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Binuclear Cobalt Thiocarbonyl Carbonyl Derivatives: Comparison with Homoleptic Binuclear Cobalt Carbonyls

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Density functional theory studies on $Co_2(CS)_2(CO)_8$ show the structure with two bridging CS groups to be the global minimum. Furthermore, swapping a terminal CO group with a bridging CS group to give a terminal CS group and a bridging CO group increases the energy of the structure by 7 ± 2 kcal/mol. Thus, unbridged $Co_2(CS)_2(CO)_8$ structures lie at least 11 kcal/mol above the doubly bridged global minimum $Co_2(\mu\text{-CS})_2(CO)_6$, unlike $Co_2(CO)_8$ where the doubly bridged and unbridged structures are significantly closer in energy. The lowest energy unsaturated $Co_2(CS)_2(CO)_n$ ($n = 5, 4, 3$) structures are predicted to contain four-electron donor bridging η^2-μ-CS groups, unlike the corresponding homoleptic carbonyls $Co_2(CO)_{n+2}$, which contain only two-electron donor carbonyl groups. For example, the three lowest energy $Co_2(CS)_2(CO)_5$ structures contain a single η^2-μ-CS group accompanied by a Co−Co distance of ~2.7 Å, consistent with the single bond required to give both cobalt atoms the favored 18-electron configuration.

1. Introduction

The simplest stable cobalt carbonyl is $Co_2(CO)_8$, which is commercially available and frequently used as a reagent in synthetic organocobalt chemistry. The structure of crystalline $Co_2(CO)_8$ has been shown by X-ray diffraction to have two bridging carbonyl groups and six terminal carbonyl groups (Figure 1).[1−3] However, infrared ν(CO) spectra of solutions of $Co_2(CO)_8$ indicate that in solution this doubly bridged isomer of $Co_2(CO)_8$ is in equilibrium with an unbridged structure.[4−8] Both cobalt atoms in $Co_2(CO)_8$ have the favored 18-electron configuration.

Unsaturated cobalt carbonyls such as $Co_2(CO)_7$ and $Co_2(CO)_6$ require formal cobalt−cobalt multiple bonds to maintain the favored 18-electron configuration of both cobalt atoms and have not been synthesized as stable compounds. However, matrix photolysis studies indicate the existence of $Co_2(CO)_7$ in low-temperature matrices. The infrared ν(CO) frequencies of $Co_2(CO)_7$ suggest a structure with exclusively terminal carbonyl groups (Figure 1).[9] A similar unbridged structure has been suggested for the isoelectronic mixed metal carbonyl $CoRh(CO)_7$, which has been isolated in the crystalline state at low temperatures.[10] However, $CoRh(CO)_7$ has proven to be too unstable for experimental determination of its structure by X-ray crystallography. The matrix photolysis studies on homoleptic cobalt carbonyls also provide evidence for the even more unsaturated $Co_2(CO)_6$, which requires a Co≡Co triple bond to give both cobalt atoms the favored 18-electron configuration.[9] The kinetics of the thermal conversion of $Co_2(CO)_8$ to $Co_4(CO)_{12}$, which occurs only slightly above room temperature, also suggests a $Co_2(CO)_6$ reaction intermediate.[11,12]

A number of metal thiocarbonyl derivatives have been synthesized in which one or more carbonyl groups of a well-known homoleptic metal carbonyl have been replaced by thiocarbonyl groups. These include $M(CS)(CO)_5$ (M = Cr, Mo, W),[13] isoelectronic with $M(CO)_6$, as well as $Fe(CS)(CO)_4$ (ref 14), isoelectronic with $Fe(CO)_5$. However, binuclear cobalt carbonyl thiocarbonyls with the general formula $Co_2(CS)_n(CO)_{8-n}$ isoelectronic with $Co_2(CO)_8$ remain unknown. Attempts to synthesize such cobalt carbonyl

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(1) Sumner, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.
(2) Leung, P. C.; Coppens, P. *Acta Crystallogr.* **1983**, *B39*, 535.
(3) Braga, D.; Grepioni, F.; Sabatino, P.; Gavezzotti, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1185.
(4) Noack, K. *Spectrochim. Acta* **1963**, *19*, 1925.
(5) Noack, K. *Helv. Chim. Acta* **1964**, *47*, 1064.
(6) Noack, K. *Helv. Chim. Acta* **1964**, *47*, 1554.
(7) Bor, G. *Spectrochim. Acta* **1963**, *14*, 1209.
(8) Bor, G. *Spectrochim. Acta* **1963**, *14*, 2065.
(9) Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 421.
(10) Horváth, I. T.; Bor, G.; Garland, M.; Pino, P. *Organometallics* **1986**, *5*, 1441.
(11) Ungváry, F.; Markó, L. *Inorg. Chim. Acta* **1970**, *4*, 324.
(12) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1974**, *71*, 283.
(13) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1978**, *95*, 7516.
(14) Petz, W. *J. Organomet. Chem.* **1978**, *146*, C23.

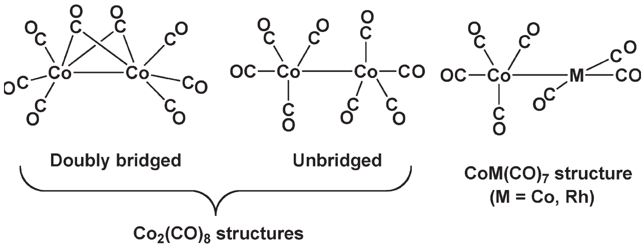

Figure 1. Structures of $Co_2(CO)_8$ and $CoM(CO)_7$ (M = Co, Rh).

thiocarbonyls by the reaction of $Co_2(CO)_8$ with CS_2 under various conditions gave complicated mixtures of products, most of which have structures built from stable tetrahedral Co_3C or Co_3S cluster units.[15−21] However, Morris and coworkers[22] have synthesized and structurally characterized the related dithiolene cobalt thiocarbonyl phosphine complexes $[Co_2(\mu\text{-}CS)(\mu\text{-}S_2C_2R_2)(CO)_3(\mu\text{-dppm})]$ [R = CO_2Me, CO_2Et; dppm = $(C_6H_5)_2PCH_2P(C_6H_5)_2$] with a single bridging CS group. In addition, the binuclear cyclopentadienyliron carbonyl thiocarbonyl $Cp_2Fe_2(\mu\text{-}CS)_2(CO)_2$ has been synthesized[23,24] and shown by X-ray diffraction[25] to containing two bridging thiocarbonyl groups in preference to bridging carbonyl groups. Note that $Cp_2Fe_2(\mu\text{-}CS)_2(CO)_2$ can be derived formally from $Co_2(CS)_2(CO)_6$ by replacement of each $Co(CO)_2$ unit with a CpFe unit.

This paper describes a density functional theory (DFT) study of possible structures of the "saturated" $Co_2(CS)_2(CO)_6$, isoelectronic with $Co_2(CO)_8$, as well as corresponding "unsaturated" derivatives of the type $Co_2(CS)_2(CO)_n$ (n = 5, 4, 3), in which each cobalt atom interacts with at least one of the two CS groups in some way. Comparison of the present results with a 2001 study[26] on the isoelectronic homoleptic cobalt carbonyl derivatives $Co_2(CO)_{n+2}$ reveals some important differences between the chemistry of the isoelectronic cobalt carbonyl and thiocarbonyl derivatives. In particular, the greater tendency of bridging thiocarbonyl groups, relative to bridging carbonyl groups, to serve as four-electron donors, as was previously observed for iron carbonyl thiocarbonyl derivatives,[27] is also observed for the binuclear cobalt carbonyl thiocarbonyls. The first stable compound containing such a four-electron donor thiocarbonyl group was $[HB(pz)_3](CO)_2W(\eta^2\text{-}\mu\text{-}CS)Mo(CO)_2$ synthesized by Angelici and co-workers in 1989.[28]

2. Theoretical Methods

Electron correlation effects were considered using DFT methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[29−31,30,32−37] Two DFT methods were used in this study. The first functional is the popular B3LYP method, which is the hybrid HF/DFT method using a combination of the three-parameter Becke exchange functional (B3) with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[38,39] The other DFT method used in the present paper is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).[40,41] It has been noted elsewhere that the BP86 method may be somewhat more reliable than B3LYP for the type of organometallic systems considered in this paper.[42−44]

Our DZP basis sets used for carbon, oxygen, and sulfur add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, and $\alpha_d(S) = 0.70$ to the standard Huzinaga−Dunning−Hay contracted DZ sets.[45−47] Therefore, the C and O basis sets are designated as (9s5p1d/4s2p1d), and the S basis set is designated as (12s8p1d/6s4p1d). For Co, in our loosely contracted DZP basis set, the Wachters primitive set[48] is used augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer, and Schaefer,[49] and designated (14s11p6d/10s8p3d). For $Co_2(CS)_2(CO)_6$, $Co_2(CS)_2(CO)_5$, $Co_2(CS)_2(CO)_4$, and $Co_2(CS)_2(CO)_3$ there are 354, 324, 294, and 264 contracted Gaussian functions, respectively, in the basis sets.

