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Unusual Effects of the Bulky 1-Norbornyl Group in Cobalt Carbonyl Chemistry: Low-Energy Structures with Agostic Hydrogen Atoms

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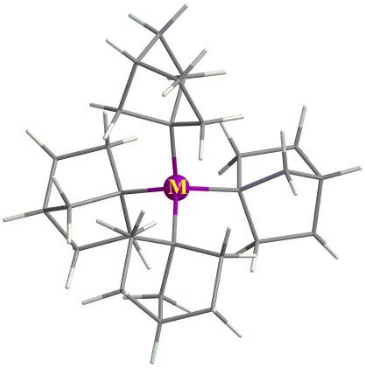
Abstract

The 1-norbornyl (nor) ligand is known experimentally to form stable transition metal alkyl derivatives through direct metal-carbon bond formation. This appears to be related to its steric bulk and inaccessibility towards β-hydrogen elimination, as exemplified by the tetraalkyls $(nor)_4M$, some of which are very stable. In this connection we have used density functional theory and the DLPNO-CCSD(T) method to investigate the 1-norbornylcobalt carbonyl derivatives $(nor)Co(CO)_n$ (n = 4, 3, 2, 1) and $(nor)_2Co_2(CO)_n$ (n = 7, 6, 5). Low-energy structures of the unsaturated systems $(nor)Co(CO)_n$ (n = 3, 2) and $(nor)_2Co_2(CO)_n$ (n = 6, 5) are found to have agostic hydrogen atoms from a CH_2 group adjacent to the Co–C bond. Such agostic hydrogen atoms form a C–H–Co bridge with a bonding Co–H distance less than ~2 Å. In such structures unsaturation is relieved by donation of an additional two electrons from the C–H bond of this norbornyl CH_2 group. In addition, structures in which carbonyl migration from cobalt to carbon has occurred to form acyl norCO ligands are among the lowest energy structures. The resulting acyl carbonyl groups of the norCO ligands serve as spacers between the bulky 1-norbornyl ligand and the cobalt carbonyl moiety. Furthermore, such neutral norCO acyl ligands can either be one-electron donors to a cobalt atom, bonding solely through the carbonyl carbon, or three-electron donor η^2-μ-norCO groups bridging a central Co_2 unit through both the acyl carbon and oxygen atoms. The strengths of the agostic C–H–Co interactions have been characterized by their reduced density gradient (RDG) values.

Key words: Cobalt carbonyls; 1-norbornyl; agostic hydrogen atoms; metal-metal bonding; density functional theory

1. Introduction

The 1-norbornyl ligand was discovered by Bower and Tennett in 1972)[1] to possess an exceptional capability of stabilizing homoleptic tetraalkyl derivatives of the first-row transition metals of stoichiometry $(C_7H_{11})_4M$ (designated as $(nor)_4M$) (Figure 1). Thus the chromium derivative $(nor)_4Cr$ is stable to air and to temperatures as high as 250°C. Later the analogous tetra-1-norbornyl derivative of the second row transition metal molybdenum $(nor)_4Mo$ was found to possess similar high stability.[2] X-ray crystallographic studies on $(nor)_4M$ (M = Fe,[3] Co[4]) indicate tetrahedral coordination of the central metal atom by forming four metal-carbon σ-bonds. Further elucidation by X-ray crystallography of the structural details of these systems, such as the position of the ligand hydrogen atoms relative to the central metal atom, is complicated by disorder problems. However, the $(nor)_4M$ molecules clearly can be regarded as spherical hydrocarbon blobs with a transition metal in the center. The stability of the $(nor)_4M$ complexes contrasts with the thermal and oxidative instability of most homoleptic transition metal alkyls and is related to dispersion effects involving a central metal encapsulated by four bulky 1-norbornyl groups.[5,6] In addition decomposition by β-hydrogen elimination is disfavored for 1-norbornyl metal derivatives because of the extreme strain of the corresponding olefin 1-norbornene by Bredt's rule.[7]



$(nor)_4M$
(M=Ti,V, Cr, Mn, Fe, Co;
Zr, Hf, Mo)

Figure 1. The $(nor)_4M$ complexes.

Despite the unusually high stability of some of the homoleptic $(nor)_4M$ complexes, transition metal complexes containing both 1-norbornyl ligands and carbonyl groups appear to be unknown, or at least they are not reported in the literature. This is surprising since the resistance of 1-norbornylmetal derivatives towards decomposition by β-hydrogen elimination to give 1-norbornene because of Bredt's rule[7] suggests that a wide range of 1-norbornylmetal derivatives other than the tetrahedral $(nor)_4M$ should be viable species. However, reports of 1-norbornylmetal complexes other than the $(nor)_4M$ derivatives cited above are limited to the stable nickel(IV) bromide $(nor)_3NiBr$, the rather labile cyclopentadienyl $(\eta^5\text{-}C_5H_5)Ni(nor)$ (Figure 2),[8,9] the surprisingly thermally stable but air-sensitive copper(I) derivative (1-nor)Cu,[10]and the extremely stable titanium compounds $CpTi(1\text{-}nor)_3$, $Cp_2Ti(1\text{-}nor)_2$ and $C_{p2}Ti(1\text{-}nor)Cl$.[11]

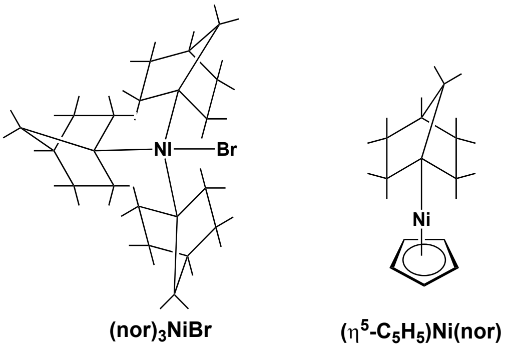


Figure 2. Two nickel 1-norbornyl complexes among the few examples of heteroleptic 1-norbornyl transition metal complexes.

Among possible 1-norbornyl metal carbonyls the cobalt derivatives are of particular interest for a number of reasons. The alkylcobalt tetracarbonyls $RCo(CO)_4$ with the favored 18-electron configuration exhibit a wide range of thermal stabilities depending upon the nature of the alkyl group. Thus the methyl derivative $CH_3Co(CO)_4$ is very unstable, decomposing at –40°C,[12] whereas the trifluoromethyl derivative $CF_3Co(CO)_4$ is a stable yellow liquid distillable at atmospheric pressure with similar physical properties to $Fe(CO)_5$.[13,14] The analogy between stable alkylcobalt carbonyls with a 1:1 alkyl/cobalt ratio to iron carbonyls could potentially be extended to stable 1-norbornylcobalt carbonyls where $(nor)Co(CO)_4$ and $(nor)_2Co_2(CO)_7$ are analogues to the well-known $Fe(CO)_5$ and $Fe_2(CO)_9$, respectively.

Previous studies, both experimental and theoretical, show that unsaturation in metal carbonyl derivatives can be accommodated in three different ways:

(1) Metal-metal multiple bonding;

(2) Four-electron donor bridging η^2-μ-CO carbonyl groups;

(3) Metal electron configurations less than the favored 18-electron configuration.

The theoretical work on the mononuclear $(nor)Co(CO)_n$ ($n = 4, 3, 2, 1$) and binuclear $(nor)_2Co_2(CO)_n$ ($n = 7, 6, 5$) derivatives described in this paper shows the 1-norbornyl ligand can accommodate unsaturation in transition metal complexes in a different way through interaction of ligand agostic hydrogen atoms[15] with the metal atom. In addition, carbonyl insertion into the norbornyl Co–C bond is found to occur in some low-energy structures to relieve the steric congestion between the bulky norbornyl group and the cobalt carbonyl moieties.

2. Theoretical Methods

Dispersion effects are found to be important in structures with sterically demanding groups.[16.17,18] Thus computational studies have shown that some molecules can be stabilized by dispersion effects.[19,20] The B3PW91-D3 method has been used successfully in investigating the first row transition metal tetrakis-1-norbornyl complexes $(nor)_4M$.[5,6] For this reason the B3PW91-D3 method with Grimme's D3 dispersion scheme[21] was also used with the Gaussian 09 program[22] to optimize the geometries of all structures in the present paper.

