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A Carbonyl Group Bridging Four Metal Atoms in a Homoleptic Carbonylmetal Cluster: The Remarkable Case of $Co_4(CO)_{11}$

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The unsaturated $Co_4(CO)_{11}$ is predicted by density functional theory (B3LYP and BP86 functionals) to have a structure with one μ_4-CO group bridging all four cobalt atoms in a Co_4 butterfly, with five Co–Co bonds in the range 2.44–2.56 Å. This μ_4-CO group is predicted to have a relatively long C–O bond of 1.226 Å (BP86) with a correspondingly low ν(CO) frequency of 1636 cm^{-1}. $Co_4(CO)_{11}$ structures of higher energy have Co_4 tetrahedra (6 Co–Co bonds) or Co_4 butterflies (5 Co–Co bonds) with a collection of terminal, edge-bridging, and face-bridging CO groups forming a total of 15 or 16 Co–C bonds. The predicted molecular structures show no signs of cobalt–cobalt multiple bonding.

1. Introduction

The first homoleptic tetranuclear carbonylmetal derivative to be prepared was the cobalt cluster $Co_4(CO)_{12}$, which was first reported in 1932.[1] Subsequent X-ray crystallographic studies[2–4] show $Co_4(CO)_{12}$ to contain a Co_4 tetrahedron with Co–Co distances of 2.50 Å for the three edges bridged by CO groups and 2.48 Å for the three unbridged edges leading to overall C_{3v} symmetry (Figure 1; M = Co). Because the cobalt atoms in $Co_4(CO)_{12}$ have the favored 18-electron configuration if all of the Co–Co edges in the Co_4 tetrahedron correspond to single bonds, these Co–Co distances around 2.50 Å can be taken as indicative of single bonds in these metal-cluster structures.

The alternative, more symmetrical T_d structure for $Co_4(CO)_{12}$ without bridging CO groups (Figure 1; M = Co) is predicted to be of higher energy than the C_{3v} structure and has not been found experimentally.[5] However, the corresponding valence-isoelectronic carbonyliridium compound $Ir_4(CO)_{12}$ has this more symmetrical unbridged structure (Figure 1; M = Ir).[6] The $M(CO)_3$ (M = Co, Rh, Ir) vertex units in these tetranuclear carbonylmetal groups are isoelectronic and isolobal with phosphorus atoms. The $M_4(CO)_{12}$ derivatives, particularly the symmetrical T_d structures (Figure 1), are thus closely related to P_4 (white phosphorus), which is a spherically aromatic system.[7] For this reason the $M_4(CO)_{12}$ derivatives (M = Co, Rh, Ir) are significant in carbonylmetal chemistry in representing the prototypical spherically aromatic carbonylmetal clusters. Spherical aromaticity has also been suggested for the isoelectronic tetrahedral clusters $M_4(CO)_{14}$ (M = Fe, Ru, Os).[8]

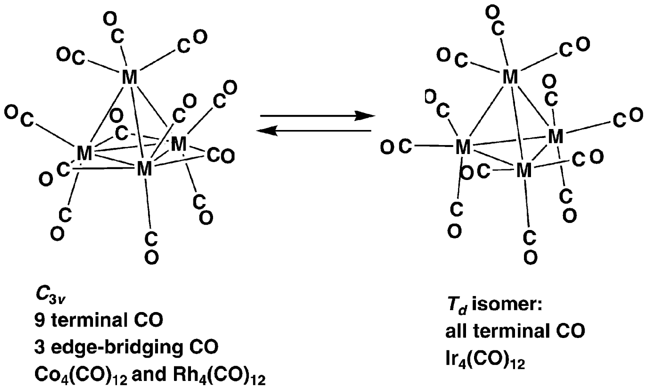

Figure 1. $M_4(CO)_{12}$ structures.