The geometries of all structures were fully optimized using the DZP B3LYP and DZP BP86 methods. Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All of the computations were carried out with the Gaussian 03 program,[50] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically,[51] while the tight (10^{-8} hartree)

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(15) Klumpp, E.; Bor, G.; Markó, L. *J. Organomet. Chem.* **1968**, *11*, 207.

(16) Bor, G.; Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Chem. Commun.* **1978**, 841.

(17) Stanghellini, P. L.; Gervasio, G.; Rossetti, R.; Bor, G. *J. Organomet. Chem.* **1980**, *187*, C37.

(18) Bor, G.; Dietler, U. K.; Stanghellini, P. L.; Gervasio, G.; Rossetti, R.; Sbrignadello, G.; Battiston, G. A. *J. Organomet. Chem.* **1981**, *213*, 277.

(19) Gervasio, G.; Rossetti, R.; Stanghellini, P. L.; Bor, G. *Inorg. Chem.* **1982**, *21*, 3781.

(20) Gervasio, G.; Rossetti, R.; Stanghellini, P. L.; Bor, G. *Dalton Trans.* **1983**, 1613.

(21) Wei, C. H. *Inorg. Chem.* **1984**, *23*, 2973.

(22) Adams, H.; Guio, L. V. Y.; Morris, M. J.; Pratt, J. A. *Dalton Trans.* **2000**, 3489.

(23) Angelici, R. J.; Dunker, J. W. *Inorg. Chem.* **1985**, *24*, 2209.

(24) Choi, M. G.; Danield, L. M.; Angelici, R. J. *J. Organomet. Chem.* **1990**, *383*, 321.

(25) Dunker, J. W.; Finer, J. S.; Clardy, J.; Angelici, R. J. *J. Organomet. Chem.* **1976**, *114*, C49.

(26) Kenny, J. P.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2001**, *40*, 900.

(27) Zhang, Z.; Li, Q.-S.; Xie, Y.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2009**, *48*, 1974.

(28) Doyle, R. A. D.; Daniels, L. M.; Angelici, R. J.; Stone, F. G. A. *J. Am. Chem. Soc.* **1989**, *111*, 4995.

(29) Ehlers, A. W.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 1514.

(30) Delley, B.; Wrinn, M.; Lüthi, H. P. *J. Chem. Phys.* **1994**, *100*, 5785.

(31) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

(32) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1995**, *102*, 8474.

(33) Barckholtz, T. A.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 1926.

(34) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353.

(35) Macchi, P.; Sironi, A. *Coord. Chem. Rev.* **2003**, *238*, 383.

(36) Carreon, J.-L.; Harvey, J. N. *Phys. Chem. Chem. Phys.* **2006**, *8*, 93.

(37) Bühl, M.; Kabrede, H. *J. Chem. Theory Comput.* **2006**, *2*, 1282.

(38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(39) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(40) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(41) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(42) See especially Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, *124*, 044103.

(43) Wang, H. Y.; Xie, Y.; King, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **2005**, *127*, 11646.

(44) Wang, H. Y.; Xie, Y.; King, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **2006**, *128*, 11376.

(45) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(46) Dunning, T. H.; Hay, P. J. *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977; pp 1−27.

(47) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(48) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(49) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 705.

(50) Frisch, M. J. et al. *Gaussian 03*, Revision C 02; Gaussian, Inc.: Wallingford, CT, 2004 (see Supporting Information for details).

(51) Papas, B. N.; Schaefer, H. F. *J. Mol. Struct.* **2006**, *768*, 175.

Table 1. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), and Numbers of Imaginary Frequencies (*Nimg*) for the Seven Optimized $Co_2(CS)_2(CO)_6$ Structures

		26−1 (C_{2v})	**26−2** (C_1)	**26−3** (C_{2v})	**26−4** (C_2)	**26−5** (C_2)	**26−6** (D_{3d})	**26−7** (C_2)
B3LYP	*E*	−4318.39417	−4318.38405	−4318.37015	−4318.38016	−4318.37477	−4318.37683	−4318.37022
	Δ*E*	0.0	6.4	15.1	8.8	12.2	10.9	15.0
	Nimg	0	0	0	0	0	0	0
BP86	*E*	−4318.98391	−4318.97620	−4318.96504	collapses to **26−1**	collapses to **26−3**	−4318.96504	−4318.95781
	Δ*E*	0.0	4.8	11.8			11.8	16.4
	Nimg	0	0	0			0	0

Table 2. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), and Numbers of Imaginary Frequencies (*Nimg*) for the Optimized $Co_2(CS)_2(CO)_5$ Structures

		25−1 (C_s)	**25−2** (C_s)	**25−3** (C_1)	**25−4** (C_s)	**25−5** (C_s)	**25−6** (C_{2v})	**25−7** (C_s)
B3LYP	*E*	−4205.03015	−4205.02927	−4205.02837	−4205.01153	−4205.01069	−4205.00728	−4204.99663
	Δ*E*	0.0	0.6	1.1	11.7	12.2	14.4	21.0
	Nimg	0	0	0	0	1 (5*i*)	0	1 (29*i*)
BP86	*E*	−4205.60983	−4205.60884	−4205.60792	−4205.58834	−4205.58663	−4205.59836	−4205.58118
	Δ*E*	0.0	0.6	1.2	13.5	14.6	7.2	18.0
	Nimg	0	0	0	1(26*i*)	1 (43*i*)	0	1 (172*i*)

Table 3. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), and Numbers of Imaginary Frequencies (*Nimg*) for the Optimized $Co_2(CS)_2(CO)_4$ Structures

		24−1 (C_2/D_2)	**24−2** (C_1)	**24−3** (C_s)	**24−4** (C_{2v})	**24−5** (C_1)	**24−6** (C_{2h})	**24−7**(D_{2d})	**24−8** (C_s)
B3LYP	*E*	−4091.66814	−4091.66151	−4091.65950	−4091.65942	−4091.65616	−4091.65241	−4091.64275	−4091.63528
	Δ*E*	0.0	4.2	5.4	5.5	7.5	9.9	15.9	20.6
	Nimg	1(8*i*)	1(4*i*)	0	0	0	0	2(12*i*, 12*i*)	1(28*i*)
BP86	*E*	−4092.24594	−4092.23943	−4092.22962	−4092.23642	−4092.23998	−4092.22921	−4092.20712	−4092.20633
	Δ*E*	0.0	4.1	10.2	6.0	3.7	10.5	24.4	24.9
	Nimg	1(32*i*)	0	1(51*i*)	1(63*i*)	0	1(29*i*)	2(50*i*, 50*i*)	1(54*i*)

Table 4. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), and Numbers of Imaginary Frequencies (*Nimg*) for the Optimized $Co_2(CS)_2(CO)_3$ Structures

		23−1 (C_1)	**23−2** (C_s)	**23−3** (C_s)	**23−4** (C_1)
B3LYP	*E*	−3978.30180	−3978.27668	−3978.27133	−3978.26470
	Δ*E*	0.0	15.8	19.1	23.3
	Nimg	0	46*i*	28*i*	0
BP86	*E*	−3978.86554	−3978.84483	−3978.83685	−3978.83073
	Δ*E*	0.0	13.0	18.0	21.8
	Nimg	0	26*i*	55*i*	0

designation is the default for the self-consistent field (SCF) convergence. The finer grid (99, 590) was used for investigating small imaginary vibrational frequencies.[52]

In the search for minima using all currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations. Thus, all imaginary vibrational frequencies with a magnitude less than 100*i* cm^{-1} are considered questionable and are given less weight in the analysis.[51,53,54] Therefore, we do not always follow the normal modes of such low imaginary vibrational frequencies.