Double-ζ plus polarization (DZP) basis sets and cc-pVTZ basis sets were used in this research. For carbon one set of pure spherical harmonic d functions with orbital exponent $\alpha_d(C) = 0.75$ is added to the standard Huzinaga-Dunning contracted DZ sets. This basis set is designated (9s5p1d/4s2p1d).[23,24] For hydrogen, a set of p polarization functions $\alpha_p(H) = 0.75$ is added to the Huzinaga-Dunning DZ sets. For the transition metal cobalt, in our loosely contracted DZP basis sets, the Wachters' primitive sets are used, but augmented by two sets of p functions and one set of d functions, contracted following Hood *et al.*, and designated (14s11p6d/10s8p3d).[25,26] Preliminary optimizations were first done by the B3PW91-D3/DZP method. The resulting structures were optimized further at the B3PW91-D3/cc-pVTZ level. The final relative energies at the B3PW91-D3/cc-pVTZ level are discussed in the text.

3. Results and Discussion

3.1 Mononuclear derivatives.

In order to benchmark the DFT relative energy orders predicted by the B3PW91-D3/cc-pVTZ method, the single point energies for the mononuclear structures $(nor)Co(CO)_n$ ($n = 4, 3, 2$) were also calculated by the DLPNO-CCSD(T)/-def2-TZVP method based on the geometries obtained by the B3PW91-D3/DZP method. The comparisons suggest that the B3PW91-D3/cc-pVTZ relative energy orderings are consistent with those obtained by the more computationally demanding DLPNO-CCSD(T) /def2-TZVP method.

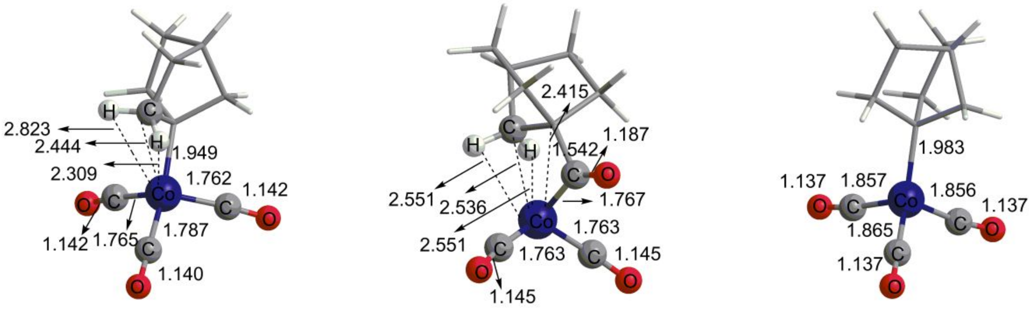
Two low-energy structures are found for the mononuclear tetracarbonyls $(nor)Co(CO)_4$ (Figure 3). The lower energy of these two structures is the singlet **4S-1** with four terminal carbonyl groups and one directly bonded norbornyl group thereby giving the cobalt atom the favored 18-electron configuration. The second $(nor)Co(CO)_4$ structure is the singlet **4S-2**, lying 5.0 kcal/mol (B3PW91-D3/cc-pVTZ) or 15.9 kcal/mol (DLPNO-CCSD(T)/def2-TZVP) in energy above **4S-1**. In **4S-2** three terminal carbonyl groups are bonded to the cobalt atom. The fourth carbonyl group functions as an acyl carbonyl bridge between the cobalt atom and the norbornyl group to give a norCO ligand. The Co-C and Co-H distances of ~2.7 Å predicted for 4**S-2** suggest only weak interactions. Ignoring such weak interactions gives the cobalt atom in **4S-2** only a 16-electron configuration. The Co-C(nor) distance of 2.085 Å in **4S-1** is longer than the average Co-C distance of 1.920 Å for the experimental (nor)$_4$Co structure.[4] This may relate to a minimal dispersion effect in the (nor)Co(CO)$_n$ structures with only one bulky 1-norbornyl group rather than four bulky 1-norbornyl groups in the (nor)$_4$M structures.

Three low-energy structures are obtained for the mononuclear tricarbonyl (nor)Co(CO)$_3$ (Figure 4). The lowest energy structure is the singlet **3S-1** with three terminal carbonyl groups. In **3S-1** the cobalt atom is σ-bonded directly to the norbornyl group with a Co-C distance of 1.949 Å. In addition, the norbornyl C–H bond closest to the cobalt atom in **3S-1** forms a three-center two-electron C–H–Co bond with a Co–C distance of 2.393 Å and a Co–H distance of 2.215 Å implying an agostic interaction. Supplementing the six electrons from the three carbonyl groups and the single electron from the Co–C σ bond of the norbornyl ligand with the two electrons from the norbornyl C–H bond through the agostic hydrogen interaction gives the cobalt atom the favored 18-electron configuration.

4S-1 (C_1)
(0.0, 0.0, 0.0)

4S-2 (C_s)
(2.9, 5.0, 15.9)

Figure 3. Optimized (nor)Co(CO)$_4$ structures. Internuclear distances are given in Å in Figures 3 through 8. The numbers in parentheses are the relative energies by the B3PW91-D3/DZP method, the B3PW91-D3/cc-pVTZ method and the DLPNO-CCSD(T)/def2-TZVP //B3PW91-D3/DZP method.



3S-1 (C_1)
(0.0, 0.0, 0.0)

3S-2 (C_s)
(7.5, 9.9, 20.3)

3T-3 (C_1)
(9.0, 8.2, 10.1)

Figure 4. Optimized (nor)Co(CO)$_3$ structures.

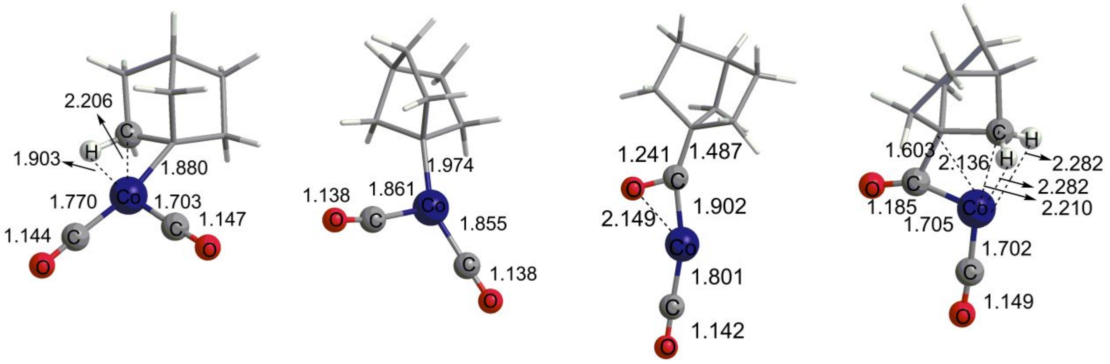
The second (nor)Co(CO)$_3$ structure is the singlet C_s structure **3S-2** lying 9.9 kcal/mol (B3PW91-D3/cc-pVTZ) or 20.3 kcal/mol (DLPNO-CCSD(T)/-def2-TZVP) in energy above **3S-1** (Figure 4). Structure **3S-2** has two terminal carbonyl groups and an acyl carbonyl group connecting the norbornyl group with the cobalt atom. In addition **3S-2** has an agostic interaction between two C–H bonds of a norbornyl CH$_2$ group and the cobalt atom with Co-H distances of 2.551 Å and a Co-C distance of 2.536 Å. If this type of CH$_2$–Co interaction results in donation of four norbornyl electrons to the cobalt atom using the electron pairs of both C–H bonds, then the cobalt atom in **3S-2** has the favored 18-electron configuration.

