no direct Co–Co or S–S bond to constitute the "body" of the butterfly. The non-planar configuration of the Co_2S_2 unit leads to two possible orientations of the R substituents, namely "up" (**u**) pointing away from the cobalt–cobalt vector and "down" (**d**) pointing towards the cobalt–cobalt vector. There are thus three possible arrangements of the two R groups in the open $Co_2(CO)_6(SR)_2$ derivatives, namely "up–down" (**ud**), "down–down" (**dd**), and "up–up" (**uu**). Additionally, the $Co(CO)_3$ moieties in these open structures can have either the staggered (**s**) or the eclipsed (**e**) arrangement. Within the butterfly $Co_2(CO)_5(\mu\text{-SR})(\mu\text{-CO})(SR)$ structure (**B**) both types of RS groups can have similar orientations. Thus not only the bridging, but also the terminal RS groups can point "up" (**u**) or "down" (**d**) from the Co–Co bond, leading to four different stereoisomers (Figure 3). All of these $Co_2(CO)_6(SR)_2$ (R = CH_3, CF_3) structures have very similar energies, lying within 8 kcal/mol of each other.

The lowest energy $Co_2(CO)_6(SCH_3)_2$ structure is the **O-ud-s** isomer, followed closely by the **O-ud-e** isomer lying only 0.4 kcal/mol above **O-ud-s** (Figure 3 and Figure 4). The highest energy of the six open $Co_2(CO)_6(\mu\text{-SCH}_3)_2$ structures is the **O-uu-e** isomer, lying 2.2 kcal/mol above the global minimum **O-ud-s**. The **O-TS** transition state is characterized by a planar Co_2S_2 central unit and an imaginary frequency corresponding to the inversion of the non-planar open $Co_2(CO)_6(\mu\text{-SCH}_3)_2$ structures. The energy barrier of only 1.9 kcal/mol suggests a readily achievable conversion between the various types of open $Co_2(CO)_6(\mu\text{-SCH}_3)_2$ structures.

The lowest lying butterfly $Co_2(CO)_5(\mu\text{-SCH}_3)(\mu\text{-CO})(SCH_3)$ structures are the **B-ud** and **B-dd** isomers, again with a relative energy difference of only 0.4 kcal/mol between them. The remaining butterfly structures with their

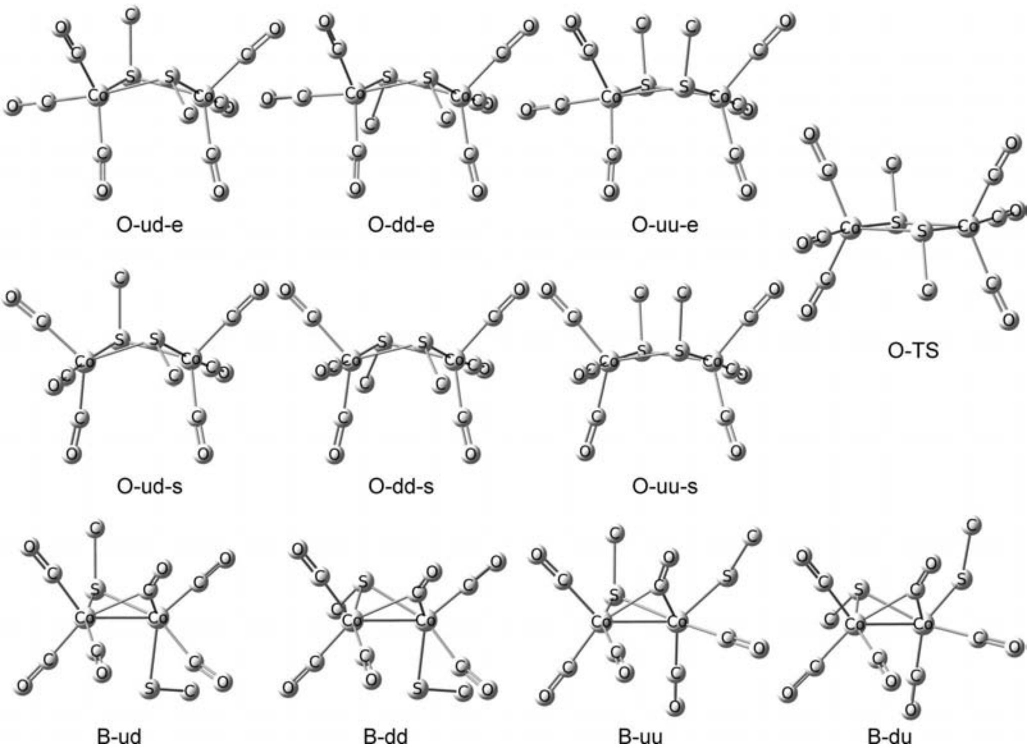

Figure 3. The 11 optimized $Co_2(CO)_6(SR)_2$ structures (R = CH_3 or CF_3). The hydrogen and fluorine atoms have been omitted for the sake of clarity.