The optimized structures are reported in Tables 1 to 4 and depicted in Figures 2 to 5. A given $Co_a(CS)_a(CO)_b$ structure is designated as **ab-c** where **a** is the number of cobalt atoms (the same as the number of CS groups), **b** is the number of CO groups, and **c** orders the structures according to their relative energies. Thus the lowest energy structure of $Co_2(CS)_2(CO)_6$ is designated **26−1**.

3. Results

3.1. Coordinately Saturated Derivatives. Seven structures were optimized for $Co_2(CS)_2(CO)_6$ (shown in Figure 2 and Table 1). All of these seven structures were predicted to have only real harmonic vibrational frequencies. The global minimum for $Co_2(CS)_2(CO)_6$, namely **26−1**, is a C_{2v} structure $Co_2(\mu\text{-}CS)_2(CO)_6$ with two bridging CS groups similar to the structure of $Co_2(CO)_8$ characterized by X-ray diffraction.[1−3] The Co−C(S) and C−S distances of **26−1** are predicted to be ∼1.94 Å and ∼1.59 Å, respectively, with both methods, which are similar to the corresponding geometrical parameters of $Co_2(\mu\text{-}CS)(\mu\text{-}S_2C_2R_2)(CO)_3(\mu\text{-dppm})$ (1.912 Å and 1.609 Å), determined by X-ray diffraction.[22] Moreover, replacement of the bridging CO groups by bridging CS groups reduces the experimentally determined Co−Co distance of 2.528 Å in $Co_2(CO)_6(\mu\text{-}CO)_2$ to the predicted Co−Co distance of 2.489 Å (B3LYP) or 2.497 Å (BP86) in $Co_2(CO)_6(\mu\text{-}CS)_2$ (**26−1**). This is consistent with the experimentally determined[22] CS bridged Co−Co distance of 2.449 Å in $Co_2(\mu\text{-}CS)(\mu\text{-}S_2C_2R_2)(CO)_3(\mu\text{-dppm})$.

A second doubly bridged $Co_2(CS)_2(CO)_6$ structure **26−2**, having one bridging CS group and one bridging CO group, is predicted to lie 6.4 kcal/mol (B3LYP) or 4.8 kcal/mol (BP86) above **26−1**. The last doubly bridged $Co_2(CS)_2(CO)_6$ structure, **26−3** with two CO bridges, is predicted to lie in energy above **26−1** by 15.1 kcal/mol (B3LYP) or 11.8 kcal/mol (BP86). From **26−1** to **26−3**, the Co−Co bond distances are predicted to increase gradually by ∼0.035 Å for each bridging CS group switched with a CO group, starting from 2.489 Å (B3LYP) or 2.497 Å (BP86) in **26−1** to 2.564 Å (B3LYP) or 2.559 Å (BP86) in **26−3**.

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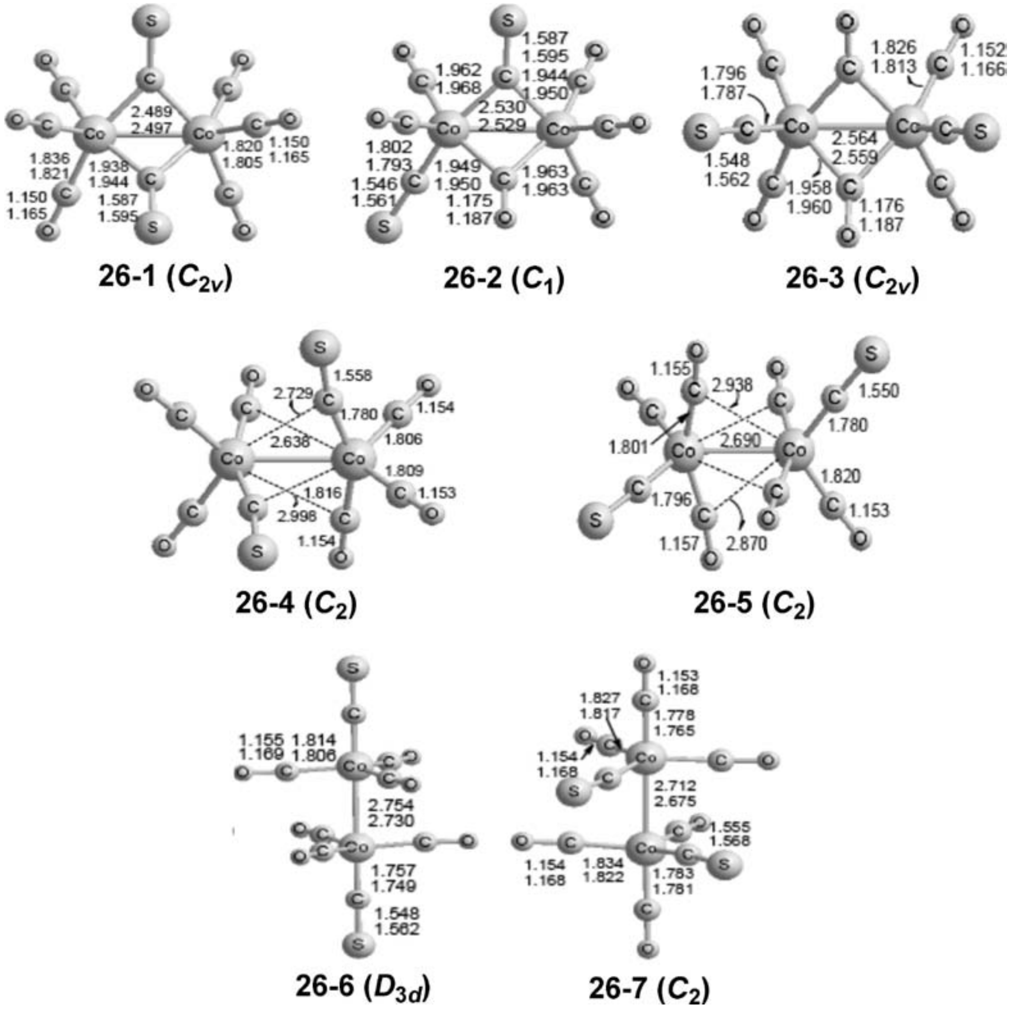
[52] Papas, B. N.; Schaefer, H. F. *J. Mol. Struct.* **2006**, *768*, 275.

[53] Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 4631.

[54] Martin, J. M. L.; Bauschlicher, C. W.; Ricca, A. *Comput. Phys. Commun.* **2001**, *133*, 189.



26-1 (C_{2v}) **26-2** (C_1) **26-3** (C_{2v})

26-4 (C_2) **26-5** (C_2)

26-6 (D_{3d}) **26-7** (C_2)

Figure 2. Optimized structures of $Co_2(CS)_2(CO)_6$. In Figures 2 to 5 the upper distances were predicted by the B3LYP method and the lower distances by the BP86 method.