The lowest energy triplet (nor)Co(CO)$_3$ structure **3T-3**, lying 8.2 kcal/mol (B3PW91-D3/cc-pVTZ) or 10.1 kcal/mol (DLPNO-CCSD(T)/def2-TZVP) in energy above **3S-1**, has three terminal carbonyl groups and a norbornyl ligand directly bonded to the cobalt atom. This gives the cobalt atom a 16-electron configuration, consistent with a triplet spin state in a high-spin configuration.

Four low energy structures were found for the dicarbonyl (nor)Co(CO)$_2$ (Figure 5). The lowest energy such structure is the singlet **2S-1** with two terminal carbonyl groups. In addition the cobalt atom in **2S-1** receives two electrons from an agostic interaction with the nearest C–H bond of the norbornyl ligand with a Co-C distance of 2.206 Å and a Co-H distance of 1.903 Å. This gives the cobalt atom in **2S-1** a 16-electron configuration.

Two low-energy triplet (nor)Co(CO)$_2$ structures were found (Figure 5). The lower energy of these structures, namely **2T-2** lying 4.2 kcal/mol (B3PW91-D3/cc-pVTZ) or 9.0 kcal/mol (DLPNO-CCSD(T)/def2-TZVP) in energy above **2S-1**, has two terminal carbonyl groups and the norbornyl ligand directly bonded to the cobalt atom through a Co–C σ bond. This gives the cobalt atom in **2T-2** a 14-electron configuration, not unreasonable for a triplet spin state structure. The other low-energy triplet (nor)Co(CO)$_2$ structure **2T-3**, lying 7.7 kcal/mol (B3PW91-D3/cc-pVTZ) or 16.7 kcal/mol (DLPNO-CCSD(T)/def2-TZVP) in energy above **2S-1**, has one terminal carbonyl group and one acyl carbonyl group connecting the cobalt atom with the norbornyl group.

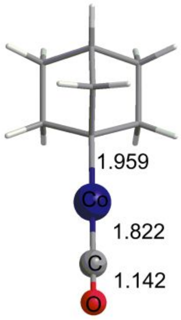
The final low-energy (nor)Co(CO)$_2$ structure is the C_s singlet **2S-4**, lying 13.5 kcal/mol (B3PW91-D3/cc-pVTZ) or 20.2 kcal/mol (DLPNO-CCSD(T)/-def2-TZVP) in energy above **2S-1** (Figure 5). Structure **2S-4** has one terminal carbonyl group and one acyl carbonyl group connecting the cobalt atom to the norbornyl group. In addition the nearest CH$_2$ group is bonded to the cobalt atom through both C–H bonds with a Co–C distance of 2.210 Å and two Co–H distances of 2.282 Å. The four electrons from the two C–H bonds of the CH$_2$ group coupled with two electrons from the terminal carbonyl group and a single electron from the norbornylacyl group gives the cobalt atom in **2S-4** a 16-electron configuration.



2S-1 (0.0, 0.0, 0.0) **2T-2** (5.1, 4.2, 9.0) **2T-3** (5.8, 7.7, 16.7) **2S-4** (11.5, 13.5, 20.2)

Figure 5. Optimized (nor)Co$(CO)_2$ structures.

Only one low-energy (nor)Co(CO) structure was found, namely the triplet **1T-1**, which lies ~14 kcal/mol below the next lowest energy (nor)Co(CO) structure (Figure 6). Structure **1T-1** has linear coordination of the cobalt atom with a terminal carbonyl group and a norbornyl group. The Co–C(nor) distance of 1.959 Å in the (nor)Co(CO) structure **1T-**1 is 0.13 Å shorter than that of 2.085 Å in the lowest energy (nor)Co$(CO)_4$ structure **4S-1**.

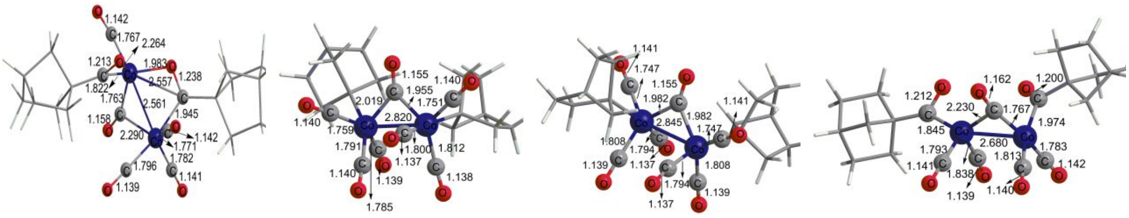


1T-1

Figure 6. The single low-energy (nor)Co(CO) structure.

3.2 Binuclear derivatives.

Four low-energy structures were found for the binuclear complex $(nor)_2Co_2(CO)_7$ (Figure 7) . The lowest energy such structure is the singlet **7S-1** with three terminal carbonyl groups and a norbornylacyl group on one cobalt atom, a terminal carbonyl group and a norbornylacyl group on the other cobalt atom. The central Co_2 unit is bridged by a two-electron donor carbonyl group and a three-electron donor η^2-μ-norCO norbornylacyl group. The cobalt atom bearing only one terminal carbonyl group is also bonded by a three-electron donor η^2-μ-norCO norbornylacyl group with a bonding Co–O distance of 2.264 Å. The carbonyl carbon atom of the bridging norbornylacyl group is bonded to both cobalt atoms whereas the oxygen atom of this carbonyl group is bonded only to one cobalt atom with a bonding Co–O distance of 1.983 Å. Interpreting the relatively short predicted Co-Co distance of 2.561 Å in **7S-1** as a formal single bond gives each cobalt atom the favored 18-electron configuration.



7S-1 (0.0, 0.0) **7S-2** (16.6, 22.2) **7S-3** (16.9, 22.3) **7T-4** (19.0, 27.9)

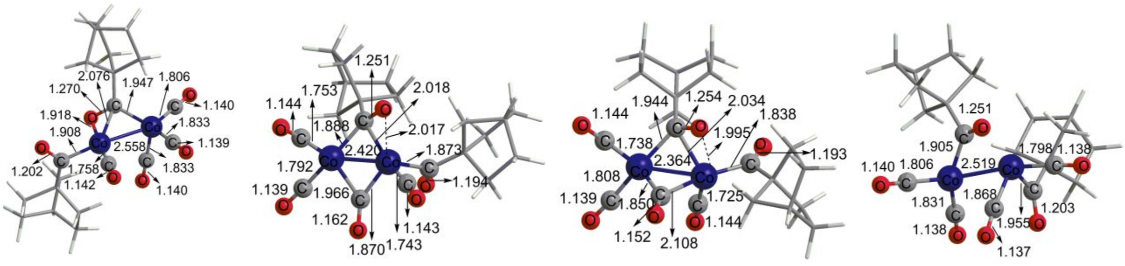
Figure 7. Optimized $(nor)_2Co_2(CO)_7$ structures. In Figures 7 to 9, the numbers in parentheses are first the relative energies by the B3PW91-D3/DZP method, and the relative energies at the B3PW91-D3/cc-pVTZ level.

The other three predicted $(nor)_2Co_2(CO)_7$ structures are much higher in energy than the lowest energy structure **7S-1**, indicating that **7S-1** is a particularly favorable structure. Structure **7S-2**, lying 22.2 kcal/mol (B3PW91-D3/cc-pVTZ) in energy above **7S-1**, has one bridging carbonyl group (Figure 7). Each cobalt atom in **7S-2** has three terminal carbonyl groups and one terminal norbornyl ligand. The Co–Co distance of 2.820 Å can be interpreted as a formal single bond, thereby giving each cobalt atom the favored 18-electron configuration. Structure **7S-3**, lying 22.3 kcal/mol in energy above **7S-1**, is similar to **7S-2** but with a different ligand stereochemistry. Thus in **7S-2** the two norbornyl ligands are on the same side of the Co–Co bond whereas in **7S-3** the two norbornyl ligands are on opposite sides of the Co–Co bond.