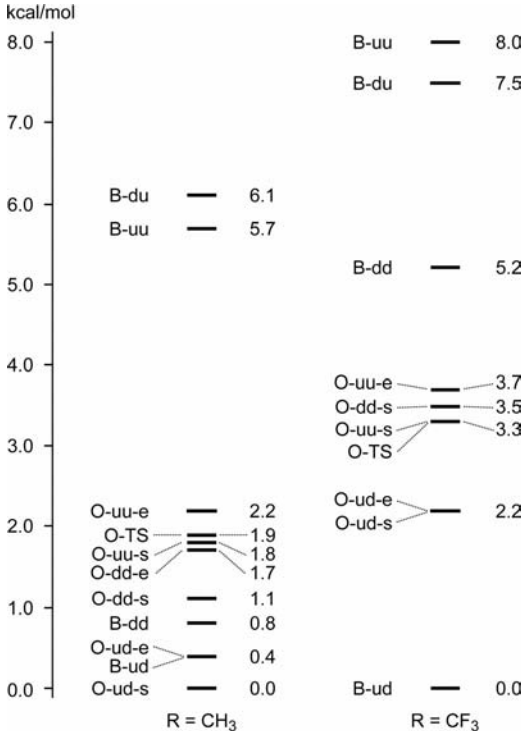

Figure 4. Relative energies [kcal/mol] for the investigated $Co_2(CO)_6(SR)_2$ structures.

terminal RS groups oriented "up" (**B-uu** and **B-du**) lie at ca. 5 kcal/mol higher energies. There is no significant difference, with respect to relative energy, between the **B-ud** and the open **O-ud-e** isomers, indicating that there is a competition between the $Co_2(CO)_6(SCH_3)_2$ structures with and without a direct metal–metal bond.

The $Co_2(CO)_6(SCF_3)_2$ system is rather different from the $Co_2(CO)_6(SCH_3)_2$ system since the lowest lying structure is not one of the open geometries but instead the **B-ud** butterfly isomer. In addition, the separation between the butterfly and open structures is more than five times higher than for $Co_2(CO)_6(SCH_3)_2$, namely 2.2 kcal/mol. There thus appears to be a greater preference for metal–metal bonding in the $Co_2(CO)_6(SCF_3)_2$ structures than in the $Co_2(CO)_6(SCH_3)_2$ structures. However, the electronegativity of the SR group does not appear to have a high impact on the geometrical parameters of both the butterfly and open $Co_2(CO)_6(SR)_2$ stereoisomers, as indicated by the very similar Co···Co and Co–S distances in both $Co_2(CO)_6(SCF_3)_2$ and $Co_2(CO)_6(SCH_3)_2$ structures (Table 1). The transition state **O-TS** (Figure 3) between the open $Co_2(CO)_6(\mu\text{-}SCF_3)_2$ structures is again readily accessible energetically, with a low lying inversion energy barrier of 1.1 kcal/mol. The remaining three butterfly $Co_2(CO)_5(\mu\text{-}SCF_3)(\mu\text{-}CO)(SCF_3)$ structures (**B-dd**, **B-du** and **B-uu**) lie at 5.2, 7.5 and 8.0 kcal/mol relative energy values, respectively, above the **B-ud** global minimum. The Co–S–S–Co dihedral angles in the **O-uu-e** and **O-uu-s** open $Co_2(CO)_6(\mu\text{-}SCF_3)_2$ structures are almost planar (177.0 and 175.5°, respectively), in contrast to the ca. 159° Co–S–S–Co dihedral of the corresponding $Co_2(CO)_6(\mu\text{-}SCH_3)_2$ structures. Attempted optimization of the **O-dd-e** $Co_2(CO)_6(\mu\text{-}SCF_3)_2$ led instead to the corresponding **O-uu-e** geometry.