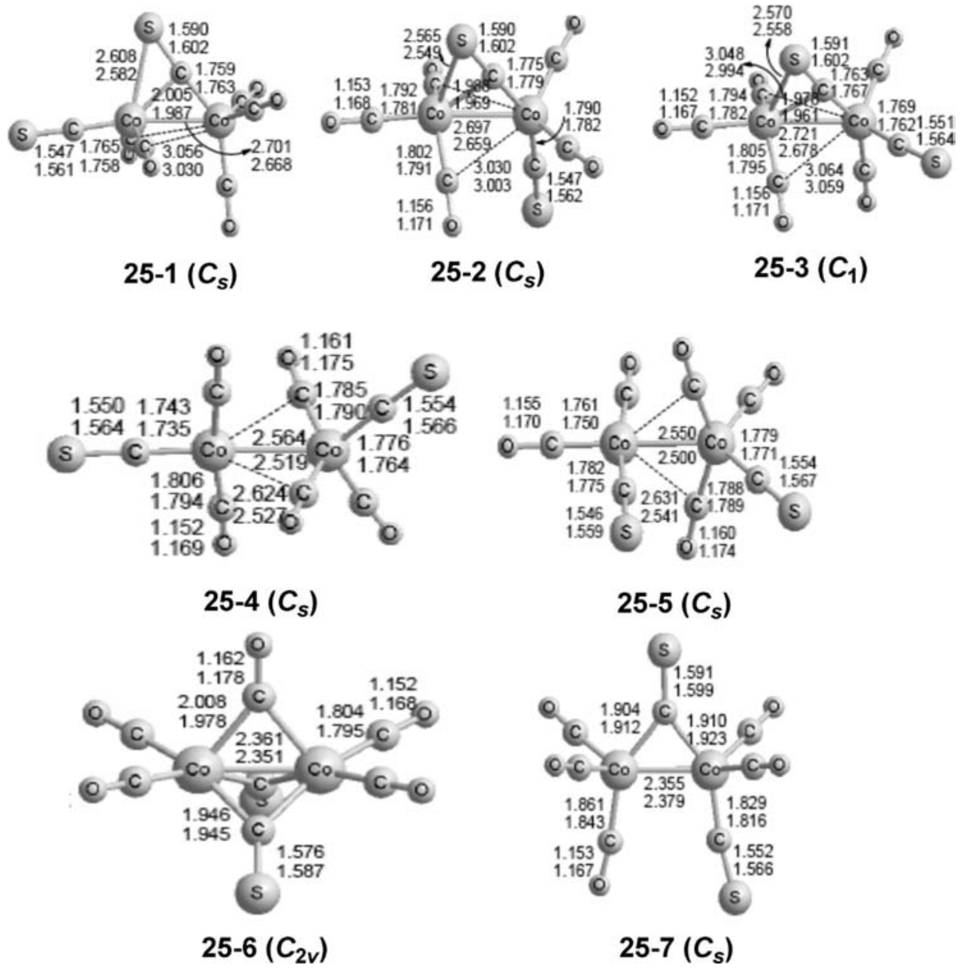
Using the B3LYP method two C_2 structures of $Co_2(CS)_2(CO)_6$, namely, **26−4** and **26−5** (Figure 2 and Table 1), with four weakly semibridging groups were predicted as local minima. Two of these weakly semibridging groups are CS groups and the other two are CO groups for **26−4**, while all of the semibridging groups are CO groups in **26−5**. If the BP86 rather than the B3LYP method is used, these two $Co_2(CS)_2(CO)_6$ structures are not local minima but collapse to **26−1** and **26−3**, respectively. With B3LYP, structures **26−4** and **26−5** lie 8.8 and 12.2 kcal/mol, respectively, above the global minimum **26−1** of $Co_2(CS)_2(CO)_6$. The Co−Co distances in **26−4** and **26−5** are 2.638 Å and 2.690 Å, respectively, which are significantly longer than those in the doubly bridged $Co_2(CS)_2(CO)_6$ structures **26−1**, 26−**2**, and **26−3**.

The final two structures of $Co_2(CS)_2(CO)_6$, namely **26−6** and **26−7** (Figure 2 and Table 1), have an unbridged Co−Co bond and a linear EC−Co−Co−CE (E = S or O) unit. The D_{3d} structure **26−6** with two axial terminal CS groups (E = S) is predicted to lie 10.9 kcal/mol (B3LYP) or 11.8 kcal/mol (BP86) higher in energy than **26−1**. The C_2 structure **26−7** with two axial terminal CO groups (E = O) lies somewhat higher in energy at 15.0 kcal/mol (B3LYP) or 16.5 kcal/mol (BP86) above **26−1**. The Co−Co distances in the two related structures **26−6** and **26−7** range from 2.754 Å (B3LYP) or 2.730 Å (BP86) in **26−6** to 2.712 Å (B3LYP) or 2.675 Å (BP86) in **26−7**.

3.2. Coordinately Unsaturated Derivatives.

3.2.1. $Co_2(CS)_2(CO)_5$. The seven structures optimized for $Co_2(CS)_2(CO)_5$ include four singly bridged structures, two doubly semibridged structures, and a triply bridged structure (Figure 3 and Table 2). The global minimum for $Co_2(CS)_2(CO)_5$ (**25−1**) is a C_s structure with a four-electron donor bridging CS group. Structure **25−1** can be derived from the $Co_2(CS)_2(CO)_6$ structure **26−2** by loss of a bridging CO group with concurrent bending of the bridging CS group. In this way the sulfur atom approaches within ~2.6 Å of the cobalt atom thereby converting a two-electron donor bridging CS group into a four-electron donor bridging CS group. The following two $Co_2(CS)_2(CO)_5$ structures in terms of energy, namely, **25−2** and **25−3**, also have a four-electron donor bridging CS group and lie only ~1 kcal/mol above **25−1**, suggesting a highly fluxional system. The Co−Co bond lengths of the $Co_2(CS)_2(CO)_5$ structures **25−1**, **25−2**, and **25−3** fall in the range 2.69 ± 0.03 Å corresponding to formal single bonds. These structures with a four-electron donor bridging CS group have the favored 18-electron configuration for both cobalt atoms.

The remaining $Co_2(CS)_2(CO)_5$ structures do not contain four-electron donor CS or CO groups and lie



25-1 (C_s) **25-2** (C_s) **25-3** (C_1)

25-4 (C_s) **25-5** (C_s)

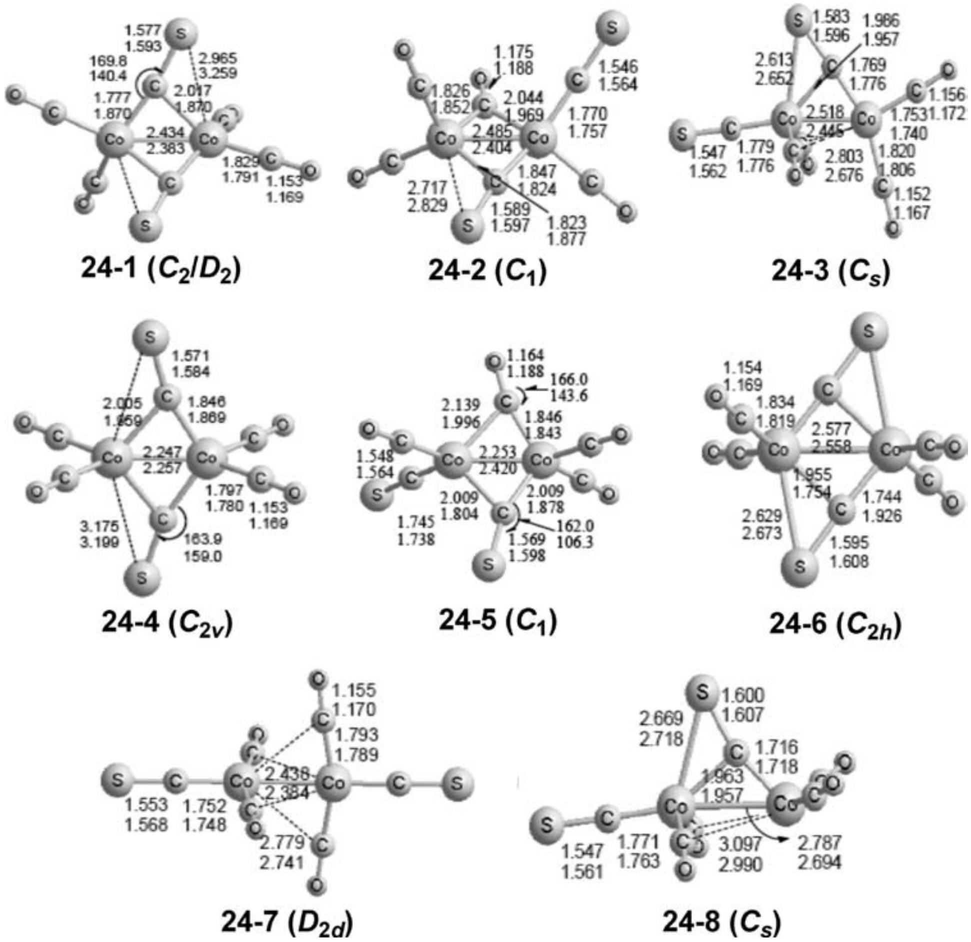
25-6 (C_{2v}) **25-7** (C_s)

Figure 3. Optimized structures of $Co_2(CS)_2(CO)_5$.