The fourth $(nor)_2Co_2(CO)_7$ structure **7T-4**, lying 27.9 kcal/mol in energy above **7S-1**, is actually a triplet $(norCO)_2Co_2(CO)_4(\mu\text{-}CO)$ structure in which two of the carbonyl groups have inserted into a nor-Co bond to form norCO acyl groups exhibiting ν(CO) frequencies at 1728 and 1769 cm^{-1} (B3PW91-D3/DZP) (Figure 7). Each cobalt atom bears two terminal carbonyl groups and a norbornylacyl ligand. The remaining carbonyl group bridges the Co_2 unit. Interpreting the Co=Co distance of 2.680 Å as a formal double bond gives each cobalt atom the 17-electron configuration for a binuclear triplet.

Four low energy structures were found for (nor)$_2$Co$_2$(CO)$_6$ (Figure 8). The lowest energy structure is the triplet **6T-1** with three terminal carbonyl groups bonded to one of the two cobalt atoms and one terminal carbonyl group bonded to the other cobalt atom. The remaining two carbonyl groups in **6T-1** are inserted between the norbornyl group and a cobalt atom to form norbornylacyl groups. One of these norbornylacyl groups is bonded as a terminal ligand to the cobalt atom bearing only one terminal carbonyl group. The other norbornylacyl group is a three-electron donor bridging η^2-μ-norCO ligand with the carbonyl carbon bridging the Co$_2$ unit. Interpreting the Co=Co distance of 2.559 Å as a formal double bond gives each metal atom the 17-electron configuration for a binuclear triplet. The (nor)$_2$Co$_2$(CO)$_6$ structure **6T-4**, lying 5.5 kcal/mol in energy above **6T-1**, is similar to **6T-1** except for the stereochemistry of the ligands around the central Co$_2$ unit.

The singlet (nor)$_2$Co$_2$(CO)$_6$ structure **6S-2**, lying only 2.9 kcal/mol above **6T-1**, has a bridging carbonyl group, two terminal carbonyl groups bonded to one cobalt atom, and one terminal carbonyl group bonded to the other cobalt atom (Figure 8). The remaining two carbonyl groups in **6S-2** are inserted into norbornyl Co–C bonds to give norbornylacyl groups. One of these norbornylacyl groups is a terminal ligand bonded to the cobalt atom bearing only a single terminal carbonyl group. The other norbornylacyl group is a three-electron donor bridging η^2-μ-norCO group. The Co≡Co distance of 2.420 Å in **6S-2** is ~0.14 Å shorter than the Co=Co double bond in **6T-1** and thus can be interpreted as a formal triple bond. This gives each cobalt atom in **6S-2** the favored 18-electron configuration. The singlet (nor)$_2$Co$_2$(CO)$_6$ structure **6S-3**, lying 5.3 kcal/mol in energy above **6T-1**, has the same set of ligands as **6S-2** and differs only in the stereochemistry of the ligands placed around the central Co$_2$ unit.



6T-1 (0.0, 0.0) **6S-2** (1.3, 2.9) **6S-3** (3.8, 5.3) **6T-4** (5.3, 5.5)

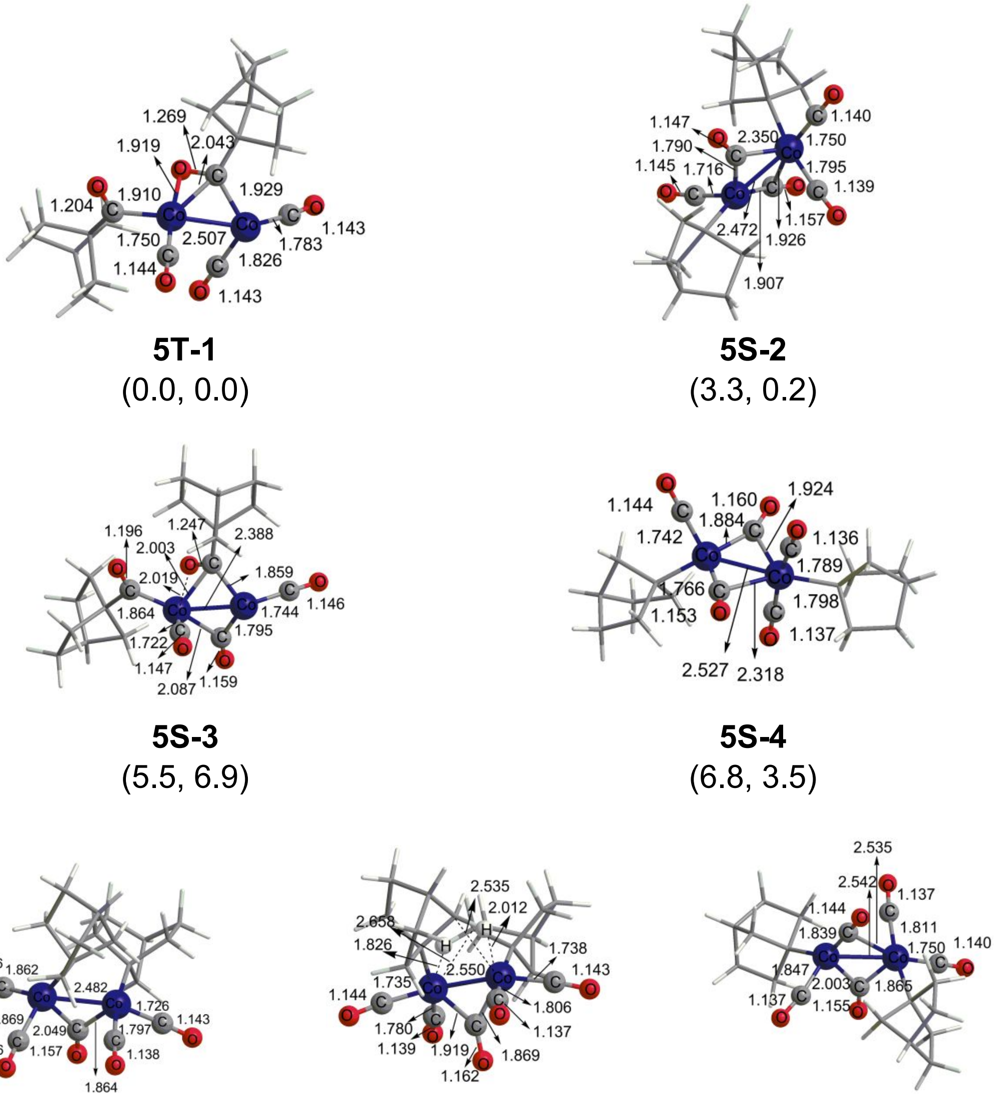
Figure 8. Optimized (nor)$_2$Co$_2$(CO)$_6$ structures.

A total of seven low-energy (nor)$_2$Co$_2$(CO)$_5$ structures were found (Figure 9). The lowest energy structure is the triplet **5T-1** with two terminal carbonyl groups bonded to one cobalt atom and another terminal carbonyl group bonded to the other cobalt atom. The remaining two carbonyl groups are inserted into the two norbornyl Co–C bonds to give norbornylacyl groups. One of the norbornylacyl groups bridges the central Co_2 unit as a three-electron donor η^2-μ-norCO group, whereas the other norbornylacyl group is a terminal ligand bonded to the cobalt atom bearing only one terminal carbonyl group. In fact the $(nor)_2Co_2(CO)_5$ structure **5T-1** can be derived from the $(nor)_2Co_2(CO)_6$ structure **6T-1** by removal of a carbonyl group from the cobalt atom bearing three terminal carbonyl groups. However, one of the two remaining terminal groups becomes a weakly semibridging CO group with the longer Co-C bond distance of 2.748 A. The Co=Co distance of 2.507 Å in **5T-1** is only slightly shorter than the Co=Co distance of 2.559 A in **6T-1** and can likewise be interpreted as a formal double bond. In **5T-1** with the three-electron donor bridging η^2-μ-norCO group the cobalt atom bearing two terminal carbonyl groups acquires the 17-electron configuration and the other cobalt atom has a 15-electron configuration, which is reasonable for a binuclear triplet.