Removal of CO groups from $Co_4(CO)_{12}$ to give $Co_4(CO)_n$ (n = 11, 10, 9, 8, etc.) is expected to lead to unsaturated derivatives. Analogy with dinuclear carbonylmetal derivatives, which we have studied extensively by density functional theory (DFT),[9,10] suggests that this unsaturation will be reflected in one of the following three ways: (1) some short metal–metal bond lengths indicative of metal–metal multiple bonding, (2) four-electron donor bridging CO groups with short metal–oxygen distances, (3) metal stereochemistries (e.g., square-planar) suggesting 16-electron rather than 18-electron configurations. However, the pres-

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ent DFT study on $Co_4(CO)_{11}$ reveals an unexpected new structural feature requiring a minimum of four metal atoms, namely a μ_4-carbonyl group bridging all four metal atoms. Such a CO group is of particular interest since its carbon–oxygen bond order is relatively low as indicated by its low predicted ν(CO) stretching frequency. Related μ_4-carbonyl groups are found in the more complicated heterometallic derivatives $(\eta^5\text{-}C_5H_5)_4Mo_2Ni_2S_2(\mu_4\text{-}CO)$ (ref.[11]) and $Rh_4(CO)_4(\mu\text{-}CO)_4(\mu_4\text{-}CO)(PtBu_3)_2[Pt(PtBu_3)]$ (ref.[12]).

2. Theoretical Methods

Electron-correlation effects were considered by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[13–21] Two DFT methods, namely B3LYP and BP86, were used in this study. The B3LYP method is the hybrid HF/DFT method using the combination of the three-parameter Becke functional (B3) with the Lee–Yang–Parr (LYP) generalized gradient correlation functional.[22,23] The BP86 method is a pure DFT method which is the combination of Becke's 1988 exchange functional with Perdew's 1986 correlation functional.[24,25] The BP86 method has been shown to be somewhat more reliable than the B3LYP method for first-row transition metal organometallic systems.[16,26–28] In the present study, the B3LYP and BP86 methods agree with each other fairly well in predicting the structural characteristics of $Co_4(CO)_{11}$.

All computations were performed using double-ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents $a_d(C) = 0.75$ and $a_d(O) = 0.85$ to the standard Huzinaga–Dunning contracted DZ sets[29,30] and are designated (9s5p1d/4s2p1d). The loosely contracted DZP basis set for cobalt is the Wachters primitive set[31] augmented by two sets of p functions and a set of d functions, contracted according to Hood, Pitzer and Schaefer,[32] namely (14s11p6d/10s8p3d).

The geometries of all structures were fully optimized using both the DZP B3LYP and DZP BP86 methods, and the 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,[33] exercising the fine-grid option (75 radial shells, 302 angular points) for evaluating integrals numerically, while the tight (10^{-8} hartree) designation is the default for the self-consistent-field (SCF) convergence. In cases where small imaginary vibrational frequencies were found, the calculations were repeated using the finer (120,974) grid.

3. Results

Five energetically low-lying structures were found for $Co_4(CO)_{11}$ (Tables 1, 3–7). The infrared ν(CO) frequencies are listed in Table 2.

3.1 The Lowest-Energy Structure for $Co_4(CO)_{11}$: A μ_4-Fourfold Bridging Carbonyl Group

The lowest-energy structure found for $Co_4(CO)_{11}$ (**1S**) is a C_2 structure containing a butterfly array of cobalt atoms with a unique CO group bridging all four metal atoms, two edge-bridging CO groups, and eight terminal CO groups (Table 3). Structure **1S** has all real harmonic vibrational frequencies (Table 1).

The Co(1)–Co(2) distance, an edge of the butterfly skeleton, is predicted to be 2.444 Å by B3LYP and 2.455 Å by BP86 (Table 3), while for the other non-equivalent edge, the Co(1)–Co(4) distance is 2.553 Å (B3LYP) or 2.538 Å (BP86). The diagonal Co(1)–Co(3) distance is 2.489 Å (B3LYP) or 2.509 Å (BP86). All of these five Co–Co distances are reasonable for single bonds in accord with the butterfly structure. The other diagonal Co(2)–Co(4) distance is very long, i.e., 3.894 Å (B3LYP) or 3.860 Å (BP86), indicating little direct interaction between these two cobalt atoms. The unique μ_4-CO group bridging all four cobalt atoms [C(26)–O(25) in Table 3] has Co–C distances of 1.971 Å and 2.031 Å (B3LYP) or 1.979 Å and 2.011 Å (BP86). This μ_4-CO group exhibits an unusually low ν(CO) frequency (Table 2), namely 1636 cm^{-1} (BP86), consistent with a very long C–O bond, namely 1.209 Å (B3LYP) or 1.226 Å (BP86). This compares with the lowest bridging ν(CO) frequency[34] of $Co_4(CO)_{12}$ [= $Co_4(CO)_9(\mu\text{-}CO)_3$] at 1866 cm^{-1}. The Co–C distances to the two edge-bridging CO groups in **1S** are 1.888 Å and 1.941 Å (B3LYP) or 1.919 Å and 1.893 Å (BP86), and the corresponding ν(CO) frequencies are 1878 cm^{-1} (BP86). The C–O distances for the edge-bridging CO groups are 1.172 Å (B3LYP) or 1.187 Å (BP86). For the eight terminal CO groups, the Co–C distances are in the range of 1.788–1.804 Å (B3LYP) or