$>$10 kcal/mol above structures **25−1**, **25−2**, and **25−3** (Figure 3 and Table 2). Thus the doubly semibridged structures **25−4** (C_s symmetry) and **25−5** (C_s symmetry) lie ~12.0 kcal/mol (B3LYP) or ~14.0 kcal/mol (BP86) higher in energy than **25−1**. The Co−Co distances of **25−4** and **25−5** fall in the range 2.53 ± 0.03 Å. This corresponds to a Co−Co single bond leading to an 18-electron configuration for the five-coordinate cobalt atom (the "right" cobalt atom in Figure 3) but only a 16-electron configuration for the square planar cobalt atom (the "left" cobalt atom in Figure 3). The C_{2v} triply bridged $Co_2(CS)_2(CO)_5$ structure **25−6**, with one CO bridge and two CS bridges, was found to be a genuine minimum with all real harmonic vibrational frequencies. The structure **25−6** lies 14.4 kcal/mol (B3LYP) or 7.2 kcal/mol (BP86) above **25−1**. The Co═Co distance in 25−**6** is predicted to be 2.361 Å (B3LYP) or 2.351 Å (BP86), which is $>$0.15 Å shorter than the Co−Co distances in the $Co_2(CS)_2(CO)_5$ structures **25−1** through 25−**5**. This suggests the formal double bond in **25−6** required to provide the favored 18-electron configuration for each cobalt atom.

The remaining $Co_2(CS)_2(CO)_5$ structure **25−7** (Figure 3 and Table 2), at 21.0 kcal/mol (B3LYP) or 18.0 kcal/mol (BP86) above the global minimum **25−1**, has a single two-electron donor CS bridge. The B3LYP method predicts a small imaginary vibrational frequency of 29*i* cm^{-1} for **25−7** suggesting that this structure is close to a local minimum. However, the BP86 method predicts a much larger imaginary vibrational frequency for **25−7**, namely 172*i* cm^{-1}, suggesting a transition state. Following the corresponding normal mode leads to **25−2** by the two-electron donor bridging CS group in **25−7** becoming a four-electron donor CS group in **25−2**. This process is accompanied by stretching of the Co═Co double bond distance of 2.355 Å (B3LYP) or 2.379 Å (BP86) in **25−7** to a Co−Co single bond distance of 2.67 ± 0.02 Å in **25−2**, thereby maintaining the favored 18-electron configuration for both cobalt atoms.

3.2.2. $Co_2(CS)_2(CO)_4$. Eight structures were found for $Co_2(CS)_2(CO)_4$ within 25 kcal/mol of the global minimum (Figure 5 and Table 3). The lowest energy $Co_2(CS)_2(CO)_4$ structure **24−1** has two asymmetric CS bridges and can be derived from **26−1** by removal of a terminal CO ligand from each cobalt atom. The B3LYP method gives a **24−1** structure with C_2 symmetry whereas the BP86 method gives a **24−1** structure with D_2 symmetry. The small imaginary vibrational frequency of **24−1** at 8*i* cm^{-1} (B3LYP) or 32*i* cm^{-1} (BP86) is reduced to 3*i* cm^{-1} upon recalculation by the B3LYP method using the ultrafine grid (99,590). This suggests that **24−1** is a genuine minimum with the small imaginary frequency arising from numerical errors. The S···Co distances in **24−1** are predicted to be 2.965 Å (B3LYP) or 3.259 Å (BP86), which are clearly too long for a direct interaction, implying that both bridging CS groups are two-electron

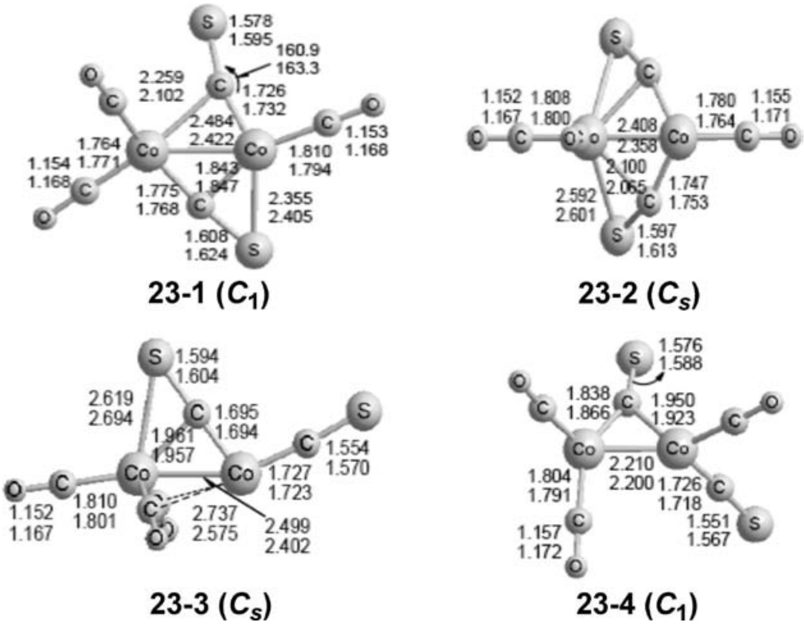


24-1 (C_2/D_2) **24-2** (C_1) **24-3** (C_s)

24-4 (C_{2v}) **24-5** (C_1) **24-6** (C_{2h})

24-7 (D_{2d}) **24-8** (C_s)

Figure 4. Optimized structures of $Co_2(CS)_2(CO)_4$.



23-1 (C_1) **23-2** (C_s)

23-3 (C_s) **23-4** (C_1)

Figure 5. Optimized structures of $Co_2(CS)_2(CO)_3$.

donors. The doubly CS-bridged Co−Co distance in **24−1** is predicted to be 2.434 Å (B3LYP) or 2.383 Å (BP86), which is only ~0.05 Å (B3LYP) or ~0.12 Å (BP86) shorter than the doubly CS-bridged Co−Co single bond distance in **26−1**.

The next $Co_2(CS)_2(CO)_4$ structure **24−2** is derived from **24−1** by swapping a bridging CS with a CO group. Structure **24−2** can be considered as a genuine minimum since only a tiny imaginary vibrational frequency of $4i$ cm^{-1} was found by the B3LYP method, and no imaginary vibrational frequencies were found by the BP86 method. Structure **24−2** of $Co_2(CS)_2(CO)_4$ lies 4.2 kcal/mol (B3LYP) or 4.1 kcal/mol (BP86) above **24−1**, which is consistent with our previous observations that replacing a bridging CS group by a CO group leads to an increase in energy. The predicted Co−Co distance in **24−2** of 2.485 Å (B3LYP) or 2.404 Å (BP86) accords with a formal single bond, thereby giving both cobalt atoms a 16-electron configuration. However, the Co···S distance in **24−2**, although probably too long at 2.717 Å (B3LYP) or 2.829 Å (BP86) for a four-electron donor CS group, is short enough to suggest a weak cobalt−sulfur interaction involving one of the coordinately unsaturated (16-electron) cobalt atoms.

Two $Co_2(CS)_2(CO)_4$ structures were found containing four-electron donor bridging η^2-μ-CS groups, namely **24−3** and **24−8** (Figure 4 and Table 3). Structure **24−3** of $Co_2(CS)_2(CO)_4$ is predicted to be a genuine minimum by B3LYP but to have a small imaginary frequency of $51i$ cm^{-1} by BP86. Structure **24−8** is predicted by either method to have a small imaginary frequency, namely, $28i$ cm^{-1} (B3LYP) or $54i$ cm^{-1} (BP86). Structures **24−3** and **24−8** can arise from the global minimum **25−1** of $Co_2(CS)_2(CO)_5$ by loss of a terminal CO group from the cobalt atom not bonded to the sulfur atom of the bridging η^2-μ-CS group. Structure **24−3** lies 5.4 kcal/mol (B3LYP) or 10.2 kcal/mol (BP86) above **24−1**. Structure **24−8** is a significantly higher energy structure at 20.6 kcal/mol (B3LYP) or 24.9 kcal/mol (BP86) above **24−1**.

We also investigated D_{2h} structures of $Co_2(CS)_2(CO)_4$ containing two CS bridges. Such structures were found to be transition states with large imaginary frequencies. Following the corresponding normal modes led to the C_{2v} structure **24−4** (Figure 4 and Table 3) with two unsymmetrical CS bridges at 5.5 kcal/mol (B3LYP) or 6.0 kcal/mol (BP86) above **24−1**. The Co≡Co distance in **24−4** is very short at 2.247 Å (B3LYP) or 2.257 Å (BP86) corresponding to the formal triple bond required to give both cobalt atoms the favored 18-electron configuration. The $Co_2(CS)_2(CO)_4$ structure **24−5**, at 7.5 kcal/mol (B3LYP) or 3.7 kcal/mol (BP86) above **24−1**, is similar to **24−4** except one of the bridging groups is a CO group rather than a CS group. By the B3LYP method the predicted Co≡Co distance in **24−5** is 2.253 Å corresponding to the formal triple bond required to give both cobalt atoms the favored 18-electron configuration. However, by the BP86 method the Co−Co distance in **24−5** is appreciably longer at 2.420 Å, which is closer to a formal single bond thereby giving both cobalt atoms only a 16-electron configuration.