The singlet $(nor)_2Co_2(CO)_5$ structure **5S-3**, lying 6.9 kcal/mol in energy above **5T-1**, has the same set of ligands as **5T-1** with approximately the same stereochemistry (Figure 9). The Co≡Co distance of 2.388 Å in **5S-3** is ~0.2 Å shorter than the Co=Co double bond in **6T-1** and thus can be interpreted as a formal triple bond. This gives one cobalt atom in **5S-3** the favored 18-electron configuration but the other cobalt atom only a 16-electron configuration. The cobalt atom not bearing the terminal norbornylacyl group has an obvious hole in its coordination sphere *trans* to the bridging norbornylacyl group and thus is assumed to be the cobalt atom with the 16-electron configuration.

The five remaining low-energy $(nor)_2Co_2(CO)_5$ structures have both norbornyl groups directly bonded to cobalt atoms without insertion of any of the five carbonyl groups into norbornyl Co–C bonds. This maximizes the electrons donated by the five carbonyl groups to the central Co_2 unit in these highly unsaturated systems.

The singlet $(nor)_2Co_2(CO)_5$ structure **5S-2**, lying 0.2 kcal/mol in energy above **5T-1,** has the two cobalt atoms bridged by two two-electron donor carbonyl ligands (Figure 9). In **5S-2** one cobalt atom is bonded to two terminal carbonyl groups whereas the other cobalt atom is bonded to only one terminal carbonyl group. In addition **5S-2** has an agostic interaction between the C–H bond of a norbornyl CH_2 group with the cobalt atom bearing one terminal group with Co-H distances of 2.653 Å and a Co-C distance of 2.715 Å. This agostic interaction coupled with the Co–C σ-bond makes this norbornyl group a three-electron donor. Interpreting the predicted Co=Co distance of 2.472 Å as a formal double bond gives each cobalt atom in **5S-2** the favored 18-electron configuration. The $(nor)_2Co_2(CO)_5$ structure **5S-4**, lying 3.5 kcal/mol in energy above **5T-1** with a predicted Co=Co distance of 2.527 Å, has a similar geometry to **5S-2**, including an agostic C–H–Co bond. Structures **5S-2** and **5S-4** differ only in the stereochemistry resulting from the orientations of the norbornyl groups.



5T-1
(0.0, 0.0)

5S-2
(3.3, 0.2)

5S-3
(5.5, 6.9)

5S-4
(6.8, 3.5)

5T-5
(9.7, 5.9)

5S-6
(10.4, 7.8)

5T-7
(10.6, 6.9)

Figure 9. Optimized $(nor)_2Co_2(CO)_5$ structures.

The fifth $(nor)_2Co_2(CO)_5$ structure, namely the triplet **5T-5** lying 5.9 kcal/mol in energy above **5T-1**, has a bridging carbonyl group (Figure 9). Each cobalt atom in **5T-5** is bonded to two terminal carbonyl groups and one terminal norbornyl group. Interpreting the Co=Co distance of 2.482 Å in **5T-5** as a formal double bond gives each cobalt atom a 17-electron configuration for a binuclear triplet.

The sixth $(nor)_2Co_2(CO)_5$ structure, namely the singlet **5S-6** lying 7.8 kcal/mol in energy above **5T-1**, has a similar arrangement of ligands as the triplet structure **5T-5** (Figure 9). However the Co–Co distance of 2.550 Å in **5S-6** is ~0.07 Å longer than that in **5T-1** suggesting a formal single bond in **5S-6**. In addition to the usual Co–C σ-bond each norbornyl ligand in **5S-**6 is also bonded to the same cobalt atom through an agostic C–H–Co bond, so that each (neutral) norbornyl ligand with these agostic interactions is a three-electron donor rather than the usual one-electron donor. One of these agostic interactions has a Co–H distance of 1.826 Å and a Co–C distance of 2.658 Å whereas the other agostic interaction has a Co–H distance of 2.012 Å and a Co–C distance of 2.535 Å. The combination of a three-electron donor norbornyl group and two terminal carbonyl groups bonded to each cobalt atom and a Co–Co single bond bridged by the fifth carbonyl group gives each cobalt atom in **5S-6** the favored 18-electron configuration.

The $(nor)_2Co_2(CO)_5$ structure **5T-7**, lying 6.9 kcal/mol in energy above **5T-1**, is the triplet state corresponding to the singlet structure **5S-2** (Figure 9). However, **5T-7** lacks the agostic C–H–Co interaction from the norbornyl group to a cobalt atom. Furthermore, the Co–Co distance of 2.542 Å in **5T-7** is ~0.07 Å longer than that in **5S-2** suggesting a formal single bond in **5T-7**. The absence of any C–H–Co agostic interactions coupled with lowering the Co–Co bond order from 2 to 1 in **5T-7** gives one cobalt atom a 17-electron configuration and the other cobalt atom only a 15-electron configuration, consistent with a binuclear triplet.

3.3 Cobalt-cobalt bonding

The Wiberg bond indices (WBIs) obtained by the NBO method[27] are listed in Table 1. In general formal single bonds between d-block metals lead to WBI values of 0.2 to 0.3 with those for double and triple bonds proportionately higher.[28] However, bridging groups across metal-metal bonds can lead to multicenter bonding thereby lowering the WBI values.[29] Spin states and metal electron configurations other than the favored 18-electrons can also affect WBI values.

The WBI values along with the Co-Co distances and bridging groups for the $(nor)_2Co_2(CO)_n$ (n = 7, 6, 5) derivatives are listed in Table 1. Considering only singlet structures, those with a single bridging μ-CO group and a formal Co–Co single bond (**7S-2**, **7S-3**, and **5S-6**) have WBI values ranging from 0.18 to 0.23. The singlet structures with two bridging CO groups and a formal Co=Co double bond (**5S-2** and **5S-4**) have somewhat higher WBI values of 0.28 to 0.30. These WBI values are higher than those for the singlet structures with Co–Co single bonds but the difference between the WBIs for single and double cobalt-cobalt bonds is reduced because of the additional delocalization of the bond between the cobalt atoms because of the second bridging carbonyl group. The singlet $(nor)_2Co_2(CO)_n$ structures with a bridging η^2-μ-norCO group and a bridging μ-CO group are found to have WBI values ranging from 0.24 to 0.39 regardless of whether the formal cobalt-cobalt bond order appears to be two or three. This appears to be a consequence of extensive delocalization in the interaction of the bridging η^2-μ-norCO group with the central Co_2 unit.

Table 1. The Co-Co distances (Å), Wiberg bond indices (WBIs), the corresponding bond orders, and bridging groups for the $(nor)_2Co_2(CO)_n$ structures calculated at the B3PW91-D3/cc-pVTZ level.

	Cobalt-cobalt bond				Natural charges
Structure	Å	WBIs	Bond order	Bridging groups	Co1/Co2
7S-1	2.561	0.27	1	η^2-norCO, μ-CO	-1.437/-0.462
7S-2	2.820	0.18	1	μ-CO	-1.332/-1.268
7S-3	2.845	0.18	1	μ-CO	-1.300/-1.300
7T-4	2.680	0.24	1	μ-CO	-1.016/-0.456
6T-1	2.558	0.24	1	η^2-norCO, μ-CO	-1.047/+0.098
6S-2	2.420	0.27	3	η^2-norCO, μ-CO	-0.865/-0.436
6S-3	2.364	0.39	3	η^2-norCO, μ-CO	-0.970/-0.432
6T-4	2.519	0.28	1	η^2-norCO	-0.373/-0.523
5T-1	2.507	0.25	1	η^2-norCO	-0.271/-0.016
5S-2	2.472	0.30	2	2 μ-CO	-0.850/-0.642
5S-3	2.388	0.33	3	η^2-norCO, μ-CO	-0.267/-0.479
5S-4	2.527	0.28	2	2 μ-CO	-0.753/-0.773
5T-5	2.482	0.23	2	μ-CO	-0.790/-0.302
5S-6	2.550	0.23	1	μ-CO	-0.796/-0.796
5T-7	2.542	0.26	1	2 μ-CO	-0.796/-0.285

3.4. CO vibrational frequencies

The terminal CO groups in the $(nor)_2Co_2(CO)_n$ (n = 7, 6, 5) structures exhibit unscaled ν(CO) frequencies from 2042 to 2164 cm^{-1}, which is the typical region for terminal CO groups (Table 2). The ν(CO) frequencies for the two-electron donor μ-CO groups bridging the two cobalt atoms are significantly lower, from 1942 to 2044 cm^{-1}. The ν(CO) frequencies for acyl carbonyl groups in the one-electron donor norCO ligands bonded to the cobalt atom only through carbon are still lower, ranging from 1766 to 1852 cm^{-1}. However, the three-electron donor bridging η^2-μ-norCO groups bonded to the central Co_2 unit through both carbon and oxygen exhibit much lower ν(CO) frequencies than the two-electron donor bridging carbonyl groups, ranging from 1467 to 1560 cm^{-1}. The decrease of ~300 cm^{-1} in the range of the ν(CO) frequencies for one-electron donor norCO ligands relative to three-electron donor bridging η^2-μ-CO ligands relates to the involvement of the C-O π-bond of the carbonyl group in the bonding to the Co_2 unit thereby reducing significantly the effective C–O bond order.

