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Modeling Intermediates in Carbon Monoxide Coupling Reactions Using Cyclooctatetraene Thorium Derivatives

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Abstract

The interaction of carbon monoxide with organoactinides has recently been shown experimentally, particularly by Cloke and co-workers, to result in coupling to give the oligomeric anions $C_nO_n^{2-}$ (n = 2, 3, 4). In order to model possible intermediates in reactions of this type, we have used density functional theory to explore the systems $(C_8H_8)Th(CO)_n$ (n = 1 to 5) and $(C_8H_8)_2Th_2(CO)_n$ (n = 2 to 7) related to the known "thorocene," $(\eta^8\text{-}C_8H_8)_2Th$. Thorium was chosen as the actinide for this work since its chemistry almost entirely involves the single diamagnetic +4 oxidation state. All of the binuclear $(C_8H_8)_2Th_2(CO)_n$ structures found in this work have long Th···Th distances ranging from 4.4 to 5.0 Å suggesting the absence of direct Th-Th bonds. Two $(C_8H_8)_2Th_2(CO)_2$ isomers of similar energies in which the two CO groups have coupled to form *trans* and *cis* isomers of a bridging η^4-μ-C_2O_2 ligand are low energy structures. These bridging η^4-μ-C_2O_2 ligands exhibit ultralow ν(CO) frequencies around 1000 cm^{-1} indicating strong back donation of thorium d and f electrons into C-O antibonding orbitals. Most of the carbonyl richer $(C_8H_8)_2Th_2(CO)_n$ (n = 3 to 7) structures are derived from one of these basic $(C_8H_8)_2Th_2(CO)_2$ structures by addition of terminal CO groups. An exception is the lowest energy $(C_8H_8)_2Th_2(CO)_4$ structure which has C_{4v} symmetry with four equivalent separate η^2-μ-CO groups bridging the thorium atoms. The thermochemistry of these systems suggest $(C_8H_8)Th(CO)_4$ and $(C_8H_8)_2Th_2(CO)_n$ (n = 2, 4) to be the most promising synthetic objectives, which are potentially obtainable by reductive carbonylation of the known $(C_8H_8)ThCl_2$.

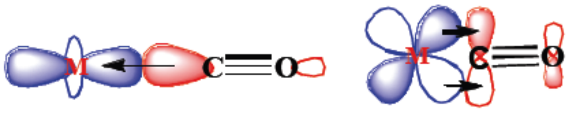
1. Introduction

There are major differences between the carbonyl chemistry of the d-block and f-block metals. Thus the d-block transition metals form thousands of stable metal carbonyl derivatives including well-known binary formally zerovalent metal carbonyl derivatives such as $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, and $M(CO)_6$ (M = Cr, Mo, and W).[1] However, the carbonyl chemistry of the f-block lanthanide and actinide metals is much more limited. Thus no binary $M_x(CO)_y$ derivatives (M = lanthanide or actinide) stable under ambient conditions are known. For the actinides the binary thorium carbonyls $Th(CO)_n$ (n = 1 to 6)[2,3] and uranium carbonyls $U(CO)_n$ (n = 1, 2, 6),[4] generated by reactions of laser-ablated metal atoms with CO, are only observed in low-temperature matrices and characterized by their ν(CO) frequencies under such conditions. A few stable actinide carbonyl derivatives, such as the uranium derivative[5,6] $(Me_4C_5H)_3U(CO)$, have been isolated but all of these stable derivatives contain only a single carbonyl group.

One of the features limiting the scope of actinide carbonyl chemistry appears to be the tendency for carbon monoxide to undergo coupling reactions in organoactinide systems. Thus the reaction of CO with uranium(III) sandwich compounds of the type $(\eta^5\text{-}Me_5C_5)U(\eta^8\text{-}C_8H_6\{SiR_3\}_2)$ leads to reductive coupling to give ethynediolate ($C_2O_2^{2-}$), deltate ($C_3O_3^{2-}$) and squarate ($C_4O_4^{2-}$) derivatives of uranium(IV).[7,8,9,10,11,12,13,14] Also, the activation of CO and other small molecules by uranium(III) has attracted much recent interest.[15,16] Related coupling reactions in the carbonyl chemistry of d-block transition metals are almost non-existent.

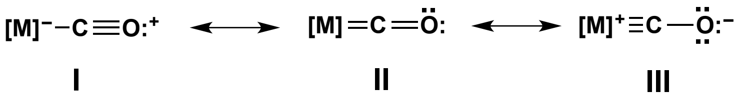
These differences in the carbonyl chemistry of d-block and f-block metals can be related to the well-known back bonding from filled metal orbitals of suitable symmetry into empty π* antibonding orbitals of the CO ligands (Figure 1).[17] For the d-block metals such back bonding necessarily involves metal d orbitals and can lead to dramatic stabilization of low formal metal oxidation states. For example, chromium hexacarbonyl, $Cr(CO)_6$, can be steam distilled in air despite the low chromium formal oxidation state of zero. Since this back-bonding increases the electron density in the π* antibonding orbitals of the CO ligands, it reduces the effective C-O bond order of these ligands (Figure 2). This can be recognized in lower ν(CO) stretching frequencies as the amount of back-bonding is increased.

The f-block metals, including the actinides, also have d and f valence orbitals of suitable symmetry to participate in back bonding, similar to the d-block metals. However, such back bonding in actinide carbonyl chemistry appears to be much stronger than the back bonding in d-block transition metal chemistry. This relates to the stronger reducing properties of actinide metals and low actinide oxidation states relative to d-block transition metals. The added electron density on the CO ligands not only reduces the effective C-O formal bond order but also provides electrons for C-C bond formation leading to coupling of the CO ligands. This can account for the tendency of organoactinides to promote CO coupling reactions.