Table 1. Total energies (E, in hartree), relative energies (ΔE, in kcal/mol), number of imaginary vibrational frequencies (N_{img}) for the stationary points of $Co_4(CO)_{11}$.

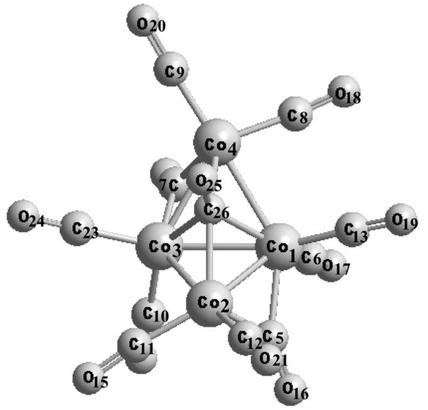
		1S (C_2)	**2S** (C_{2v})	**3S** (C_1)	**4S** (C_s)	**5S** (C_{2v})
B3LYP	E	–6778.32287	–6778.32125	–6778.31539	–6778.30917	–6778.30808
	ΔE	0.0	1.0	4.7	8.6	9.3
	N_{img}	0	1 (7*i*)	0	0	1 (23*i*)
BP86	E	–6779.38495	–6779.37817	–6779.37741	–6779.36385	–6779.34588
	ΔE	0.0	4.3	4.7	13.2	24.5
	N_{img}	0	0	0	0	3 (41*i*,31*i*,30*i*)

Table 2. ν(CO) vibrational frequencies [cm^{-1}] predicted for the five lowest-lying stationary points of $Co_4(CO)_{11}$ [infrared intensities in parentheses are in km/mol; ν(CO) frequencies of bridging CO groups are in **bold**].

	B3LYP	BP86
1S (C_2)	**1710** (**201**), **1956** (**387**), **1957** (**444**), 2078 (399), 2081 (3), 2091 (1), 2098 (141), 2110 (1591), 2115 (2687), 2120 (2889), 2162 (1)	**1636** (**178**), **1878** (**327**), **1878** (**297**), 1987 (387), 1989 (11), 2005 (89), 2012 (128), 2024 (1306), 2025 (2289), 2035 (2026), 2069 (28)
2S (C_{2v})	**1880** (**750**), **1886** (**162**), **1962** (678), 2071 (229), 2076 (83), 2094 (290), 2102 (0), 2116 (2137), 2116 (2676), 2119 (1877), 2161 (8),	**1797** (**547**), **1799** (**162**), **1891** (**535**), 1985 (19), 1993 (118), 2006 (0), 2006 (101), 2024 (2573), 2026 (1826), 2035 (1368), 2068 (12)
3S (C_1)	**1899** (**612**), **1946** (**444**), **1969** (**396**), **2011** (**577**), 2071 (323), 2087 (136), 2098 (93), 2107 (2463), 2113 (1984), 2118 (2049), 2158 (23)	**1820** (**420**), **1878** (**205**), **1893** (**667**), **1902** (**322**), 1975 (308), 1999 (82), 2010 (298), 2020 (1701), 2026 (1616), 2032 (1635), 2064 (30)
4S (C_s)	**1874** (**436**), **1966** (**118**), **1994** (**928**), 2064 (7), 2077 (247), 2082 (10), 2095 (74), 2100 (1037), 2113 (2826), 2119 (2826), 2159 (32)	**1829** (**315**), **1879** (**73**), **1904** (**746**), 1975 (38), 1995 (2), 1999 (125), 2007 (195), 2014 (814), 2031 (2074), 2032 (2203), 2067 (26)
5S (C_{2v})	**1958** (**961**), **1981** (**61**), **2002** (**359**), 2070 (0), 2077 (380), 2084 (202), 2094 (0), 2099 (1235), 2114 (3040), 2114 (2286), 2156 (2)	**1858** (**154**), **1862** (**700**), **1900** (**172**), 1986 (0), 1992 (437), 2001 (102), 2009 (0), 2020 (997), 2028 (2552), 2031 (1725), 2065 (12)