The predicted Co–Co bond lengths in the butterfly $Co_2(CO)_5(\mu\text{-}SR)(\mu\text{-}CO)(SR)$ structures (R = CH_3 and CF_3) (see Table 1) agree well with the experimental value of 2.559(3) Å, determined by X-ray diffraction for the Co–Co single bond of $Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$), one of the few experimentally available compounds containing a $Co_2(\mu\text{-}CO)(\mu\text{-}S)$ core.[20] The open $Co_2(CO)_6(\mu\text{-}SR)_2$ structures, on the other hand, are predicted to have long Co···Co distances of ca. 3.39 Å (Table 1). This clearly indicates the absence of a direct metal–metal bond. For the open $Co_2(CO)_6(\mu\text{-}SR)_2$ structures the favored 18-electron configuration for the cobalt atoms can be attained without a direct cobalt–cobalt bond. The predicted Co–S distances of ca. 2.25 and ca. 2.29 Å for the $Co_2(CO)_5(\mu\text{-}SR)(\mu\text{-}CO)(SR)$ structures also agree well with the experimental values of 2.262(6) and 2.275(5) Å.[20] However, while the experimental distances between the cobalt atoms and the carbon of the bridging CO group are practically equal [1.94(1) and 1.95(1) Å],[20] the calculations predict a more unsymmetrical μ-CO group for the $Co_2(CO)_5(\mu\text{-}SR)(\mu\text{-}CO)(SR)$ structures, with Co–C bond lengths of ca. 1.86 and ca. 2.08 Å, suggesting a displacement of the bridging CO group towards the cobalt center bearing the terminal SR group.

Even though the nature of the SR group does not appear to have a high impact on the geometrical parameters, its

Table 1. Calculated Co–Co and Co–S distances [Å], imaginary frequencies [cm^{-1}] and HOMO–LUMO gaps [eV] for the $Co_2(CO)_6(SR)_2$ structures. Terminal Co–S distances are printed in *italics*.

	Co–Co		Co–S		Imaginary frequency		HOMO–LUMO	
	R = CH_3	R = CF_3	R = CH_3	R = CF_3	R = CH_3	R = CF_3	R = CH_3	R = CF_3
O-ud-s	3.359	3.387	2.314, 2.323, 2.342, 2.362	2.313, 2.315, 2.357, 2.360	none		1.6	1.6
O-ud-e	3.402	3.417	2.292, 2.369	2.292, 2,364	none		1.7	1.7
B-ud	2.523	2.523	2.242, 2.289, *2.363*	2.222, 2.278, *2.361*	none		1.8	1.5
B-dd	2.514	2.514	2.272, 2.288, *2.356*	2.262, 2.277, *2.350*	none		1.8	1.4
O-dd-s	3.402	3.457	2.326, 2.351	2.320, 2.358	none	8*i*	1.6	1.6
O-dd-e	3.419	–	2.299, 2.373	–	none	–	1.5	–
O-uu-s	3.393	3.433	2.320, 2.354	2.314, 2.360	none		1.5	1.6
O-TS	3.472	3.469	2.325, 2.347	2.320, 2.358	31*i*	16*i*	1.5	1.5
O-uu-e	3.396	3.436	2.305, 2.362	2.301, 2.363	none		1.7	1.8
B-uu	2.518	2.510	2.271, 2.296, *2.303*	2.269, 2.278, *2.296*	none		0.9	1.1
B-du	2.522	2.515	2.240, 2.311, *2.309*	2.257, 2.282, *2.303*	none		1.0	1.2

effect is felt in the atomic charge distributions. For instance, in the **O-ud-e** structures, the charge on the methyl carbon shifts from –0.70 to +1.05 (an increase of ca. 1.75) after switching from hydrogen to fluorine, while the positive charge on the sulfur atoms slightly decreases by almost 0.1. The charges on the cobalt atom and the CO ligands remain essentially the same. On the other hand, the atomic charge distribution of the **B-ud** geometry behaves in a different way: while the methyl carbon charge follows the same trend as in **O-ud-e**, only the terminal sulfur charge decreases (by 0.15) while the charge on the bridging S atom remains the same. In addition, the charge on the cobalt atom bearing the terminal SR group decreases by ca. 0.1, while the charge on the other cobalt remains unaltered. The equatorial CO carbon charge in the vicinity of the terminal SR group is also influenced by the change in electronegativity of the thio group (see the Supporting Information for more details).