A C_{2h} $Co_2(CS)_2(CO)_4$ structure **24−6** was also found, which clearly has two four-electron bridging η^2-μ-CS groups as indicated by short Co−S distances of 2.629 Å (B3LYP) or 2.673 Å (BP86). Structure **24−6** is predicted to lie above **24−1** by 9.9 kcal/mol (B3LYP) or 10.5 kcal/mol (BP86). The Co−Co bond length is 2.577 Å (B3LYP) or 2.558 Å (BP86), consistent with the formal Co−Co single bond required to give both cobalt atoms the favored 18-electron configuration.

A single essentially unbridged $Co_2(CS)_2(CO)_4$ structure was found, namely, the D_{2d} structure **24−7** at 15.9 kcal/mol (B3LYP) or 24.4 kcal/mol (BP86) above **24−1** (Figure 4 and Table 3). Structure **24−7** was found have to have a doubly degenerate imaginary vibrational frequency at $12i$ cm^{-1} (B3LYP) or $50i$ cm^{-1} (BP86). The unbridged Co≡Co distance in **24−7** is predicted to be 2.438 Å (B3LYP) or 2.384 Å (BP86), which is 0.2 to 0.3 Å shorter than the Co−Co distances in the unbridged $Co_2(CS)_2(CO)_6$ structures **26−4** through **26−8**, which clearly have formal single bonds. This suggests the formal Co≡Co triple bond in **24−7** required to give both cobalt atoms the favored 18-electron configuration.

3.2.3. $Co_2(CS)_2(CO)_3$. Four structures were optimized for $Co_2(CS)_2(CO)_3$ (Figure 5 and Table 4). The global minimum of $Co_2(CS)_2(CO)_3$, namely, **23−1**, has one four-electron donor bridging CS group and one two-electron donor bridging CS group and is a genuine minimum without any imaginary vibrational frequencies. The four-electron donor η^2-μ-CS group in **23−1** is indicated by a short Co−S distance of 2.355 Å (B3LYP) or 2.405 Å (BP86). The Co−Co distance in **23−1** (Table 4) is predicted to be 2.484 Å (B3LYP) or 2.422 Å (BP86), which is similar to the doubly bridged Co−Co single bond distance in the $Co_2(CS)_2(CO)_6$ structure **26−1** (Table 1), namely, 2.489 Å (B3LYP) or 2.497 Å (BP86). This suggests that the Co−Co bond is a formal single bond in **23−1**, leading to a 16-electron configuration for both cobalt atoms. The $Co_2(CS)_2(CO)_3$ structure **23−1** can be derived from the $Co_2(CS)_2(CO)_4$ **24−4** by loss of a terminal CO group on the "right" Co atom in Figure 4 with concurrent conversion of a two-electron bridging CS ligand to a four-electron donor bridging η^2-μ-CS group.

All of the other $Co_2(CS)_2(CO)_3$ structures lie 13 kcal/mol or more above the global minimum **23−1**, suggesting that structure **23−1** is particularly favorable. The next $Co_2(CS)_2(CO)_3$ structure **23−2**, at 15.8 kcal/mol (B3LYP) or 13.0 kcal/mol (BP86) above **23−1**, has a small imaginary vibrational frequency at $46i$ cm^{-1} (B3LYP) or $26i$ cm^{-1} (BP86), with two four-electron donor bridging η^2-μ-CS groups, as indicated by the relatively short Co−S distances at 2.592 Å (B3LYP) or 2.601 Å (BP86). The pair of η^2-μ-CS groups in **23−2** is different from that in **24−6** (Figure 4) since in **23−2** the short Co−S distances are to the same cobalt atom whereas in **24−6** the short Co−S distances are to different cobalt atoms. The $Co_2(CS)_2(CO)_3$ structure **23−2** can be derived from the $Co_2(CS)_2(CO)_4$ structure **24−4** by loss of one of the terminal CO groups (from the "right" cobalt atom in Figure 4) with concurrent conversion of both of the bridging CS groups from two-electron donors to four electron donors. In this conversion of **24−4** to **23−2** the two Co−S distances are shortened and the Co−Co distance is lengthened. In **23−2** (Figure 5) the doubly bridged Co═Co distance of 2.408 Å (B3LYP) or 2.358 Å (BP86) is ~0.1 Å shorter than the doubly bridged clearly formal single Co−Co bond in the $Co_2(CS)_2(CO)_6$ structure **26−1** at 2.489 Å (B3LYP) or 2.497 Å (BP86). This 2.38 Å distance could correspond to the formal double bond needed to give both cobalt atoms in **23−2** the favored 18-electron configuration.

The next $Co_2(CS)_2(CO)_3$ structure (Figure 5 and Table 4) is the singly bridged unsymmetrical structure **23−3** at 19.1 kcal/mol (B3LYP) or 18.0 kcal/mol (BP86) with a small imaginary vibrational frequency at $28i$ cm^{-1}

(B3LYP) or 55*i* cm^{-1} (BP86). The bridging group in **23−3** is a four-electron donor η^2-μ-CS group as indicated by a relatively short Co−S distance at 2.619 Å (B3LYP) or 2.694 Å (BP86). One of the cobalt atoms in **23−3** (the "left" cobalt atom in Figure 5) bears three CO groups, two of which are slightly semibridging with the "long" Co−C distance at 2.737 Å (B3LYP) or 2.575 Å (BP86). The other cobalt atom in **23−3** (the "right" cobalt atom in Figure 5) has a terminal CS group. The Co−Co distance in **23−3** is predicted to be 2.499 Å (B3LYP) or 2.402 Å (BP86), which is very similar to that in **26−1** (Figure 2 and Table 1) and thus corresponds to a formal single bond. This gives the cobalt atom in **23−3** bearing three CO groups the favored 18-electron configuration but the cobalt atom bearing the terminal CS group only a 14-electron configuration. A large gap is evident in the coordination sphere of this latter, highly unsaturated cobalt atom.

The remaining structure of $Co_2(CS)_2(CO)_3$, namely, **23−4** (Figure 5 and Table 4), is also a singly bridged structure, at 23.3 kcal/mol (B3LYP) or 21.8 kcal/mol (BP86) above **23−1**. Structure **23−4** is a genuine minimum with no imaginary vibrational frequencies predicted by both methods. The bridging group in **23−4** is a two-electron donor CS group. The Co−Co distance in **23−4** is predicted to be 2.210 Å (B3LYP) or 2.200 Å suggesting a cobalt−cobalt bond of high formal order. In this connection a formal quadruple bond between the two cobalt atoms in **23−4** would give both cobalt atoms the favored 18-electron configuration.

We also tried to optimize triply bridged structures of $Co_2(CS)_2(CO)_3$. However, such optimization led either to one of the structures in Figure 5 or to structures more than 30 kcal/mol above the global minimum **23−1**.

3.3. Dissociation Energies. The CO removal energies (BDEs) of the lowest energy structures of $Co_2(CS)_2(CO)_n$ (n = 6, 5, 4) derivatives are reported in Table 5 as the following series of reactions:

$$Co_2(CS)_2(CO)_n \rightarrow Co_2(CS)_2(CO)_{n-1} + CO \ (n = 6, 5, 4)$$

These predicted CO dissociation energies are generally somewhat lower than the experimental dissociation energies[55] of 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively, as well as that of 51 ± 4 kcal/mol predicted for $Fe(CS)(CO)_4$ using similar DFT methods.[27] However, the CO dissociation energies of the $Co_2(CS)_2(CO)_n$ derivatives are comparable to the 33 ± 3 and 19 ± 5 kcal/mol predicted for the binuclear derivatives $Fe_2(CS)_2(CO)_7$ and $Fe_2(CS)_2(CO)_6$, respectively, using analogous DFT methods.[27] In general, the CO dissociation energies of the binuclear metal carbonyl thiocarbonyl derivatives appear to be significantly lower than those of similar mononuclear metal carbonyl thiocarbonyl derivatives, possibly owing to the driving force of the thiocarbonyl group to become a four-electron donor bridging η^2-μ-CS derivative in the binuclear complexes.