σ forward bonding π back bonding

Figure 1. Forward and back bonding of a CO ligand to a metal atom. For a d-block transition metal the back bonding uses metal d orbitals whereas for an f-block metal, such as an actinide, symmetry considerations allow the back bonding to use either metal d or f orbitals.



$$[\mathrm{M}]^{-}{-}\mathrm{C}{\equiv}\mathrm{O}{:}^{+} \longleftrightarrow [\mathrm{M}]{=}\mathrm{C}{=}\ddot{\mathrm{O}}{:} \longleftrightarrow [\mathrm{M}]^{+}{\equiv}\mathrm{C}{-}\underset{\cdot\cdot}{\ddot{\mathrm{O}}}{:}^{-}$$

I II III

Figure 2. Resonance structures illustrating the effect of back bonding on removing electron density from the metal atom and lowering the formal C-O bond order. The designation [M] refers to the metal atom with all associated ligands other than the CO group in question.

The experimental work on CO coupling with organoactinide derivatives involves almost entirely uranium chemistry. However, the chemistry of uranium is complicated by the presence of four reasonably stable oxidation states ranging from U(III) to U(VI).[18] In aqueous media only U(IV) and U(VI) are stable, since U(III) is typically oxidized by water and U(V) disproportionates into U(IV) + U(VI). However, in non-aqueous media all four uranium oxidation states from U(III) to U(VI) can be chemically significant. Furthermore, the two stable uranium oxidation states have different spins with the f^2 U(IV) typically having the triplet spin state and the f^0 U(VI) having the singlet spin state.

In order to avoid the complications of the multiple oxidation and spin states of uranium chemistry, we have chosen thorium as the actinide to use for our initial theoretical studies to explore the chemistry of actinide carbonyl intermediates involved in carbon monoxide coupling reactions. Although there are some examples of organothorium(III) derivatives,[19] almost all thorium chemistry involves the singlet f^0 Th(IV) oxidation state. We therefore anticipate that higher spin states and lower formal oxidation states are not likely to be involved in relevant organothorium chemistry. Our initial studies[20] used the binuclear cyclopentadienyl thorium carbonyl derivatives $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_n$ (n = 2 to 9). The presence of the cyclopentadienyl ligand in such derivatives was chosen in order to have experimentally accessible systems. Thus these $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_n$ systems can be obtained from reactions of the cyclopentadienyl anion with thorium halides or other Th(IV) derivatives followed by reductive carbonylation.

Our theoretical studies on $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_n$ (n = 2 to 9) systems[20] revealed two fundamental types of low-energy structures containing unusual carbonyl bridges between a pair of thorium atoms (Figure 3). Thus the lowest energy structure of the tricarbonyl $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_3$ has three bridging $\eta^2\text{-}\mu\text{-}CO$ groups linking the pair of thorium atoms. Each of these $\eta^2\text{-}\mu\text{-}CO$ groups is bonded to one thorium atom through its carbon atom and to the other thorium atom through both its carbon and oxygen atoms. This $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_3$ structure is analogous to the lowest energy $(\eta^5\text{-}C_5H_5)_2Ti_2(CO)_3$ structure of the d-block metal titanium, which was the subject of earlier theoretical study.[21] Comparison of the predicted ν(CO) frequencies of 1350, 1396, and 1513 cm^{-1} for the lowest energy $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_3$ structure with those of 1501, 1540, and 1603 cm^{-1} for the lowest energy $(\eta^5\text{-}C_5H_5)_2Ti_2(CO)_3$ structure clearly indicates the stronger back bonding of the f-block metal thorium to the CO groups as compared with that of the d-block metal titanium. Furthermore considering the CO groups in $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_3$ as CO^{2-} dianions arising from double deprotonation of hydroxy-carbene, :C(H)(OH), gives the thorium atoms the favored +4 formal oxidation state.

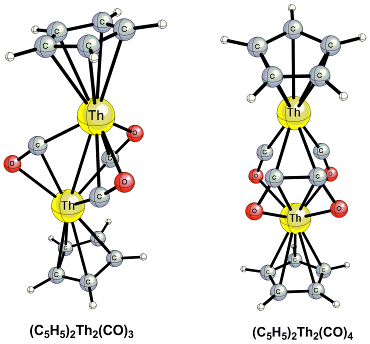
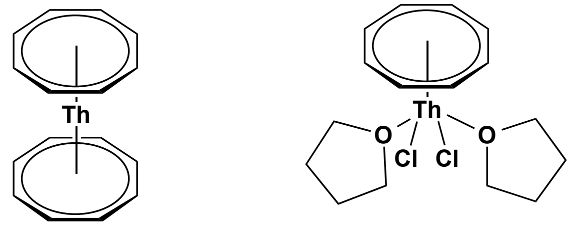


Figure 3. The lowest energy $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_n$ (n = 3, 4) structures.

Coupling of the carbonyl ligands was observed in the lowest energy structure of the tetracarbonyl $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_4$, which can be more accurately written as $(\eta^5\text{-}C_5H_5)_2Th_2(\eta^4\text{-}\mu\text{-}C_2O_2)(\eta^2\text{-}\mu\text{-}CO)_2$ (Figure 3).[20] Considering the bridging $\eta^4\text{-}\mu\text{-}C_2O_2$ ligand as arising from the double deprotonation of ethynediol, HOC≡COH, gives each thorium atom in this $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_4$ the favored formal +4 oxidation state. The carbonyl-richer species $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_n$ (n = 5 to 9) have three or four CO units bridging the two thorium atoms with the "extra" CO groups being terminal CO groups similar to the CO group in $(Me_4C_5H)_3U(CO)$[5,6,22] or the terminal CO groups in thousands of d-block transition metal carbonyl derivatives.[1] Such terminal CO groups bonded to f-block metals have similar ν(CO) frequencies as similar terminal CO groups bonded to d-block transition metals.