1.774–1.799 Å (BP86). The corresponding ν(CO) frequencies are 1987–2069 cm^{-1}. The Co–C–O bond angles of these terminal CO groups are almost linear.

Table 3. Lowest-energy structure **1S** of $Co_4(CO)_{11}$. The μ_4-CO group is C(26)–O(25).



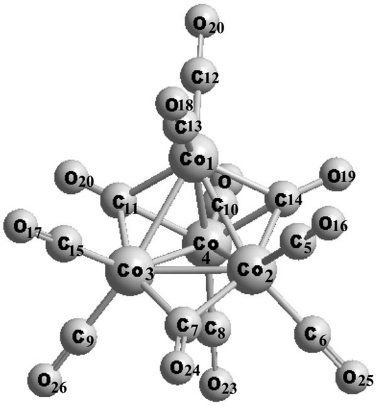
1S

Bond length	B3LYP	BP86
Co(1)–Co(2)	2.444	2.455
Co(1)–Co(3)	2.489	2.509
Co(1)–Co(4)	2.553	2.538
Co(2)–Co(4)	3.894	3.860

3.2 Structure of $Co_4(CO)_{11}$ with a Tetrahedral Array of Cobalt Atoms

The next energetically low-lying $Co_4(CO)_{11}$ structure **2S** (Table 4) is only 1.0 kcal/mol (B3LYP) or 4.3 kcal/mol (BP86) above the global minimum **1S**. It has all real vibrational frequencies by BP86, but a negligibly small[35] imaginary vibrational frequency (7*i* cm^{-1}) by B3LYP. This small imaginary vibrational frequency becomes 10*i* cm^{-1} when the finer (120,974) integration grid is used for the B3LYP calculation.

Table 4. Tetrahedral structure **2S** of $Co_4(CO)_{11}$.



2S

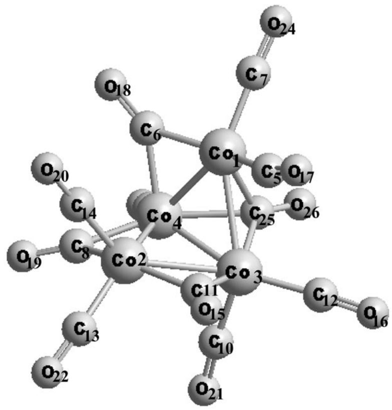
Bond length	B3LYP	BP86
Co(1)–Co(2)	2.605	2.560
Co(2)–Co(3)	2.366	2.410
Co(1)–Co(4)	2.378	2.365

Structure **2S** has C_{2v} symmetry with a tetrahedral array for the four cobalt atoms. It has two face-bridging μ_3-CO groups, one edge-bridging μ-CO group, and eight terminal CO groups. This arrangement of bridging CO groups in **2S** contrasts with the presence of three edge-bridging μ-CO groups in the known[2–4] tetrahedral structure of $Co_4(CO)_{12}$. The tetrahedral structure **2S** of $Co_4(CO)_{11}$ (Table 4) contains two distinct cobalt environments. The Co(2)–Co(3) distance, with one edge-bridging CO group on it, is 2.366 Å (B3LYP) or 2.410 Å (BP86). The Co(1)–Co(4) distance, without an edge-bridging CO group, is 2.378 Å (B3LYP) or 2.365 Å (BP86). The Co(1)–Co(2) distances are predicted to be 2.605 Å (B3LYP) or 2.560 Å (BP86). The Co–C distances for the face-bridging μ_3-CO groups are 2.002 Å and 2.047 Å (B3LYP) or 2.011 Å and 1.999 Å (BP86). The C–O distance for these two groups is 1.180 Å (B3LYP) or 1.197 Å (BP86). The low vibrational frequencies of 1797 and 1799 cm^{-1} (BP86) found in **2S** (Table 2) can be assigned to these two face-bridging μ_3-CO groups. The Co–C distance for the symmetrical edge-bridging CO group is 1.936 Å (B3LYP) or 1.941 Å (BP86). The related C–O bond length is 1.171 Å (B3LYP) or 1.185 Å (BP86), and its ν(CO) frequency is 1891 cm^{-1} (BP86). For the eight terminal CO groups, the Co–C distances are in the range of 1.782–1.795 Å (B3LYP) or 1.774–1.780 Å (BP86). The corresponding ν(CO) frequencies are 1993–2068 cm^{-1} (BP86). The Co–C–O bond angles of these terminal CO groups are almost linear.