Not only are the geometries not affected significantly by the nature of the SR group, the electronic structure of the corresponding conformers is also only weakly influenced by it. Both the highest occupied (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the corresponding methyl or trifluoromethyl-substituted **O-ud-e** structures have very similar shapes and compositions. While the HOMOs are mainly composed of σ(Co–S) and π(Co–CO) bonding orbitals and also by σ*(Co–CO) antibonding ones, the LUMOs are dominated by the σ*(Co–S) and σ*(Co–CO) antibonding orbitals (Figure 5). As expected, the composition of the **B-ud** frontier orbitals differs in character from the corresponding **O-ud-e** orbitals. However, they again remain similar with respect to the change of the SR group from methyl to trifluoromethyl. Both **B-ud** HOMOs are mainly composed of the lone pair on the terminal S atom and of the σ bonding orbitals between the μ-CO group and the cobalt centers. In contrast, the LUMOs of **B-ud** are dominantly σ*(Co–μ-CO) in character (Figure 5). This similarity between the frontier orbitals of the methyl and trifluoromethyl-substituted structures could explain the observed almost equal HOMO–LUMO gaps (Table 1).

More important is the fact that the butterfly structures with a direct metal–metal bond are nearly isoenergetic to open structures without a Co–Co bond, and their HOMO–LUMO gaps and individual orbital energies are almost identical (Table 1 and Figure 5).

The theoretical vibrational ν(CO) frequencies for the $Co_2(CO)_6(SR)_2$ compounds are listed in Tables 2 and 3. The terminal ν(CO) frequencies were found in the 1927–2060 cm^{-1} range for the $Co_2(CO)_6(SCH_3)_2$ structures and in the 1996–2076 cm^{-1} range for the $Co_2(CO)_6(SCF_3)_2$ compounds. The bridging ν(CO) frequencies for the $Co_2(CO)_5(\mu\text{-}SR)(\mu\text{-}CO)(SR)$ compounds are significantly lower, in the ranges of 1848–1885 cm^{-1} for R = CH_3 and 1886–1894 cm^{-1} for R = CF_3. In general the ν(CO) frequencies of either type are slightly but significantly higher for the $Co_2(CO)_6(SCF_3)_2$ structures relative to the corresponding $Co_2(CO)_6(SCH_3)_2$ structures. This is an effect of the greater electronegativity of the CF_3 group relative to the CH_3 group leading to lower back-bonding in the $Co_2(CO)_6(SCF_3)_2$ structures relative to the corresponding $Co_2(CO)_6(SCH_3)_2$ structures. The predicted vibrational ν(CO) frequencies for the terminal CO groups in the $Co_2(CO)_6(SR)_2$ structures are fairly close to the C–O stretching frequencies of $Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8$.[9]