The $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_n$ (n = 2 to 5) structures can be generated by combining two $\eta^5\text{-}C_5H_5Th$ units with various numbers of CO groups. If the CO groups are initially considered as neutral ligands, then the thorium atoms in the $\eta^5\text{-}C_5H_5Th$ units of the $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_n$ structures must initially be considered to have the +1 formal oxidation state. The bridging and coupling modes of the CO groups found in the $(\eta^5\text{-}C_5H_5)_2Th_2(CO)_n$ (n = 2 to 5) structures can be considered to be the effects of the low oxidation state Th(I) reducing the neutral CO species to anionic CO species. Such anionic CO species can either bridge the thorium atoms through their oxygen atoms to form $\eta^2\text{-}\mu\text{-}CO$ groups or couple through C-C bond formation to form C_2O_2 units.

The theoretical results reported in this paper reflect changes in the reducing properties of the formally low oxidation state thorium atoms by changing the hydrocarbon from cyclopentadienyl (C_5H_5) to cyclooctatetraene (C_8H_8). Cyclooctatetraene is well known to form the stable dianion $C_8H_8^{2-}$ with ten π electrons corresponding to the Hückel $4n + 2$ (n = 2) rule for stable aromatic systems.[23] Thus the thorium atom in a neutral C_8H_8Th unit has the +2 formal oxidation state and might be expected to have different reducing properties towards CO ligands than the neutral C_5H_5Th unit with the thorium atom in the +1 oxidation state. Furthermore cyclooctatetraene thorium derivatives are known experimentally including the sandwich compound "thorocene",[24,25] $(\eta^8\text{-}C_8H_8)_2Th$, and half-sandwich compounds such as $(\eta^8\text{-}C_8H_8)ThX_2$ (X = Cl, BH_4) (Figure 4).[26,27] Thus the $(C_8H_8)_2Th_2(CO)_n$ systems discussed in this paper can potentially be generated by the reductive carbonylation of such systems.



$(\eta^8\text{-}C_8H_8)_2Th$

$(\eta^8\text{-}C_8H_8)ThCl_2(OC_4H_8)_2$

Figure 4. Cyclooctatetraenethorium derivatives that have been synthesized and structurally characterized by X-ray crystallography.

2. Theoretical Methods

Electron correlation effects have been included to some degree using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool for organometallic compounds[28,29,30,31,32,33,34] including actinide derivatives.[35,36,37] Two differently constructed DFT functionals, namely the BP86 and the M06-L functionals, were used in the present study. The BP86 method combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient-corrected correlation functional method (P86).[38,39] This method has been shown to be effective for the study of transition metal and actinide complexes.[40,41] The second functional used in this work is a hybrid *meta*-GGA DFT method, M06-L, developed by Truhlar's group.[42,43] The studies in Truhlar's group suggest that M06-L is one of the best functionals for the study of organometallic and inorganic thermochemistry, and perhaps the best current functional for transition metal energetics. When these two conceptually different DFT methods agree, confident predictions can be made.

Scalar relativistic effects were incorporated using an (14s13p10d8f6g/10s9p5d4f3g) effective core potential (ECP) basis set with 60 core electrons for the thorium atoms.[44] The Ahlrichs TZVP valence triple-ζ basis sets with polarization functions were used for all of the other atoms.[45,46]

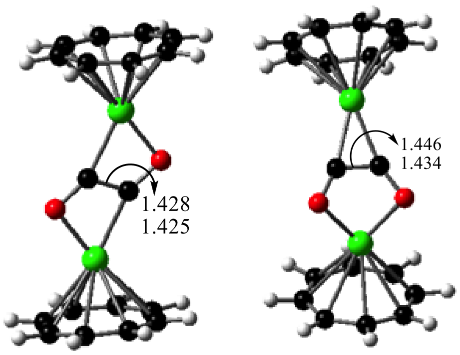
The geometries of all structures were fully optimized using both functionals with the (120, 974) grid for evaluating integrals numerically in the Gaussian09 program.[47] In all of the computations no symmetry constraints were imposed on the starting geometries. Harmonic vibrational frequencies and infrared intensities were determined at the same levels. The tight designation is the default for the SCF energy convergence. In the search for minima, low-magnitude imaginary vibrational frequencies may be suspect, because the numerical integration procedures used in existing DFT methods have significant limitations.[48] All of the final optimized structures reported in this paper have only real vibrational frequencies unless otherwise indicated.

Extensive searches for the global and local minima $(C_8H_8)_2Th_2(CO)_n$ structures (n = 1 to 7) were made using the BP86 and M06-L methods and starting geometries with different numbers of terminal CO groups attached to each thorium atom. However, most of the low-lying optimized structures were found to have two or four bridging CO groups. High-energy structures, especially many triplet structures, have questionable significance and thus are excluded from the discussion in this paper. All of the $(C_8H_8)_2Th_2(CO)_n$ structures discussed in this paper are singlet spin state structures.