3.3 A Structure of $Co_4(CO)_{11}$ with a Butterfly Array of Cobalt Atoms

Another $Co_4(CO)_{11}$ structure **3S** (Table 5) lies 4.7 kcal/mol above the global minimum **1S** by both the B3LYP and BP86 methods. It has all real vibrational frequencies, indicating a genuine minimum. Structure **3S** has a butterfly array of cobalt atoms, with a long Co(1)···Co(2) distance of 2.974 Å (B3LYP) or 3.105 Å (BP86) between the wingtips of the Co_4 butterfly, indicating a very weak direct Co···Co interaction. All of the other Co–Co distances fall in the range 2.413–2.610 Å (B3LYP) or 2.374–2.565 Å (BP86). They may be interpreted as the five single bonds necessary to form the butterfly structure. Structure **3S** has one face-bridging μ_3-CO group, three edge-bridging CO groups, one semibridging CO group, and six terminal CO groups.

Table 5. Butterfly structure **3S** of $Co_4(CO)_{11}$.



3S

Bond length	B3LYP	BP86
Co(1)–Co(2)	2.974	3.105
Co(1)–Co(3)	2.610	2.511
Co(1)–Co(4)	2.425	2.374
Co(2)–Co(3)	2.413	2.451
Co(2)–Co(4)	2.480	2.420
Co(3)–Co(4)	2.557	2.565

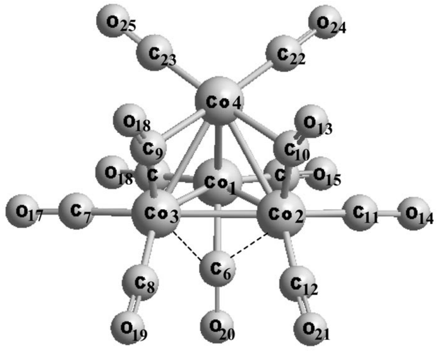
The distances from Co(1), Co(4) and Co(3) to the face-bridging carbon atom C(25) are 2.204, 1.985, and 1.966 Å (B3LYP) or 2.037, 2.034, and 2.007 Å (BP86), respectively. The C–O distance for this CO group is very long, namely 1.178 Å (B3LYP) or 1.193 Å (BP86). The low vibrational frequency of 1820 cm^{-1} (BP86, Table 2) can be assigned to this face-bridging μ_3-CO group.

For one of the edge-bridging CO groups, the Co–C(11) distances are 2.037 Å and 1.872 Å (B3LYP) or 1.997 Å and 1.915 Å (BP86). For another edge-bridging CO group the Co–C(8) distances are 1.805 Å and 2.245 Å (B3LYP) or 1.856 Å and 2.040 Å (BP86). For the third edge-bridging CO group the Co–C(6) distances are 1.997 Å and 1.851 Å (B3LYP) or 1.948 Å and 1.875 Å (BP86). The ν(CO) frequencies of these three edge-bridging CO groups are predicted to be 1878, 1893, and 1902 cm^{-1}. As for the semibridging CO group, the longer Co–C distance is 2.870 Å (B3LYP) or 2.576 Å (BP86) and the shorter one is 1.773 Å (B3LYP) or 1.782 Å (BP86).