Table 5. Bond Dissociation Energy (kcal/mol) for Successive Removal of Carbonyl Groups from $Co_2(CS)_2(CO)_n$ (n = 6, 5, 4)

dissociation processes	B3LYP	BP86
$Co_2(CS)_2(CO)_6 \rightarrow Co_2(CS)_2(CO)_5 + CO$	22.2	29.4
$Co_2(CS)_2(CO)_5 \rightarrow Co_2(CS)_2(CO)_4 + CO$	20.9	23.0
$Co_2(CS)_2(CO)_4 \rightarrow Co_2(CS)_2(CO)_3 + CO$	23.6	33.4

3.4. Vibrational Frequencies. The harmonic vibrational frequencies and the infrared intensities for all of the $Co_2(CS)_2(CO)_n$ (n = 6, 5, 4, 3) structures have been evaluated using both the B3LYP and the BP86 methods. These results were initially used to determine if a structure is a genuine minimum. The predicted ν(CO) and ν(CS) harmonic vibrational frequencies and infrared intensities for the most stable structures of $Co_2(CS)_2(CO)_n$ (n = 6, 5, 4, 3) are of particular interest, since any future experimental work to detect such species are likely to rely on relatively strong ν(CO) and ν(CS) vibrational frequencies for initial product characterization. The ν(CO) and ν(CS) stretching frequencies for the $Co_2(CS)_2(CO)_n$ (n = 6, 5, 4, 3) derivatives are listed in Table 6. These results were obtained with the BP86 method, which has been shown to be more reliable than the B3LYP method for such infrared frequencies.[56,57]

The data in Table 6 indicate that genuine terminal ν(CO) frequencies fall in the range 2070 to 1970 cm^{-1} similar to other metal carbonyl derivatives. The lack of any significant difference between the predicted terminal ν(CO) frequencies of $Co_2(\mu\text{-}CS)_2(CO)_6$ **(26−1)** and those of the analogous[26] $Co_2(\mu\text{-}CO)_2(CO)_6$ (Table 6) shows that there is very little change in the electron density on the cobalt atoms when the bridging CO groups are replaced by bridging CS groups. If a terminal ν(CO) group is weakly bonded in a semibridging manner to the other cobalt atom [e.g., the $Co_2(CS)_2(CO)_5$ structures **25−2**, **25−3**, **25−4**, and **25−5** (Figure 3); the $Co_2(CS)_2(CO)_4$ structures **24−3**, **24−7**, and **24−8** (Figure 4); and the $Co_2(CS)_2(CO)_3$ structure **23−3** (Figure 5)], then this ν(CO) frequency can be somewhat lower. Thus, the ν(CO) frequency of 1947 cm^{-1} for **23−3** is the lowest such ν(CO) frequency among the $Co_2(CS)_2(CO)_n$ structures encountered in this research. The ν(CO) frequencies for bridging carbonyl groups are significantly lower than those of terminal carbonyl groups as is generally found for metal carbonyl derivatives. Thus for the $Co_2(CS)_2(CO)_n$ structures discussed in this paper, these ν(CO) frequencies fall in the range 1930 to 1870 cm^{-1}.

The terminal ν(CS) frequencies for the $Co_2(CS)_2(CO)_n$ (n = 6, 5, 4, 3) structures are predicted to occur at 1340 to 1290 cm^{-1} (Table 6), which is similar to the predicted ν(CS) frequency range in the previous work on iron carbonyl thiocarbonyls.[27] The ν(CS) frequencies for two-electron donor bridging thiocarbonyls for the $Co_2(CS)_2(CO)_n$ structures are predicted to occur at 1230 to 1170 cm^{-1}, which is similar to the range of bridging ν(CS) frequencies predicted for the binuclear $Fe_2(CS)_2(CO)_n$ derivatives in the previous DFT study.[27] In contrast to four-electron donor η^2-μ-CO carbonyl groups, the four-electron donor η^2-μ-CS thiocarbonyl groups are predicted to exhibit

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(55) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 12060.

(56) Jonas, V.; Thiel, W. *J. Phys. Chem.* **1995**, *102*, 8474.

(57) Silaghi-Dumitrescu, I.; Bitterwolf, T. E.; King, R. B. *J. Am. Chem. Soc.* **2006**, *128*, 5342.

Table 6. ν(CO) and ν(CS) Vibrational Frequencies and Corresponding Infrared Intensities (in Parentheses) Predicted for $Co_2(CS)_2(CO)_n$ (n = 6, 5, 4, 3) Using the BP86 Method[a]

	ν(CO)	ν(CS)
	$Co_2(CS)_2(CO)_6$ Structures	
26−1 (C_{2v})	2069(110), 2043(1252), 2020(997), 2020(1347), 2012(2), 2011(0)	**1197(195)**, **1170(629)**
$Co_2(CO)_8$[b]	2079(13), 2042(1311), 2018(1203), 2018(1503), 2011(14), 2010(0)	
26−2 (C_1)	2061(183), 2034(1089), 2017(1366), 2012(556), 2009(18), **1877(437)**	1322(516), **1179(519)**
26−3 (C_{2v})	2053(837), 2022(625), 2013(1228), 2004(0), **1880(282)**, **1871(603)**	1328(690), 1314(631)
26−6 (D_{3d})	2057(0), 2006(118), 2003(1607), 2003(1606), 1986(0), 1986(0)	1341(0), 1334(1208)
26−7 (C_2)	2058(407), 2035(1471), 2013(394), 2002(1216), 1992(39), 1991(201)	1314(624), 1292(341)
26−8 (C_{2h})	2055(0), 2036(1486), 2010(0), 2003(1566), 1996(476), 1987(0)	1304(0), 1299(1068)
	$Co_2(CS)_2(CO)_5$ Structures	
25−1 (C_s)	2054(689), 2011(623), 2003(266), 2003(1430), 1979(296)	1334(643), **1228(373)**
25−2 (C_s)	2049(38), 2027(1483), 2005(1278), 1994(152), 1974(436)	1330(361),**1214(551)**
25−3 (C_1)	2052(575), 2026(1104), 2006(1010), 1993(86), 1975(596)	1326(591), **1224(419)**
25−4 (C_s)	2058(2), 2013(1347), 1986(521), 1971(138), 1953(986)	1339(327), 1320(1014)
25−5 (C_s)	2045(982), 2009(1194), 1999(52), 1977(202), 1958(1015)	1330(798), 1306(318)
25−6 (C_{2v})	2046(179), 2016(2206), 2006(1096), 2006(0), **1928(450)**	**1216(257)**, **1189(572)**
25−7 (C_s)	2049(153), 2028(1312), 2004(1326), 1996(519), 1996(4)	1283(458), **1188(616)**
	$Co_2(CS)_2(CO)_4$ Structures	
24−1 (C_2/D_2)	2038(0), 2007(2059), 1995(1339), 1990(232)	**1199(0)**, **1190(764)**
24−2 (C_1)	2035(249), 2015(1569), 1996(787), **1880(421)**	1331(507), **1194(462)**
24−3 (C_s)	2042(1045), 1999(956), 1986(32), 1967(896)	1325(726), **1224(375)**
24−4 (C_{2v})	2033(4), 2007(1788), 1992(1385), 1982(134)	**1230(1)**, **1212(836)**
24−5 (C_1)	2038(709), 2012(1360), 1995(669), **1878(390)**	1338(657), **1205(308)**
24−6 (C_{2h})	2030(0), 2006(1587), 1988(0), 1987(1805)	**1213(0)**, **1198(628)**
24−7(D_{2d})	2049(0), 2013(2), 1976(1288), 1976(1288)	1329(0), 1315(1471)
24−8 (C_s)	2026(470), 1993(717), 1983(1807), 1961(47)	1330(656), **1226(369)**
	$Co_2(CS)_2(CO)_3$ Structures	
23−1 (C_1)	2038(250), 2009(1926), 1995(640)	**1247(279)**,**1166(286)**
23−2 (C_s)	2034(368), 2002(1746), 1985(542)	**1187(154)**, **1126(340)**
23−3 (C_s)	2030(1065), 1972(310), 1947(927)	1329(562), **1250(450)**
23−4 (C_1)	2018(722), 1994(1179), 1972(834)	1331(507), **1216(480)**

[a] **boldface** means bridging CO or CS groups; **underlined bold** implies four-electron CS bridges. [b] Reference 26.