Table 2. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses, in km/mol) for the $(nor)_2Co_2(CO)_n$ (n = 7, 6, 5) structures calculated at the B3PW91-D3/DZP level. Bridging carbonyl frequencies are in **bold,** terminal acyl carbonyl frequencies are in **red**, and bridging acyl carbonyl frequencies are in **blue.**

5T-1	**1467**(*104*), **1766**(*548*), 2042(*752*), 2077(*1647*), 2107(*534*)
5S-2	**1956**(*463*), **2037**(*456*), 2084(*859*), 2089(*1360*), 2129(*417*)
5S-3	**1530**(*100*), **1812**(*587*), **1975**(*1011*), 2060(*1550*), 2090(*632*)
5S-4	**1950**(*421*), **2008**(*592*), 2089(*538*), 2091(*1491*), 2154(*158*)
5T-5	**1953**(*589*),2081(*359*),2095(*833*),2107(*1585*),2146(*725*)
5S-6	**1942**(*387*), 2074(*500*),2079(*1001*), 2113(*1484*),2138(*453*)
5T-7	**1968**(*397*) , **2044**(*756*) , 2091(*914*) , 2098(*869*) , 2137(*505*)
6T-1	**1465**(*108*),**1777**(*534*),2074(*664*),2078(*227*),2099(*1525*),2139(*772*)
6S-2	**1540**(*267*),**1792**(*287*),1941(*489*),2078(*814*),2093(*1403*), 2132(*1004*)
6S-3	**1515**(*87*),**1852**(*622*),1997(*918*),2074(*124*),2084(*1462*),2134(*1136*)
6T-4	**1552**(*178*),**1755**(*320*),2083(*971*),2089(*343*),2106(*1653*),2142(*535*)
7S-1	**1560**(*123*),**1773**(*352*),**2010**(*572*),2066(*324*),2086(*1080*),2105(*1385*),2146(*968*)
7S-2	**1960**(*393*), 2077(*71*), 2086(*497*), 2099(*968*), 2108(*769*), 2123(*824*), 2164(*721*)
7S-3	**1965**(*381*), 2075(*150*), 2089(*379*), 2097(*639*), 2106(*7323*), 2125(*1458*),2162(*288*)
7T-4	**1728**(*121*),**1779**(*395*),**1936**(*727*),2057(*266*),2074(*815*),2089(*1457*),2137(*843*)

3.4 Thermochemistry

The carbonyl dissociation energies for the reactions $(nor)Co(CO)_n \rightarrow (nor)Co(CO)_{n-1} + CO$ are reported in Table 3. The predicted dissociation energies of at least ~26 kcal/mol for the dissociation of one CO group from $(nor)Co(CO)_n$ to give $(nor)Co(CO)_{n-1}$, suggest the viability of each $(nor)Co(CO)_n$ complex. For the binuclear $(nor)_2Co_2(CO)_n$ derivatives, the predicted dissociation energy of 33.0 kcal/mol for the dissociation of one CO group from the singlet heptacarbonyl $(nor)_2Co_2(CO)_7$ (**7S-1**) to give the singlet lowest energy $(nor)_2Co_2(CO)_6$ hexacarbonyl structure **6S-2** also suggests a viable structure (Table 4). Further dissociation of a CO group from triplet $(nor)_2Co_2(CO)_6$ (**6T-1**) to give the pentacarbonyl $(nor)_2Co_2(CO)_5$ (**5T-1**) in the same triplet spin state requires 34.8 kcal/mol, suggesting a similarly viable structure. The disproportionation reaction of $(nor)_2Co_2(CO)_6$ to give $(nor)_2Co_2(CO)_7$ + $(nor)_2Co_2(CO)_5$ is endothermic by 4.7 kcal/mol also suggesting a viable structure (Table 4). Also the dissociation of binuclear $(nor)_2Co_2(CO)_n$ into the mononuclear fragments $(nor)Co(CO)_x$ + $(nor)Co(CO)_y$ ($n = x + y$) is not thermochemically favored since such dissociation reactions require at least 20 kcal/mol (Table 4).

Table 3. Energies (kcal/mol) for carbonyl dissociation from (nor)Co(CO)$_n$ structures$_n$ and (nor)Co(CO)$_n$ structures predicted at the B3PW91-D3/cc-pVTZ level.

(nor)Co(CO)$_4$ → (nor)Co(CO)$_3$+ CO	28.8
(nor)Co(CO)$_3$ → (nor)Co(CO)$_2$+ CO	30.2
(nor)Co(CO)$_2$ → (nor)Co(CO)+ CO	28.1

Table 4 Energies (kcal/mol) for carbonyl dissociation and disproportionation of (Nor)$_2$Co$_2$(CO)$_n$ derivatives predicted at the B3PW91-D3/cc-pVTZ level.

(nor)$_2$Co$_2$(CO)$_7$ (**7S-1**) → (nor)$_2$Co$_2$(CO)$_6$ (**6S-2**) + CO	33.0
(nor)$_2$Co$_2$(CO)$_6$ (**6T-1**) → (nor)$_2$Co$_2$(CO)$_5$ (**5T-1**) + CO	34.8
2(nor)$_2$Co$_2$(CO)$_6$(6T-1)→(nor)$_2$Co$_2$(CO)$_7$(7S-1)+ (nor)$_2$Co$_2$(CO)$_5$(5T-1)	4.7
(nor)$_2$Co$_2$(CO)$_7$(7S-1) → (nor)Co(CO)$_4$ + (nor)Co(CO)$_3$	27.7
(nor)$_2$Co$_2$(CO)$_6$ (6T-1) → (nor)Co(CO)$_4$ + (nor)Co(CO)$_2$	27.9
(nor)$_2$Co$_2$(CO)$_6$(6T-1) → (nor)Co(CO)$_3$ + (nor)Co(CO)$_3$	26.6
(nor)$_2$Co$_2$(CO)$_5$ (5T-1) → (nor)Co(CO)$_3$ + (nor)Co(CO)$_2$	20.8
(nor)$_2$Co$_2$(CO)$_5$ (5T-1) → (nor)Co(CO)$_4$ + (nor)Co(CO)	20.0

3.5 Reduced density gradients

The reduced density gradients (RDG),[29] implemented in Multiwfn[28] and indicating agostic attractions, Van der Waals interactions, and steric repulsion, for some representative structures are depicted in Figure 10. The agostic interactions between the cobalt atom and the C-H bonds are indicated by a blue region with different strengths being indicated by the depth of the blue color. The most unsaturated structure **2S-1** is seen to have the strongest C–H–Co agostic interaction, which is consistent with the low ν(C-H) stretching frequency of 2681 cm^{-1}. For **3S-1** with a significantly weaker C–H–Co agostic interaction, the ν(C-H) frequency is significantly higher at 2906 cm^{-1}. For the electronically saturated (nor)Co(CO)$_4$ structures **4S-1** and **4S-2**, there is no obvious agostic interaction between the cobalt atom and any C–H bonds of the 1-norbornyl ligand. However, significant Van der Waals interactions are predicted between the norbornyl and Co(CO)$_4$ groups.