3.4 A Structure of $Co_4(CO)_{11}$ with Three Distinct Cobalt Environments

The structure next-higher in energy for $Co_4(CO)_{11}$, namely **4S** (Table 6), is predicted to lie 8.6 kcal/mol (B3LYP) or 13.2 kcal/mol (BP86) above the global minimum **1S**. It also has all real vibrational frequencies. This structure has C_s symmetry with one face-bridging μ_3-CO group, two edge-bridging μ-CO groups, and eight terminal CO groups on the underlying Co_4 tetrahedron. Structure **4S** contains three distinct cobalt environments. The cobalt Co(4) is connected to two terminal and two edge-bridging CO groups. The cobalt atoms Co(2) and Co(3) are each bonded to one face-bridging, one edge-bridging, and two terminal CO groups. Another cobalt atom, Co(1), is connected to two terminal and one face-bridging CO groups.

Table 6. Structure of $Co_4(CO)_{11}$ with three distinct cobalt environments.



4S

Bond length	B3LYP	BP86
Co(1)–Co(2)	2.512	2.489
Co(2)–Co(3)	2.511	2.492
Co(1)–Co(4)	2.626	2.621
Co(2)–Co(4)	2.574	2.567

All six of the Co–Co distances in **4S** correspond to the single bonds necessary to form a Co_4 tetrahedron. Thus, the Co(1)–Co(2) distance is predicted to be 2.512 Å (B3LYP) or 2.489 Å (BP86). The Co(2)–Co(3) distance is 2.511 Å by

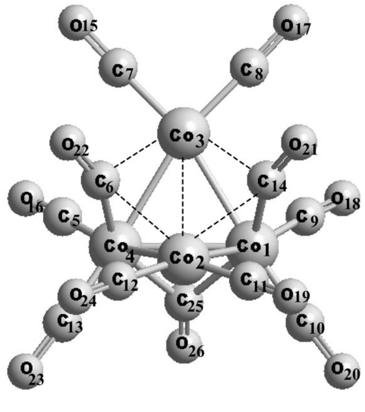
B3LYP and 2.492 Å by BP86. The Co(1)–Co(4) distance is 2.626 Å (B3LYP) or 2.621 Å (BP86). The Co(2)–Co(4) distance is 2.574 Å (B3LYP) or 2.567 Å (BP86).

For the face-bridging CO group in **4S**, the Co–C distances are 1.871 Å and 2.111 Å (B3LYP) or 1.838 Å and 2.170 Å (BP86). The long C–O distance of 1.183 Å (B3LYP) or 1.194 Å (BP86) for this CO group indicates a weak C–O bond consistent with its low vibrational frequency of 1829 cm^{-1} (BP86) (Table 2). The Co–C distances to the edge-bridging CO groups are 1.794 Å and 2.161 Å (B3LYP) or 1.799 Å and 2.097 Å (BP86), and their corresponding ν(CO) frequencies are 1879 cm^{-1} and 1904 cm^{-1}(BP86). For the eight terminal CO groups, the Co–C distances are in the range of 1.777–1.793 Å (B3LYP) or 1.766–1.786 Å (BP86), and their corresponding ν(CO) frequencies are in the range 1975–2067 cm^{-1} (BP86). The Co–C–O bond angles are almost linear.

3.5 Another Butterfly Structure of $Co_4(CO)_{11}$

The last $Co_4(CO)_{11}$ stationary point **5S** at competitive relative energies (Table 7) lies 9.3 kcal/mol (B3LYP) or 24.5 kcal/mol (BP86) above **1S**. It has a small imaginary vibrational frequency of $23i$ cm^{-1} by B3LYP or three small imaginary vibrational frequencies of $41i$, $31i$, and $30i$ cm^{-1} by BP86. Using the finer (120,974) integration grid fails to remove these small imaginary vibrational frequencies.

Table 7. Geometry of structure **5S** of $Co_4(CO)_{11}$.



5S

Bond length	B3LYP	BP86
Co(1)–Co(2)	2.511	2.464
Co(2)–Co(3)	3.547	3.200
Co(1)–Co(4)	2.581	2.538

Structure **5S** has C_{2v} symmetry with a butterfly array of cobalt atoms and two face-bridging, one edge-bridging, and eight terminal CO groups. Five of the Co–Co distances fall in the range 2.511–2.581 Å, consistent with the single bonds necessary to construct the butterfly structure. The sixth Co···Co distance of 3.547 Å (B3LYP) or 3.200 Å (BP86), corresponding to the distance between the butterfly wingtips, is too long for any significant direct metal–metal interaction.