3. Results

3.1 The Dicarbonyl $(C_8H_8)_2Th_2(CO)_2$ and the Tricarbonyl $(C_8H_8)_2Th_2(CO)_3$

Two low-lying structures were obtained for the dicarbonyl $(C_8H_8)_2Th_2(CO)_2$, namely a *trans* structure **2S-1** with the two CO groups oriented in opposite directions and a *cis* structure **2S-2** with the two CO groups oriented in the same direction (Figure 5 and Table 1). The BP86 method predicts essentially the same energy for the two structures. However, the M06-L method predicts the *trans* structure to lie 2.5 kcal/mol in energy above the *cis* structure. Each $(C_8H_8)_2Th_2(CO)_2$ structure has a long $Th\cdots Th$ distance of ~4.8 Å for **2S-1** and ~4.7 Å for **2S-2** clearly indicating the absence of a formal thorium-thorium bond. In each $(C_8H_8)_2Th_2(CO)_2$ structure the two CO groups are coupled through C–C bond formation to form a bridging C_2O_2 group. In the *trans* structure **2S-1** the μ-C_2O_2 bridging group is bonded to each thorium atom through both a carbon and an oxygen atom forming four-membered ThC_2O chelate rings. In the *cis* structure **2S-2** the μ-C_2O_2 bridging group is bonded to one thorium atom through its carbon atoms forming a three-membered ThC_2 ring and to the other thorium atom through its oxygen atoms forming a five-membered $ThOC_2O$ chelate ring. The ν(CO) frequencies of the bridging μ-C_2O_2 in both **2S-1** and **2S-2** are very low, in the ~900 to ~1100 cm^{-1} range, indicating a low formal C-O bond order consistent with extremely strong Th→CO back bonding in these systems. If the μ-C_2O_2 ligand is interpreted as a tetraanion obtained by formal removal of four protons from ethenediol, HOCH=CHOH, then each thorium atom in each structure exhibits the favored +4 oxidation state.



2S-1 (C_1)
(0.0, 2.5)

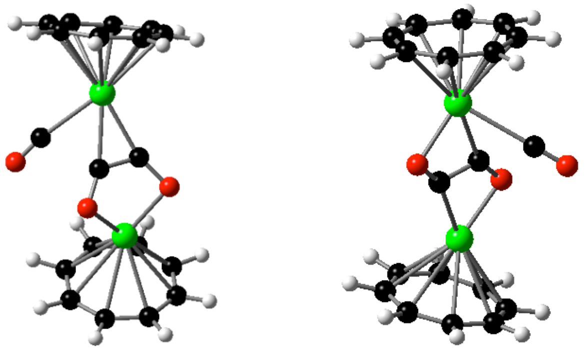
2S-2 (C_1)
(0.0, 0.0)

Figure 5. Two optimized $C_8H_8Th_2(CO)_2$ structures. In Figures 5 to 10 the upper optimized distances in Å are obtained by the BP86 method and the lower distances by the M06-L method.. The numbers in parentheses are the relative energies (ΔE in kcal/mol) predicted by the BP86 and M06-L methods.

Table 1. Total energies (E in hartree), relative energies (ΔE in kcal/mol), and Th-Th distances (Å), for the $(C_8H_8)_2Th_2(CO)_2$ structures.

	2S-1 (*C*$_1$)		**2S-2** (*C*$_1$)	
	BP86	M06-L	BP86	M06-L
Th-Th	4.830	4.813	4.709	4.663
–E	1662.05292	1661.69069	1662.05250	1661.69473
ΔE	0.0	0.0	0.3	–2.5

Two low-lying singlet structures are obtained for the tricarbonyl $(C_8H_8)_2Th_2(CO)_3$ analogous to those of the dicarbonyl (Figure 6 and Table 2). Each $(C_8H_8)_2Th_2(CO)_3$ structure can be derived from one of the $(C_8H_8)_2Th_2(CO)_2$ structures by simply adding a terminal CO group while preserving the bridging μ-C_2O_2 ligand. Thus the lowest energy $(C_8H_8)_2Th_2(CO)_3$ structure **3S-1** is derived from the *cis* dicarbonyl structure **2S-2** by adding a terminal CO group to the thorium atom bonded to the two carbon atoms of the μ-C_2O_2 ligand. Similarly the second $(C_8H_8)_2Th_2(CO)_3$ structure **3S-2**, lying 4.5 kcal/mol (BP86) or 5.8 kcal/mol (M06-L) in energy above **3S-1**, can be derived from the *trans* dicarbonyl structure **2S-1** by adding a terminal CO group.



3S-1 (*C*$_1$)
(0.0, 0.0)

3S-2 (*C*$_1$)
(4.5, 5.8)

Figure 6. Two optimized $C_8H_8Th_2(CO)_3$ structures.

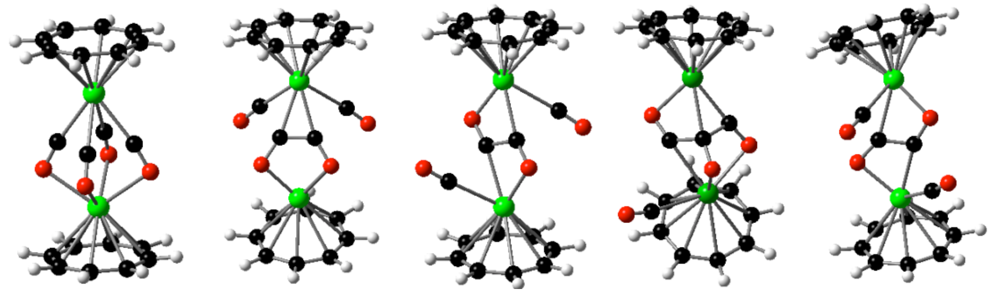
Table 2 Total energies (E in hartree), relative energies (ΔE in kcal/mol), and Th-Th distances (Å), for the $(C_8H_8)_2Th_2(CO)_3$ structures.

	3S-1 (*C*$_1$)		**3S-2** (*C*$_1$)	
	BP86	M06-L	BP86	M06-L
Th-Th	4.797	4.701	4.886	4.820
–E	1775.43204	1775.06010	1775.42480	1775.05091
ΔE	0.0	0.0	4.5	5.8

3.2 The Tetracarbonyl $(C_8H_8)_2Th_2(CO)_4$ and the Pentacarbonyl $(C_8H_8)_2Th_2(CO)_5$

The chemically relevant energy surfaces of the dicarbonyl $(C_8H_8)_2Th_2(CO)_2$ and the tricarbonyl $(C_8H_8)_2Th_2(CO)_3$ are relatively simple since the CO groups either couple to form bridging μ-C_2O_2 ligands or remain as terminal CO groups. The energy surfaces of the carbonyl-richer structures $(C_8H_8)_2Th_2(CO)_n$ (n = 4, 5) become more complicated. Thus in addition to bridging μ-C_2O_2 ligands and terminal CO groups, bridging η^2-μ-CO groups forming both Th-O and Th-C bonds are found. In addition, one of the low-lying $(C_8H_8)_2Th_2(CO)_4$ structures even has a bridging μ-C_3O_3 ligand formed by coupling three CO groups.