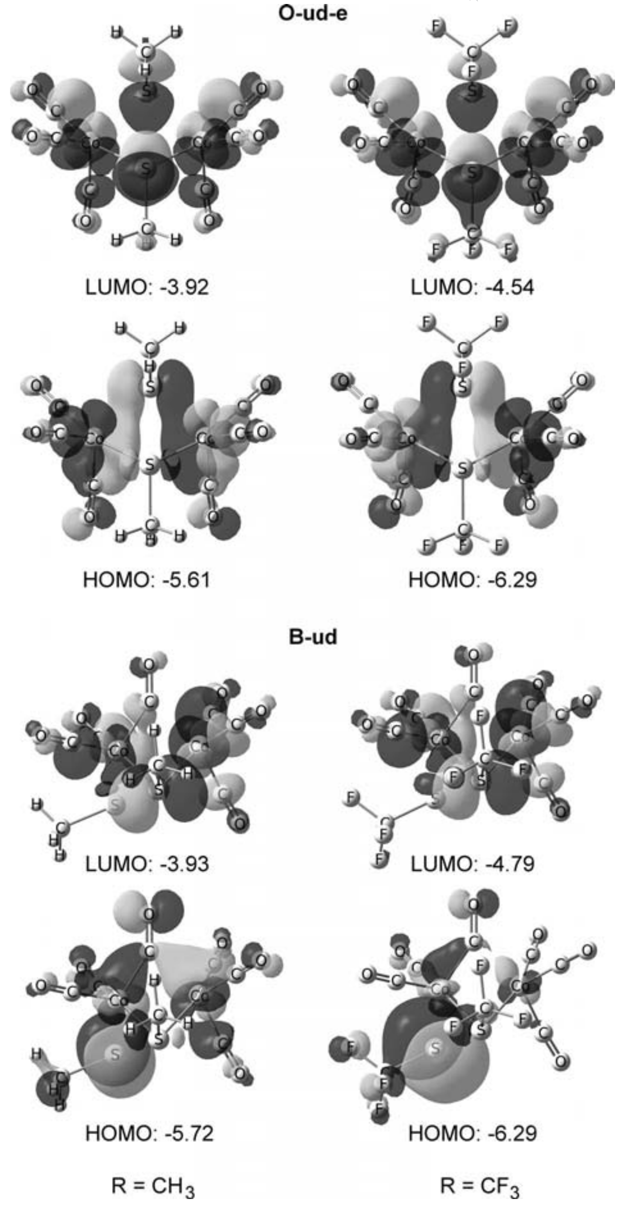

Figure 5. Energies [eV] and contours at the 0.03 isovalue of the HOMO and LUMO of some relevant $Co_2(CO)_6(SR)_2$ structures (R = CH_3 or CF_3). Positive values of the orbital contour are presented in light gray and negative values in dark gray.

We also investigated $Co_2(CO)_6(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2R_2)$ structures with a central Co_2S_2 tetrahedrane unit similar to the $Co_2(CO)_6[\mu\text{-}\eta^2{:}\eta^2\text{-}S_2(C_6X_5)_2]$ structures (X = F, Cl) originally suggested by Bor and Natile.[7] In this connection optimizations were attempted from starting $Co_2(CO)_6(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2R_2)$ geometries having tetrahedrane Co_2S_2 central units. However, all of these calculations failed to optimize towards the tetrahedrane structure. These results are consis-

Table 2. Calculated infrared ν(CO) frequencies for the $Co_2(CO)_6(SCH_3)_2$ structures. The infrared intensities are given in parentheses in km/mol. The ν(CO) frequencies for the bridging CO groups are printed in **bold**. The **O-TS** structure is omitted.

	Infrared ν(CO) frequencies [cm^{-1}]
O-ud-e	1969 (73), 1980 (1520), 1986 (71), 1992 (840), 2032 (1196), 2048 (112)
O-dd-e	1966 (29), 1980 (1554), 1986 (24), 1988 (873), 2028 (1290), 2044 (16)
O-uu-e	1971 (190), 1976 (1326), 1988 (2), 1996 (1024), 2031 (1159), 2048 (182)
O-ud-s	1972 (241), 1979 (1097), 1986 (912), 1990 (219), 2029 (1261), 2046 (112)
O-dd-s	1969 (93), 1980 (1482), 1986 (751), 1987 (135), 2028 (1369), 2044 (1)
O-uu-s	1972 (277), 1977 (1104), 1990 (723), 1995 (396), 2032 (1197), 2049 (163)
B-dd	**1885 (350)**, 1946 (414), 1998 (586), 2009 (687), 2017 (1098), 2054 (562)
B-ud	**1879 (313)**, 1927 (471), 2000 (693), 2008 (477), 2010 (1177), 2053 (516)
B-du	**1859 (389)**, 1989 (79), 2002 (974), 2006 (493), 2025 (1223), 2056 (579)
B-uu	**1848 (362)**, 2000 (25), 2005 (448), 2012 (1069), 2025 (1149), 2060 (112)

Table 3. Calculated infrared ν(CO) frequencies for the $Co_2(CO)_6(SCF_3)_2$ structures. The infrared intensities are given in parentheses in km/mol. The ν(CO) frequencies for the bridging CO groups are shown in **bold**. The **O-TS** structure is omitted.

	Infrared ν(CO) frequencies [cm^{-1}]
O-ud-e	1996 (55), 2005 (1510), 2010 (17), 2014 (733), 2054 (1190), 2069 (67)
O-uu-e	1997 (3), 2004 (1598), 2011 (26), 2014 (763), 2054 (1215), 2068 (41)
O-ud-s	1996 (94), 2004 (1439), 2009 (705), 2012 (52), 2053 (1251), 2069 (47)
O-dd-s	1999 (118), 2004 (1350), 2011 (576), 2014 (309), 2054 (1287), 2069 (1)
O-uu-s	1999 (90), 2004 (1476), 2012 (632), 2013 (167), 2055 (1249), 2069 (23)
B-ud	**1893 (341)**, 2019 (24), 2026 (538), 2028 (928), 2050 (1277), 2075 (291)
B-dd	**1887 (361)**, 2013 (31), 2024 (518), 2027 (925), 2050 (1220), 2073 (353)
B-uu	**1894 (372)**, 2015 (137), 2022 (349), 2028 (989), 2048 (1047), 2076 (493)
B-du	**1886 (381)**, 2017 (139), 2022 (330), 2028 (937), 2047 (1163), 2075 (500)

tent with the observation of $Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8$[9] rather than a $Co_2(CO)_6(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2R_2)$ tetrahedrane derivative as the reaction product from $Co_2(CO)_8$ and $(C_6F_5)_2S_2$.