In the representative binuclear (nor)$_2$Co$_2$(CO)$_5$ structures **5S-2** and **5S-6** with agostic C–H–Co interaction(s), the deeper blue regions between the cobalt atom and the C-H bond(s) are predicted for the RDG values. Stronger Van der Waals interaction and repulsion are also found between different ligands (Figure 11), which indicates that dispersion and steric effects play an important role[33] in stabilizing the binuclear (nor)$_2$Co$_2$(CO)$_n$ complexes. The more global Van der Waals interaction was found in the experimentally known compounds (nor)$_4$Co,[4] which plays a key role in stabilizing the structure. The strong agostic attraction between the cobalt atom and the C-H bond, indicated by the deep blue region, was found in the theoretical structure (nor)CoC_5H_5 related to the experimentally synthesized structure (nor)NiC_5H_5 (Figure 10).[8,9]

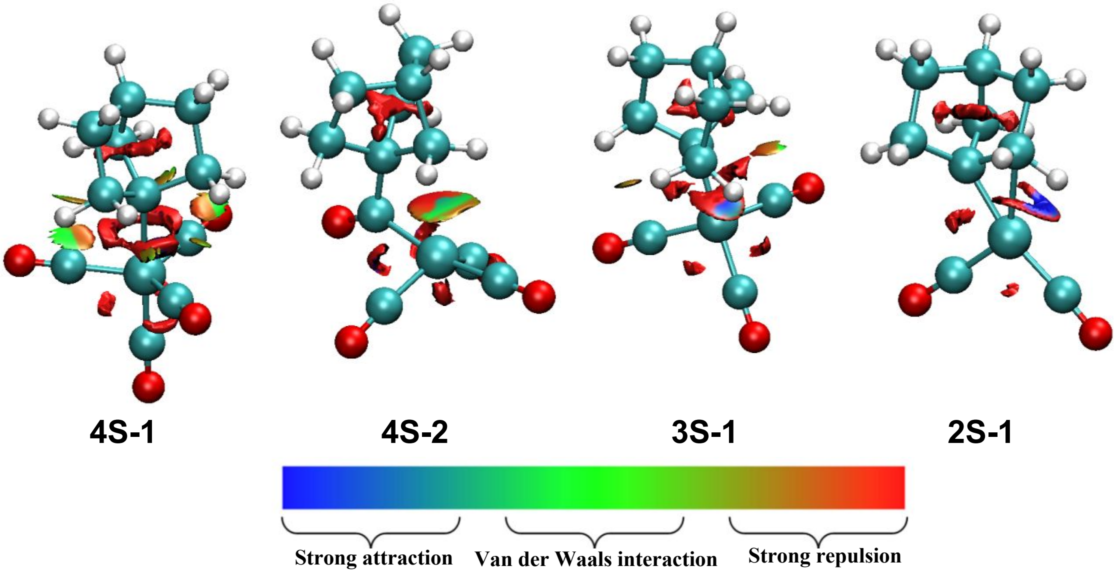


Figure 10. The reduced density gradients (RDG) for the example (nor)$Co(CO)_n$ ($n = 4$, 3, 2) structures calculated at the B3PW91-D3/DZP level.

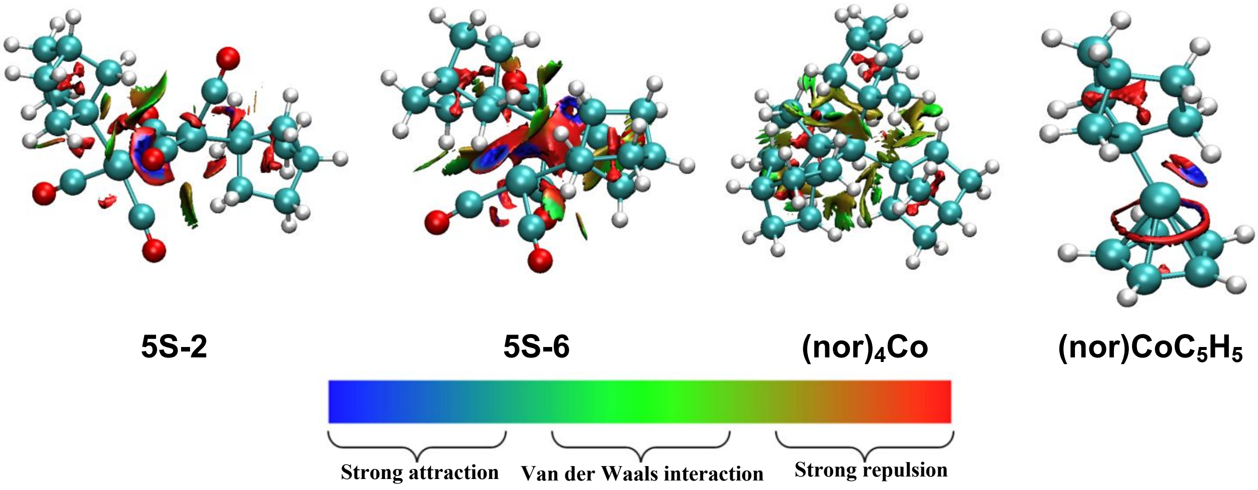


Figure 11. The reduced density gradients (RDG) for the $(nor)_2Co_2(CO)_5$ structures and $(nor)_4Co$ and (nor)CoC_5H_5 calculated at the B3PW91-D3/DZP level..

4. Summary

The bulky nature of the 1-norbornyl (nor) ligand is found to lead to the following novel features in low-energy structures of the mononuclear (nor)$Co(CO)_n$ ($n = 4$, 3, 2, 1) and the binuclear $(nor)_2Co_2(CO)_n$ ($n = 7$, 6, 5) derivatives:

(1) Formation of hydrogen bridges to a cobalt atom from a norbornyl CH_2 group next to the Co–C bond leading to a short bonding Co–H distance indicative of an agostic hydrogen atom.[15] This results in donation of two extra electrons from the C–H bond of this norbornyl group thereby making such a neutral norbornyl group a

three-electron donor. Such agostic hydrogen atoms provide alternatives to metal-metal multiple bonding and four-electron donor bridging η^2-μ-CO groups in unsaturated norbornylcobalt carbonyl derivatives.

(2) Facile migration of a norbornyl group from cobalt to a terminal carbonyl group bonded to cobalt. The resulting acyl carbonyl group acts as a spacer between the bulky norbornyl group and the cobalt carbonyl fragment, thereby decreasing steric congestion around the cobalt atom.

(3) The average Co-C distance of 1.920 Å for the experimental $(\mathrm{nor})_4\mathrm{Co}$ structure is significantly shorter than any of the Co-C distances predicted in the $(\mathrm{nor})\mathrm{Co}(\mathrm{CO})_n$ (n = 4, 3, 2, 1) structures. This may be a consequence of strong dispersion in the $(\mathrm{nor})_4\mathrm{Co}$ structure with four bulky 1-norbornyl ligand contrasted with minimal distortion in the $(\mathrm{nor})\mathrm{Co}(\mathrm{CO})_n$ structures with only a single 1-norbornyl ligand.

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The authors declare no competing financial interest.

Supporting Information

Tables S1 to S10: Optimized coordinates of the $(\mathrm{nor})\mathrm{Co}(\mathrm{CO})_n$ structures (n = 1 to 4); Tables S11 to S25: Optimized coordinates of the $(\mathrm{nor})_2\mathrm{Co}_2(\mathrm{CO})_n$ structures (n = 5 to 7); Tables S26 to S40: Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses, in km/mol) for the $(\mathrm{nor})_2\mathrm{Co}_2(\mathrm{CO})_\mathrm{n}$ structures (n = 5 to 7); Complete Gaussian09 reference (Reference 22); a separate concatenated xyz file containing the geometric coordinates of the optimized structures.

Literature References

(1) Bower, B. K.; Tennent, H. K. Transition metal bicyclo[2.2.1]hept-1-yls. *J. Am. Chem. Soc***.** **1972**, *94*, 2512–2513 .