Four low-lying $(C_8H_8)_2Th_2(CO)_4$ structures are found (Figure 7 and Table 3). The lowest energy $(C_8H_8)_2Th_2(CO)_4$ structure is the highly symmetrical C_{4v} structure **4S-1** in which the two thorium atoms are bridged by four equivalent η^2-μ-CO groups. Each of these bridging η^2-μ-CO groups in **4S-1** is bonded to one thorium atom through the carbon atom and to the other thorium atom through the oxygen atom. The long Th···Th distance of 4.477 Å (BP86) or 4.412 Å (M06-L) in **4S-1** indicates no direct interaction between the two thorium atoms.



4S-1 (C_{4v}) (0.0, 0.0) **4S-2** (C_s) (2.0, 6.7) **4S-3**-BP86 (C_1) **4S-3**-M06-L (C_1) (8.2, 11.8) **4S-4** (C_1) (9.3, 15.2)

Figure 7. Four optimized $(C_8H_8)_2Th_2(CO)_4$ structures.

Table 3 Total energies (E in hartree), relative energies (ΔE in kcal/mol), and Th-Th distances (Å), for the $(C_8H_8)_2Th_2(CO)_4$ Structures.

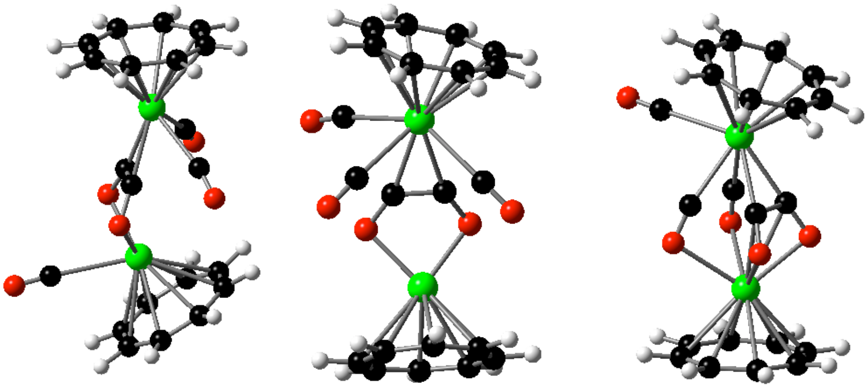
	4S-1(C_{4v})		4S-2 (C_s)		4S-3 (C_1)		4S-4(C_1)	
	BP86	M06-L	BP86	M06-L	BP86	M06-L	BP86	M06-L
Th-Th	4.477	4.412	4.850	4.749	4.945	4.779	4.898	4.887
–E	1888.81149	1888.43566	1888.80830	1888.42502	1888.79848	1888.41684	1888.79666	1888.41151
Nimg	none	none	none	1(4i)	none	none	none	none
ΔE	0.0	0.0	2.0	6.7	8.2	11.8	9.3	15.2

The next three $(C_8H_8)_2Th_2(CO)_4$ structures in terms of energy, namely **4S-2**, **4S-3**, and **4S-4**, can be derived from the $(C_8H_8)_2Th_2(CO)_2$ structures by adding terminal CO groups to the thorium atoms (Figure 7 and Table 3). Thus the $(C_8H_8)_2Th_2(CO)_4$ structure **4S-2**, lying 2.0 kcal/mol (BP86) or 6.7 kcal/mol (M06-L) in energy above **4S-1**, can be derived from the $(C_8H_8)_2Th_2(CO)_2$ structure **2S-2** by adding two terminal CO groups to the thorium atom bonded to the carbon atoms of the bridging μ-C_2O_2 ligand. The next two $(C_8H_8)_2Th_2(CO)_4$ structures **4S-3** and **4S-4**, lying 8.2 and 9.3 kcal/mol (BP86) or 11.8 and 15.2 kcal/mol (M06-L), respectively, in energy above **4S-1**, can be derived from structure **2S-1** by adding one terminal CO group to each thorium atom. These two $(C_8H_8)_2Th_2(CO)_4$ structures have very similar geometries by the BP86 method, except that in **4S-3** the two terminal CO groups are on the same side of the bridging μ-C_2O_2 group whereas in **4S-4** they are in the opposite sides of the bridging μ-C_2O_2 group. However, for **4S-3**, the M06-L method predicts that one of the terminal CO groups couples with the C_2O_2 group, forming a bridging C_3O_3 group.

Three low-lying structures closely spaced in energy are predicted for $(C_8H_8)_2Th_2(CO)_5$. The lowest energy structure **5S-1** predicted by the BP86 method can be derived from the dicarbonyl structure **2S-2** by adding two terminal CO groups to the thorium atom bonded only to the carbon atoms of the coupled C_2O_2 group and adding one terminal CO group to the other thorium atom. The second $(C_8H_8)_2Th_2(CO)_5$ structure **5S-2** is predicted either to lie only 0.4 kcal/mol above **5S-1** (BP86) or to have the same energy as **5S-1** (M06-L). In **5S-2** all of the terminal CO groups are attached to the thorium atom in **2S-1** not bonded to any oxygen atoms of the coupled C_2O_2 group. The third $(C_8H_8)_2Th_2(CO)_5$ structure **5S-3**, lying 1.9 kcal/mol (BP86) above **5S-1** or 3.2 kcal/mol (M06-L) below **5S-1**, can be derived from the lowest energy $(C_8H_8)_2Th_2(CO)_4$ structure **4S-1** by adding a terminal CO group to the thorium atom bonded exclusively to carbon atoms of the CO ligands. However, two of the four separate CO groups in **4S-1** couple to form a C_2O_2 ligand in **5S-3** when this terminal CO group is added. The long Th⋯Th distances (> 4.4 Å) in all three $(C_8H_8)_2Th_2(CO)_5$ structures indicate the absence of direct metal-metal bonds.