Structure **5S** contains two distinct cobalt environments. The Co(3) and Co(2) atoms are each bonded to two terminal and two face-bridging μ_3-CO groups. The Co(4) and Co(1) atoms are each connected to one face-bridging, one edge-bridging, and two terminal CO groups. For the two face-bridging μ_3-CO groups, the Co–C distances are 2.441 Å and 1.792 Å (B3LYP) or 2.265 Å and 1.835 Å (BP86). The face-bridging C–O distances are 1.168 Å (B3LYP) or 1.188 Å (BP86), and the corresponding vibrational frequencies are 1858 cm^{-1} and 1862 cm^{-1} (BP86). The Co–C distance to the symmetrical edge-bridging CO group is 1.967 Å (B3LYP) or 1.959 Å (BP86). The corresponding C–O distance is 1.169 Å (B3LYP) or 1.182 Å (BP86), and its ν(CO) frequency is 1900 cm^{-1}. For the eight terminal CO groups, the Co–C distances are in the range of 1.764–1.794 Å (B3LYP) or 1.757–1.782 Å (BP86). The corresponding vibrational frequencies fall in the range 1986–2065 cm^{-1} (BP86, Table 2). The Co–C–O bond angles for the terminal CO groups are almost linear.

4. Discussion

4.1 The μ_4-CO Group in the Global Minimum 1S of $Co_4(CO)_{11}$

The most unusual $Co_4(CO)_{11}$ structure found in this work is the structure of lowest energy, namely **1S** which has a CO group bridging all four cobalt atoms (Figure 2). This is an unprecedented structure for a homoleptic carbonylmetal derivative. This μ_4-carbonyl group can be regarded as being bonded to the Co_4 framework by a five-center CCo_4 bond. This leads to an unusually low ν(CO) frequency at 1636 cm^{-1} (BP86) and a corresponding low carbon–oxygen formal bond order as indicated by a relatively long C–O distance of 1.226 Å. For comparison, the ν(CO) frequency of the analogous μ_4-CO group in the Mo/Ni heterometallic derivative $(\eta^5\text{-}C_5H_5)_4Mo_2Ni_2S_2(\mu_4\text{-}CO)$ is 1654 cm^{-1} and its C–O distance is 1.18 Å.[11] Similarly, the ν(CO) frequency of the analogous μ_4-CO group in the Rh/Pt heterometallic derivative $Rh_4(CO)_4(\mu\text{-}CO)_4(\mu_4\text{-}CO)(PtBu_3)_2[Pt(PtBu_3)]$ is 1704 cm^{-1} and its C–O distance is 1.168 Å.[12] Thus, the properties of the μ_4-CO group predicted for structure **1S** of $Co_4(CO)_{11}$ are somewhat more extreme than those in the reported examples of μ_4-CO groups found in stable isolable compounds structurally characterized by X-ray diffraction. By contrast, the normal μ-CO edge-bridging CO groups in $Co_4(CO)_{12}$ [= $Co_4(CO)_9(\mu\text{-}CO)_3$] exhibit an infrared ν(CO) frequency at 1866 cm^{-1} and a C–O distance[4] of 1.133 Å.

The five-center CCo_4 bond to the μ_4-CO group accommodates the electron deficiency of $Co_4(CO)_{11}$ (**1S**), leading to effective 18-electron configurations for all four cobalt atoms without the need for any metal–metal multiple bonding or four-electron donor η^2-μ-CO groups. In $Co_4(CO)_{12}$ with either the tribridged or unbridged structures (Figure 1) the six Co–Co bonds in the underlying Co_4 tetrahedron lead to 18-electron configurations for all four cobalt atoms. Conversion of tetrahedral $Co_4(CO)_{12}$ with six Co–Co bonds

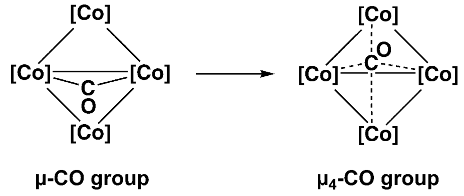


Figure 2. Relationship between a normal μ-CO group bridging a Co–Co bond and a μ$_4$-CO group bridging all four cobalt atoms in the Co$_4$ butterfly of the lowest energy structure **1S** of Co$_4$(CO)$_{11}$. The interactions of the μ$_4$-CO group with all four cobalt atoms in the five-center CCo$_4$ bond are shown by dashed lines. The designation [Co] refers to a cobalt atom with its ligands other than the μ$_4$-CO group.