The main differences between the $Fe_2(CO)_6(\mu\text{-}SR)_2$ structures and the open $Co_2(CO)_6(\mu\text{-}SR)_2$ structures (**O** in Figure 1) is the lack of a direct metal-metal bond, the lack of the semi-bridging CO groups in the open $Co_2(CO)_6(SR)_2$ structures with staggered $Co(CO)_3$ units, and much lower energy barriers by a factor of ten for the inversion of the non-planar Co_2S_2 open structures.[21] The predicted energy difference between the corresponding $Co_2(CO)_6(SR)_2$ structures with staggered and eclipsed $Co(CO)_3$ moieties is around ca. 0.5 kcal/mol, which is much smaller than that for the $Fe_2(CO)_6(\mu\text{-}SR)_2$ derivatives.[21] In addition, the predicted energy barriers for the inversion of open $Co_2(CO)_6(\mu\text{-}SR)_2$ structures is approximately twenty times lower than the energy barriers for the inversion of non-planar Fe_2S_2 butterfly structures through planar Fe_2S_2 intermediates.[21]

4. Conclusions

Density functional calculations on the $Co_2(CO)_6(SR)_2$ compounds (R = CH_3, CF_3) predict two different competing structure types, namely open structures with non-planar central Co_2S_2 units without direct Co–Co bonds and butterfly structures with a direct Co–Co bond forming the "body" of the butterfly. In the butterfly structures, one of the RS groups is a terminal RS group while the other RS group is a bridging RS group. In addition, one of the carbonyl groups in the butterfly structures is a bridging μ-CO group. The lowest energy $Co_2(CO)_6(SCH_3)_2$ structure is an open isomer. However, this open isomer lies only 0.4 kcal/mol below the corresponding butterfly isomer. For the corresponding fluorinated derivative $Co_2(CO)_6(SCF_3)_2$ a butterfly structure with a direct Co–Co bond and a bridging CO group lies at a slightly lower energy than the lowest energy open structures. This indicates a greater preference towards direct metal–metal bonding in the $Co_2(CO)_6(SCF_3)_2$ structures. The relative energy difference between open and butterfly $Co_2(CO)_6(SCF_3)_2$ structures is more than five times higher than for the $Co_2(CO)_6(SCF_3)_2$ structures. The electronegativity of the RS group in the $Co_2(CO)_6(SR)_2$ structures has little effect on the main geometric parameters but exerts a higher influence on the atomic charge distribution of both the open and the butterfly structures. However, the electronegativity of the fluorine atoms is mainly felt by the charge of the methyl carbon; the sulfur charge is a lot less influenced by it. Not only the geometries are not affected by the nature of the SR group, but the electronic structure of the corresponding conformers remains also similar. More important is the surprising fact, that the butterfly structures with a direct metal–metal bond are nearly isoenergetic to open structures without a Co–Co bond. The similar HOMO–LUMO gaps and the almost identical orbital energies of the open and butterfly structures result in the isoenergetic character of geometries with a direct metal–metal bond and geometries without such a bond. Unsuccessful attempts to reproduce theoretically the proposed $Co_2(CO)_6(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2R_2)$ structure with a central Co_2S_2 tetrahedrane unit are consistent with the reformulation of the originally claimed Co_2S_2 tetrahedranes $Co_2(CO)_6[\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2(C_6X_5)_2]$ (X = F, Cl) as the trinuclear derivative $Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8$.

Supporting Information (see footnote on the first page of this article): Tables S1 to S2: BP86/6-31G(d) total energies (E, au), relative energies (Δ*E*, kcal/mol) and Co–Co distances [Å] for the $Co_2(CO)_6(SR)_2$ (R = CH_3, CF_3) structures; Tables S3 to S24. Cartesian coordinates of the $Co_2(CO)_6(SR)_2$ (R = CH_3, CF_3) structures; Tables S25 to S45. Harmonic vibrational frequencies (cm^{-1}) and IR intensities [km/mol] for the $Co_2(CO)_6(SR)_2$ (R = CH_3, CF_3) structures. Tables S46 to S47. Atomic charge distributions from natural population analysis and relative charge differences for the $Co_2(CO)_6(SR)_2$ (R = CH_3, CF_3) structures.

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