Table 4. Total energies (E in hartree), relative energies (ΔE in kcal/mol), and Th-Th distances (Å), for the $(C_8H_8)_2Th_2(CO)_5$ structures.

	5S-1 (*C*$_1$)		**5S-2** (*C*$_1$)		**5S-3** (*C*$_1$)	
	BP86	M06-L	BP86	M06-L	BP86	M06-L
Th-Th	4.844	4.718	4.855	4.745	4.452	4.491
–E	2002.17467	2001.78173	2002.17397	2001.78176	2002.17190	2001.78681
ΔE	0.0	0.0	0.4	0.0	1.9	−3.2



5S-1 (C_1)
(0.0, 0.0)

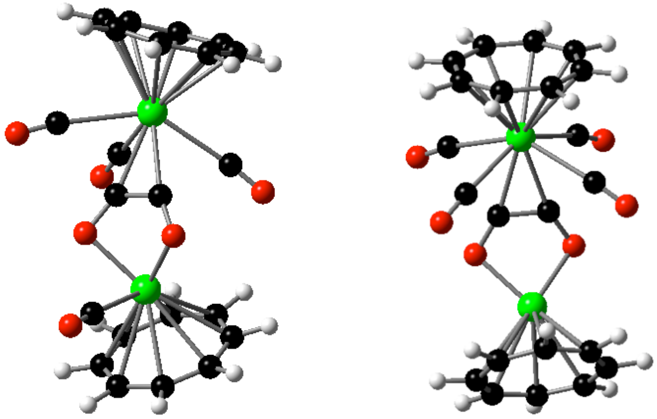
5S-2 (C_1)
(0.4, 0.0)

5S-3 (C_1)
(1.9, –3.2)

Figure 8. The optimized $C_8H_8Th_2(CO)_5$ structures.

3.3 The Carbonyl-Rich Structures $(C_8H_8)_2Th_2(CO)_6$ and $(C_8H_8)_2Th_2(CO)_7$

Two low-lying structures closely spaced in energy within 0.2 kcal/mol are obtained for the hexacarbonyl $(C_8H_8)_2Th_2(CO)_6$ (Figure 9 and Table 5). Both structures can be derived from the dicarbonyl structure **2S-2**. The lowest energy structure predicted by the BP86 method is **6S-1** with three terminal CO groups attached to the thorium atom bonded to the carbon atoms of the coupled C_2O_2 group and the remaining terminal CO group attached to the other thorium atom. The second $(C_8H_8)_2Th_2(CO)_6$ structure has a very unsymmetrical distribution of the terminal CO groups with all four attached on the thorium atom bonded only to the carbon atoms of the coupled bridging C_2O_2 group.



6S-1 (C_1)
(0.0, 0.0)

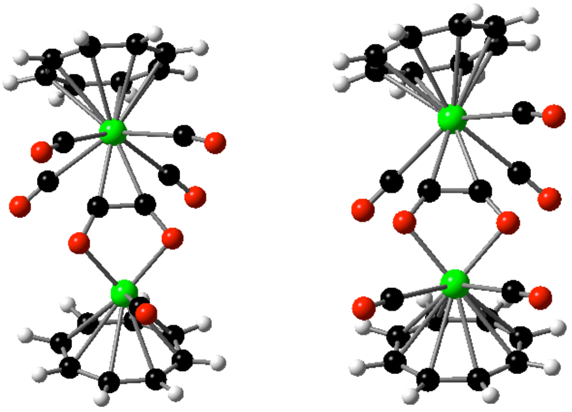
6S-2 (C_1)
(0.2,–0.1)

Figure 9. The optimized $C_8H_8Th_2(CO)_6$ structures.

Table 5. Total energies (E in hartree), relative energies (ΔE in kcal/mol), and Th-Th distances (Å), for the $(C_8H_8)_2Th_2(CO)_6$ structures.

	6S-1 (C_1)		**6S-2** (C_1)	
	BP86	M06-L	BP86	M06-L
Th-Th	4.855	4.727	4.865	4.699
–E	2115.54027	2115.13821	2115.54002	2115.13837
ΔE	0.0	0.0	0.2	-0.1

The two low-lying structures for the heptacarbonyl $(C_8H_8)_2Th_2(CO)_7$ can be derived from the dicarbonyl structure **2S-2**. The lowest energy such structure **7S-1** has four terminal CO groups attached to the thorium atom bonded to the carbon atoms of the coupled bridging μ-C_2O_2 group and the fifth terminal CO group attached to the other thorium atom (Figure 10 and Table 6). The second $(C_8H_8)_2Th_2(CO)_7$ structure, lying 5.5 kcal/mol (BP86) or 3.3 kcal/mol (M06-L) above **7S-1**, has only three terminal CO groups attached to the thorium atom bonded to the carbon atoms of the coupled bridging μ-C_2O_2 group leaving two terminal CO groups for the other thorium atom.



7S-1 (C_1)
(0.0, 0.0)

7S-2 (C_1)
(5.5, 3.3)

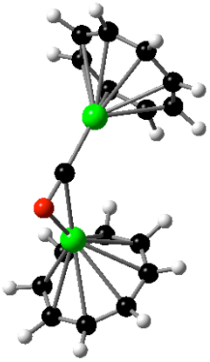
Figure 10. The optimized $C_8H_8Th_2(CO)_7$ structures.