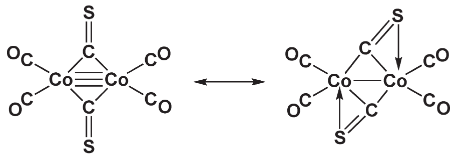
somewhat higher ν(CS) frequencies than the two-electron donor bridging CS groups in most cases. Thus, these frequencies fall in the very broad range from 1247 cm^{-1} in **23−1** to 1126 cm^{-1} in **23−2**, which overlaps with the ν(CS) range for two-electron donor bridging CS groups, as noted above. Thus a four-electron donor thiocarbonyl group cannot readily be identified by an unusual ν(CS) frequency, in contrast to four-electron donor carbonyl groups, which can be recognized by an abnormally low ν(CO) frequency.

4. Discussion

Both experimental data[4,5] and theoretical studies[26] on $Co_2(CO)_8$ suggest that a doubly bridged structure and an unbridged structure are of sufficiently similar energies to exist in equilibrium, at least in solution. However, the theoretical work in this paper indicates a much larger energy difference of ~11 kcal/mol between the lowest lying doubly bridged structure **26−1** (Figure 2 and Table 1) of $Co_2(CS)_2(CO)_6$ and the lowest lying unbridged structure **26−6**. This can be related to the greater tendency of thiocarbonyl groups to serve as bridging ligands relative to carbonyl groups, as was previously observed for binuclear iron carbonyl thiocarbonyls $Fe_2(CS)_2(CO)_n$.[27] The greater tendency of thiocarbonyls to serve as bridging ligands relative to carbonyl groups is also indicated by the predicted relative energies of the structures $Co_2(\mu\text{-}CS)_2(CO)_6$ (**26−1**), $Co_2(\mu\text{-}CS)(\mu\text{-}CO)(CS)(CO)_5$ (**26−2**), and $Co_2(\mu\text{-}CO)_2(CS)_2(CO)_4$ (**26−3**), where each exchange of a bridging CO group for a bridging CS group increases the energy of the structure by 7 ± 2 kcal/mol. The preference for bridging thiocarbonyl groups relative to bridging carbonyl groups was previously observed experimentally by Angelici and co-workers[23−25] for $Cp_2Fe_2(\mu\text{-}CS)_2(CO)_2$, for which the structure found by X-ray diffraction has two bridging thiocarbonyl groups rather than any bridging carbonyl groups.

The preferred structures for the unsaturated $Co_2(CS)_2(CO)_n$ derivatives (n = 5, 4, 3) are very different from the structures of the corresponding unsaturated carbonyl derivatives[26] $Co_2(CO)_{n+2}$ owing to the greater tendency of thiocarbonyl groups to act as four-electron donor bridging groups relative to carbonyl groups. Thus, the three lowest lying $Co_2(CS)_2(CO)_5$ structures, namely **25−1**, **25−2**, and **25−3** (Figure 3 and Table 2), all have four-electron donor bridging η^2-μ-CS groups with relatively short Co−S distances at ~2.6 Å, as well as Co−Co distances at ~2.7 Å, suggesting formal single bonds. The lowest energy unbridged $Co_2(CS)_2(CO)_5$ structure **25−4** related to the unbridged global minimum[26] of $Co_2(CO)_7$ is predicted at 12 ± 2 kcal/mol above **25−1**.

The lowest energy $Co_2(CO)_6$ structure is predicted by our previous DFT study[26] to have two bridging CO groups and a very short Co≡Co distance of 2.24 ± 0.01 Å, suggesting the formal triple bond required to give both cobalt atoms the



24-1 (Co≡Co) **24-1 (Co–Co)**

Figure 6. Possible resonance hybrids for the $Co_2(\mu\text{-}CS)_2(CO)_4$ structure **24−1** (Figure 4).

favored 18-electron rare gas configuration. A similar $Co_2(CO)_6$ structure was proposed by Sweany and Brown for one of the products that they observed in low temperature matrixes.[9] The three lowest energy $Co_2(CS)_2(CO)_4$ structures (Figure 4 and Table 3), however, have Co−Co distances in the single to double bond range and bridging CS groups with a range of Co−S distances ranging from 2.63 ± 0.02 Å in **24−3** to a rather long 3.1 ± 0.1 Å in **24−1**. The longer Co−S distances suggest some, but rather weak, Co−S interactions, implying that these bridging CS groups are resonance hybrids between four- and two-electron donors, as illustrated schematically in Figure 6 for the global minimum **24−1**. Note that in both canonical forms, namely, **24−1(Co≡Co)** with a formal metal−metal triple bond and two-electron donor CS groups and **24−1(Co−Co)** with a formal metal−metal single bond and four-electron donor CS groups, both cobalt atoms have the favored 18-electron configuration. The doubly bridged cobalt−cobalt distance in **24−1** of ~2.4 Å lies between the doubly bridged Co−Co obviously single bond distances of ~2.5 Å in the $Co_2(CS)_2(CO)_6$ structures **26−1**, **26−2**, and **26−3** (Figure 2) and the presumed doubly bridged formal Co≡Co triple bond distance of ~2.25 Å in the $Co_2(\mu\text{-}CS)_2(CO)_4$ structure **24−4** (Figure 4).

The previous DFT study[26] on $Co_2(CO)_5$ led to a singly bridged structure with a very short cobalt−cobalt distance of 2.17 Å suggesting the formal quadruple bond required to give both cobalt atoms the favored 18-electron configuration. A similar interpretation of the bonding is possible for the relative high energy $Co_2(\mu\text{-}CS)(CS)(CO)_3$ structure **23−4** at 22.5 ± 0.8 kcal/mol above the global minimum **23−1** (Figure 5 and Table 4). The lower energy $Co_2(CS)_2(CO)_3$ structures **23−1**, **23−2**, and **23−3** have one (**23−1** and **23−3**) or two (**23−2**) four-electron donor bridging $\eta^2\text{-}\mu$-CS groups and Co=Co distances of ~2.4 Å, suggesting formal double bonds. For **23−2** this gives the favored 18-electron configurations for both cobalt atoms albeit with a formal positive charge on the cobalt atom bearing two terminal CO groups (the "left" cobalt atom in Figure 5) and a formal negative charge on the cobalt atom bearing a single terminal CO group (the "right" cobalt atom in Figure 5). For the $Co_2(CS)_2(CO)_3$ structures with only a single four-electron donor bridging $\eta^2\text{-}\mu$-CS group and the formal Co=Co double bond suggested by the ~2.4 Å Co=Co distance, the cobalt atom bearing a single terminal ligand must necessarily have only a 16-electron configuration (the "right" cobalt atoms in Figure 5) leaving the favored 18-electron configuration for the other cobalt atom.

In summary, these DFT studies predict the chemistry of the binuclear cobalt carbonyl thiocarbonyls $Co_2(CS)_2(CO)_n$ (n = 6, 5, 4, 3) to be very different from that of the isoelectronic homoleptic cobalt carbonyls $Co_2(CO)_{n+2}$. This difference arises from the great tendency for the thiocarbonyl group to form low energy structures containing formal four-electron donor bridges with direct Co−S bonding, as well as Co−C bonding. No evidence for similar structures with analogous four-electron donor carbonyl groups was found in the previous DFT study[26] of the homoleptic cobalt carbonyls $Co_2(CO)_{n+2}$. Hopefully, this DFT study showing some of the lowest energy $Co_2(CS)_2(CO)_n$ (n = 5, 4, 3) structures to be very different from the corresponding low energy homoleptic carbonyl structures will stimulate experimentalists to develop methods for the syntheses of these very interesting compounds.

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Supporting Information Available: Tables S1−S4 containing theoretical harmonic vibrational frequencies for $Co_2(CS)_2(CO)_6$ (7 structures), $Co_2(CS)_2(CO)_5$ (7 structures), $Co_2(CS)_2(CO)_3$ (8 structures), $Co_2(CS)_2(CO)_3$ (4 structures) using the BP86 method; Tables S5−S32 containing theoretical Cartesian coordinates for $Co_2(CS)_2(CO)_6$ (8 structures), $Co_2(CS)_2(CO)_5$ (7 structures), $Co_2(CS)_2(CO)_3$ (8 isomers), $Co_2(CS)_2(CO)_3$ (4 structures) using the B3LYP method; complete Gaussian 03 reference (Reference 50). This material is available free of charge via the Internet at http://pubs.acs.org.