to the butterfly structure **1S** of Co$_4$(CO)$_{11}$, with only five Co–Co bonds, by loss of a CO group and a Co–Co bond leads to a loss of four electrons, two from the "missing" Co–Co bond and two from the lost CO group. The four-way bridging μ$_4$-CO group makes up for this loss of four electrons in structure **1S** of Co$_4$(CO)$_{11}$ (Figure 2). Thus, a normal symmetrical or nearly symmetrical bridging μ-CO group donates its electron pair to two metal atoms, formally one electron to each metal atom. However, the four-way bridging μ$_4$-CO group can share its electron pair with all four cobalt atoms through formation of a five-center CCo$_4$ bond. Thus, in Figure 2 only the left and right Co atoms of the Co$_4$ rhombus receive electrons from the normal bridging μ-CO group. The top and bottom Co atoms thus receive no electrons from this μ-CO group. However, the μ$_4$-CO group bridging all four cobalt atoms (Figure 2, right) effectively donates its electron pair to all four cobalt atoms at the same time through the five-center CCo$_4$ bond. In this way the top and bottom cobalt atoms as well as the left and right cobalt atoms receive electrons from this unusual μ$_4$-CO group, thereby making up for the loss of four electrons noted above in going from the stable structure of Co$_4$(CO)$_{12}$ to the global minimum **1S** of Co$_4$(CO)$_{11}$ by loss of a CO group and one of the Co–Co bonds.

4.2 The Other Structures of Co$_4$(CO)$_{11}$

One possible way for Co$_4$(CO)$_{11}$ to compensate for the unsaturation generated by the loss of a CO group from saturated Co$_4$(CO)$_{12}$ would be for one of the six Co–Co bonds in the Co$_4$ tetrahedron to become significantly shorter than the other five Co–Co bonds suggesting one Co=Co double bond in the tetrahedron. This is not observed for any of the Co$_4$(CO)$_{11}$ structures. A possible reason for this is the equalization of the Co–Co distances in Co$_4$(CO)$_{11}$ by the spherical aromaticity[7] suggested for Co$_4$(CO)$_{12}$ and M$_4$(CO)$_{14}$ (M = Fe, Ru, Os).[8]

The Co$_4$ frameworks observed for the Co$_4$(CO)$_{11}$ structures are either butterflies with five Co–Co distances in the broad single-bond range of 2.4–2.6 Å (**1S**, **3S**, and **5S**) or tetrahedra with six such Co–Co distances (**2S** and **4S**). The distribution of terminal and various types of bridging CO groups (μ$_2$, μ$_3$, and μ$_4$) leads to 15 or 16 Co–C bonds to the Co$_4$ skeleton.

4.3 Synthetic Prospects

Decarbonylation of Co$_4$(CO)$_{12}$ is an obvious way to prepare the unsaturated Co$_4$(CO)$_{11}$ provided that conditions can be found to break selectively one Co–CO bond without destroying the Co$_4$ cluster. However, Co$_4$(CO)$_{11}$ has apparently never been observed experimentally even as an unstable photolysis product in low-temperature matrices. Other possible conditions for the decarbonylation of Co$_4$(CO)$_{12}$ to Co$_4$(CO)$_{11}$ could involve selectively oxidizing one of its CO groups as CO$_2$ using stoichiometric amounts of trimethylamine *N*-oxide or iodosylbenzene at low temperatures. Alternatively, structures related to those predicted for Co$_4$(CO)$_{11}$ in this work, particularly structure **1S** (Figure 2) with the unusual μ$_4$-CO group (Figure 2), might be stabilized by replacing some of the terminal CO groups pairwise with small-bite strong π-acceptor ligands such as CH$_3$N(PF$_2$)$_2$, which can stabilize metal–metal bonds in cluster structures by forming stable five-membered M$_2$P$_2$N ring systems.[36]

Supporting Information (see footnote on the first page of this article): Theoretical harmonic vibrational frequencies for the Co$_4$(CO)$_{11}$ structures using the BP86 method, theoretical Cartesian coordinates for the Co$_4$(CO)$_{11}$ structures using the BP86 method.

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