(2) Kolodziej, R. M.; Schrock, R. R.; Davis, W. M. Synthesis and characterization of Mo(nor)$_4$ (nor = 1-norbornyl). *Inorg. Chem.* **1988**, *27*, 3253–3255.

(3) Lewis, R. A.; Smiles, D. E.; Darmon, J. M.; Stieber, S. C. E.; Wu, G.; Hayton, T. W. Reactivity and Mössbauer spectroscopic characterization of an Fe(IV) ketimide complex and reinvestigation of an Fe(IV) norbornyl complex, *Inorg. Chem.* **2013**, *52*, 8218-8227**.**

(4) Byrne, E. K.; Richeson, D. S.; Theopold, K. H. Tetrakis(1-norbornyl)cobalt, a low spin tetrahedral complex of a first row transition metal. *Chem. Commun.* **1986**, 1491–1492.

(5) Liptrot, D. J.; Guo, J.-D.; Nagase, S.; Power, P. P. Dispersion forces, disproportionation, and stable high-valent transition metal alkyls. *Angew. Chem. Int. Ed.* **2016**, 55, 14766–14769.

(6) Li, H.; Hu, Y.; Wan, D.; Zhang, Z.; Fan, Q.; King, R. B.; Schaefer, H. F. Dispersion effects in stabilizing organometallic compounds: The tetra-1-norbornyl derivatives of the first row transition metals as exceptioinal examples. *J. Phys. Chem. A.* **2019**, *123*, 9514-9519.

(7) Bredt, J. Über sterische Hinderung in Brückenringen (Bredtsche Regel) und über die *meso-trans*-Stellung in kondensierten Ringsystemen des Hexamethylens. *Liebigs Ann. Chem.* **1924**, *437*, 1–13.

(8) Dimitrov, V.; Linden, A. A pseudodetrahedral, high-oxidation state organonickel compound: synthesis and structure of bromotris(1-norbornyl)-nickel(IV). *Angew. Chem. Int. Ed.* **2003,** *42*, 2631-2633..

(9) Lehmkuhl, H.; Dimitrov, V. η^2-Alkin-Komplexe des η^5-Cyclopentadienylnickel-1-norbornyls. *J. Organometal. Chem.* **1996**, *519*, 69–73.

(10) Dimitrov, V.; Thiele, K.-H., Darstellungen und Eigenschaften von 1-Norbornylkupfer. *Z. anorg. allg. Chem*. **1984**, *610* , 7-10

(11) Dimitrov, V. Darstellung und Eigenschaften von Cyclopentadienyl-titan(IV)-1-norbornyl-verbindungen, *J. Organometal. Chem*. **1985,** *282*, 321–329.

(12) Hieber, W.; Beck, W.; Lindner, E. Trifluoroacetyl- and trifluoromethylmetal carbonyl compounds. *Z. Naturforsch.* **1961**, *16b*, 229–231.

(13) McClellan, W. R. Perfluoroalkyl and perfluoroacyl metal carbonyls. *J. Am. Chem. Soc.* **1961**, *83*, 1598–1600.

[14] D. J. Harrison, A. L. Daniels, I. Korobkov, and R. T. Baker, Tetracarbonyl-(trifluoromethyl)cobalt(I) $[Co(CO)_4(CF_3)]$ as a precursor to new cobalt trifluoromethyl and difluorocarbene complexes, *Organometallics*, 2015, **34**, 4598–4604.

(15) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc.* Agostic interactions in transition metal compounds*,Natl. Acad, Sci.* **2007**, *104*, 6908-6914.

(16) Wagner J. P; Schreiner, P. R. London dispersion decisively contributes to the thermodynamic stability of bulky NHC-coordinated main group compounds, *J. Chem. Theory Comput.* **2016**, *12*, 231−237.

(17) Liptrot D. J. ; Power P. P. London dispersion forces in sterically crowded inorganic and organometallic molecules, *Nat. Rev. Chem.* **2017**, *1*, 0004.

(18) Israelachvilli, J. N. Intermolecular and surface forces; 3 ed., Academic Press: Waltham, USA, **2011**.

(19) Li, H.; Feng, H.; Xie, Y.; Schaefer, H. F. The recently synthesized dimagnesiabutadiene and the analogous dimetalla-beryllium, -calcium, -strontium, and –barium compounds, *Chem. Eur. J.* **2016**, *22*, 15019-15026.

(20) Wagner, J. P.; Schreiner, P. R. London dispersion in molecular chemistry—reconsidering steric effects, *Angew. Chem. Int. Ed.* **2015**, *54*, 12274–12296.

(21) Grimme, S. Density functional theory with London dispersion corrections. *Sires Comput. Mol. Sci.* **2011**, *1*, 211–228.

(22) Frisch, M. J.; *et al.* Gaussian 09, Revision A.02; Gaussian, Inc., Wallingford CT, 2009.

(23) Dunning Jr., T. H. Gaussian basis functions for use in molecular calculations. I. Contraction of (9s5p) atomic basis sets for the first-row atoms. *J. Chem. Phys.* **1970**, *53*, 2823-2833.

(24) Huzinaga, S. Gaussian-type functions for polyatomic systems. I. *J. Chem. Phys.* **1965**, *42*, 1293-1302..

(25) Wachters, A. J. H. Gaussian basis set for molecular wavefunctions containing third-row atoms.. *J. Chem. Phys.* **1970**, *52*, 1033-1036.

(26) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. Electronic structure of homoleptic transition metal hydrides: TlH_4, VH_4, CrH_4, MnH_4, FeH_4, CoH_4, and NiH_4. *J. Chem. Phys*. **1979**, *71*, 705-712.

(27) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Order Donor-Acceptor Perspective*, Cambridge University Press, Cambridge, England, U. K., 2005, pp. 32–36.

(28) Wang, H.; Xie, Y.; King, R. B.; Schaefer, H. F. Remarkable aspects of unsaturation in trinuclear metal carbonyl clusters: the triiron species $Fe_3(CO)_n$ (n = 12, 11, 10, 9), *J. Am. Chem. Soc.*, **2006**, *128*, 11376-11384.

(29) Green, J. C.; Green, M. L. H.; Parkin, G. The occurrence and representation of three-centre two-electron bonds in covalent inorganic compounds *Chem. Comm.* **2012**, *48*, 11481-11503.

(28) Lu, T. Multiwfn: A multifunctional wavefunction analyzer, Version3.6, 2019; http://Multiwfn.codeplex.com.

(29) Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W.; Revealing noncovalent interactions, *J. Am. Chem. Soc.* **2010**, *132*, 18, 6498-6506

(30) Neese, F. et.al, ORCA 4.1.2, An ab initio, DFT and semiempirical SCF-MO package, Max-Planck-Institut für Kohlenforschung.

(31) Neese, F.; Atanasov, M.; Bistoni, G.; Maganas, D.; Ye, S. Chemistry and quantum mechanics in 2019: Give us insight and numbers. *J. Am. Chem. Soc.* **2019**, *141*, 2814–2824.

(32) Guo, Y.; Riplinger, C.; Becker, U.; Liakos, D. G.; Minenkov, Y.; Cavallo, L.; Neese, F. An improved linear scaling perturbative triples correction for the domain based local pair-natural orbital based singles and doubles coupled cluster method. *J. Chem. Phys.* **2018**, *148*, 011101.

(33) Lin, X.; Wu, W.; Mo, Y., Agostic interactions in early transition-metal complexes: roles of hyperconjugation, dispersion, and steric effect, *Chem. Eur. J.* **2019**, *25*, 6591–6599.

5/20

Unusual Effects of the Bulky 1-Norbornyl Group in Cobalt Carbonyl Chemistry: Low-Energy Structures with Agostic Hydrogen Atoms

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Low-energy (nor)Co(CO)$_n$ (n = 3, 2) and (nor)$_2$Co$_2$(CO)$_n$ (nor = 1-norbornyl; n = 6, 5) structures are found to have agostic hydrogen atoms from a CH$_2$ group adjacent to the Co–C bond forming C–H–Co bridges. In addition, low-energy structures are found with (nor)CO acyl ligands resulting from carbonyl migration.