Table 6. Total energies (E in hartree), relative energies (ΔE in kcal/mol), and Th-Th distances (Å) for the $(C_8H_8)_2Th_2(CO)_7$ structures.

	7S-1 (C_1)		**7S-2** (C_1)	
	BP86	M06-L	BP86	M06-L
Th-Th	4.863	4.690	4.914	4.763
–E	-2228.90650	-2228.49504	-2228.89773	-2228.48980
ΔE	0.0	0.0	5.5	3.3

3.4 Thermochemistry

In order to explore the thermochemistry of the $(C_8H_8)_2Th_2(CO)_n$ discussed above, information on the optimized structures of the monocarbonyl $(C_8H_8)_2Th_2(CO)$ and the mononuclear derivatives $(C_8H_8)Th(CO)_n$ (n = 5, 4, 3, 2, 1) is needed. For the monocarbonyl $(C_8H_8)_2Th_2(CO)$ the lowest energy structure **1S-1** was found to have a four-electron donor bridging η^2-μ-CO group and a long Th···Th distance of ~4.0 Å indicating the absence of a direct Th-Th bond (Figure 11).



1S-1 (C_s)

Figure 11. The optimized $C_8H_8Th_2(CO)$ structure.

The lowest energy structures for the mononuclear derivatives $(C_8H_8)Th(CO)_n$ (n = 5, 4, 3, 2, 1) are depicted in Figure 12. The bonding in these systems is much more conventional than that for the binuclear thorium derivatives $(C_8H_8)_2Th_2(CO)_n$. The $(C_8H_8)Th(CO)_5$ structure can be derived from a trigonal prism with the η^8-C_8H_8 ring occupying one of the triangular faces and three terminal CO groups located at the vertices of the other triangular faces. Two of the three rectangular faces of this trigonal prism are capped by the two remaining terminal CO groups. The remaining $(C_8H_8)Th(CO)_n$ structures can be derived from this $(C_8H_8)Th(CO)_5$ structure by removal of CO groups.

Table 7 lists the CO dissociation energies for both the mononuclear derivatives $(C_8H_8)Th(CO)_n$ and the binuclear derivatives $(C_8H_8)_2Th_2(CO)_n$. For the mononuclear derivatives the CO dissociation energy from $(C_8H_8)Th(CO)_5$ to give $(C_8H_8)Th(CO)_4$ is rather low at ~5 kcal/mol, whereas the CO dissociation energy from $(C_8H_8)Th(CO)_4$ to give $(C_8H_8)Th(CO)_3$ is much higher at ~20 kcal/ mol. This suggests that $(C_8H_8)Th(CO)_4$ is the favored species among the mononuclear cyclooctatetraene thorium carbonyls $(C_8H_8)Th(CO)_n$. The structure of $(C_8H_8)Th(CO)_4$ can be derived from the experimentally known "thorocene" structure $(\eta^8$-$C_8H_8)_2Th$ (Figure 4) by replacing one of the octahapto

η^8-C_8H_8 rings with four CO groups. Note that an octahapto η^8-C_8H_8 ring and four terminal CO groups are both eight-electron donors to a central transition metal atom.

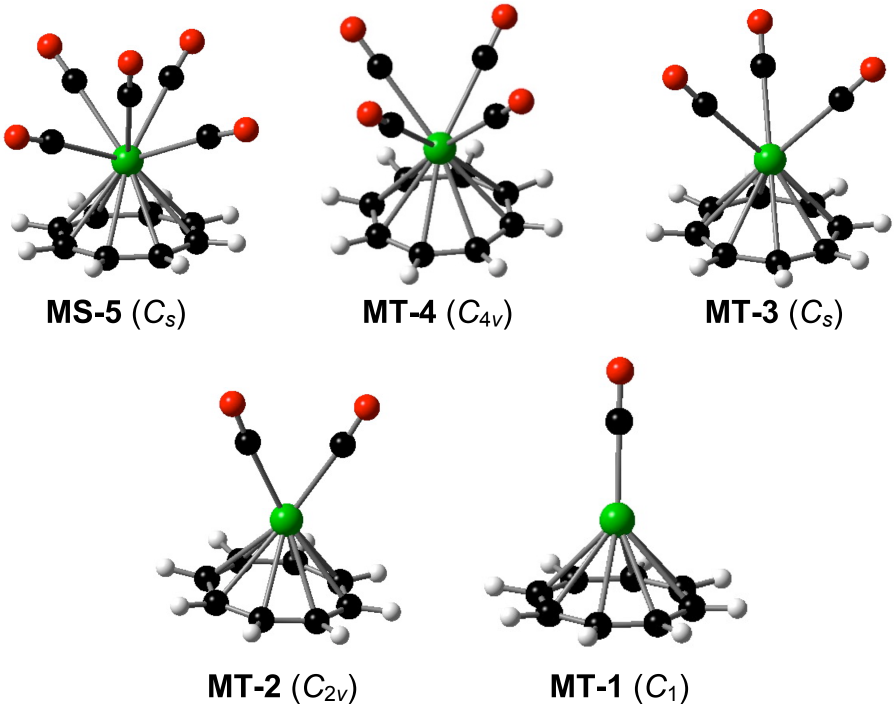


Figure 12. Optimized structures of the mononuclear fragments $C_8H_8Th(CO)_n$ (n = 5, 4, 3, 2, 1). For each **MX-n**, **M** represents a mononuclear structure, X represents the spin state (**S** = singlet, **T** = triplet), and **n** represents the number of carbonyl groups.

Table 7. Predicted carbonyl dissociation energies for the lowest energy $(C_8H_8)Th(CO)_n$ (n = 5, 4, 3, 2) and $(C_8H_8)_2Th_2(CO)_n$ (n = 7, 6, 5, 4, 3, 2) structures using the BP86 method.

	BP86	M06L
$(C_8H_8)Th(CO)_5 \rightarrow (C_8H_8)Th(CO)_4 + CO$	3.8	6.3
$(C_8H_8)Th(CO)_4 \rightarrow (C_8H_8)Th(CO)_3 + CO$	18.5	21.9
$(C_8H_8)Th(CO)_3 \rightarrow (C_8H_8)Th(CO)_2 + CO$	19.2	22.2
$(C_8H_8)Th(CO)_2 \rightarrow (C_8H_8)Th(CO) + CO$	31.6	31.0
$(C_8H_8)_2Th_2(CO)_7$(**7S-1**) → $(C_8H_8)_2Th_2(CO)_6$ (**6S-1**) + CO	7.1	11.5
$(C_8H_8)_2Th_2(CO)_6$ (**6S-1**) → $(C_8H_8)_2Th_2(CO)_5$ (**5S-1**) + CO	7.4	11.5
$(C_8H_8)_2Th_2(CO)_5$ (**5S-1**) → $(C_8H_8)_2Th_2(CO)_4$ (**4S-1**) + CO	5.9	4.9
$(C_8H_8)_2Th_2(CO)_4$ (**4S-1**) → $(C_8H_8)_2Th_2(CO)_3$ (**3S-1**) + CO	**16.1**	**23.4**
$(C_8H_8)_2Th_2(CO)_3$ (**3S-1**) → $(C_8H_8)_2Th_2(CO)_2$ (**2S-1**) + CO	15.9	19.5
$(C_8H_8)_2Th_2(CO)_2$ (**2S-1**) → $(C_8H_8)_2Th_2(CO)$ (**1S-1**) + CO	**58.7**	**52.4**

The predicted dissociation energies of terminal CO groups from carbonyl-rich $(C_8H_8)_2Th_2(CO)_n$ derivatives (n = 7, 6, 5) are relatively low, namely < 8 kcal/mol by the BP86 method and < 12 kcal/mol by the M06-L method (Table 7). This is consistent with the experimentally observed facile loss of coordinated CO groups in $Cp_3U(CO)$[5,6,22] as well as $U(CO)_n$, $U(CO)_n^+$ and $UO_2(CO)_n^+$ derivatives.[4,49] However, for the lowest energy $(C_8H_8)_2Th_2(CO)_4$ structure **4S-1**, which lacks terminal CO groups, the CO dissociation energy is significantly higher at 16.1 kcal/mol (BP86) or 23.4 kcal/mol (M06-L). The dicarbonyl $(C_8H_8)_2Th_2(CO)_2$ structure **2S-1**, in which the two CO groups couple to form a bridging μ-C_2O_2 ligand, has a very high CO dissociation energy of 58.7 kcal/mol (BP86) or 52.4 kcal/mol (M06-L). This is not surprising since CO dissociation from **2S-1** requires rupture not only of a Th-C bond but also the C-C bond in the μ-C_2O_2 ligand. For comparison, the experimental CO dissociation energies for the simple carbonyls $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ of the d-block metals are 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol, respectively.[50]

Table 8 lists the predicted energies for the disproportionation reactions $2\,(C_8H_8)_2Th_2(CO)_n \rightarrow (C_8H_8)_2Th_2(CO)_{n-1} + (C_8H_8)_2Th_2(CO)_{n+1}$. Such reactions for $(C_8H_8)_2Th_2(CO)_n$ (n = 6, 5, 3) are predicted to be mildly exothermic up to ~7 kcal/mol suggesting that these are not viable species. However, the analogous disproportionations of $(C_8H_8)_2Th_2(CO)_4$ and $(C_8H_8)_2Th_2(CO)_2$, particularly the latter, are significantly endothermic suggesting that these are the most promising synthetic targets among the molecules discussed in this paper.

Table 8. Predicted energies for the disproportionation reactions $2\,(C_8H_8)_2Th_2(CO)_n \rightarrow (C_8H_8)_2Th_2(CO)_{n-1} + (C_8H_8)_2Th_2(CO)_{n+1}$

	BP86	M06L
$2\,(C_8H_8)_2Th_2(CO)_6$ (**6S-1**) $\rightarrow (C_8H_8)_2Th_2(CO)_7$(**7S-1**) + $(C_8H_8)_2Th_2(CO)_5$ (**5S-1**)	-0.4	-0.1
$2\,(C_8H_8)_2Th_2(CO)_5$ (**5S-1**) $\rightarrow (C_8H_8)_2Th_2(CO)_6$ (**6S-1**) + $(C_8H_8)_2Th_2(CO)_4$ (**4S-1**)	-1.5	-6.7
$2\,(C_8H_8)_2Th_2(CO)_4$ (**4S-1**) $\rightarrow (C_8H_8)_2Th_2(CO)_5$ (**5S-1**) + $(C_8H_8)_2Th_2(CO)_3$ (**3S-1**)	**10.2**	**18.5**
$2\,(C_8H_8)_2Th_2(CO)_3$ (**3S-1**) $\rightarrow (C_8H_8)_2Th_2(CO)_4$ (**4S-1**) + $(C_8H_8)_2Th_2(CO)_2$ (**2S-1**)	-0.2	-3.9
$2\,(C_8H_8)_2Th_2(CO)_2$ (**2S-1**) $\rightarrow (C_8H_8)_2Th_2(CO)_3$ (**3S-1**) + $(C_8H_8)_2Th_2(CO)$ (**1S-1**)	**42.8**	**32.9**

We also examined the energies for the dissociation of the binuclear derivatives $(C_8H_8)_2Th_2(CO)_n$ (n = 7 to 2) into mononuclear fragments (Table 9). In this connection the dissociation energies for all of the $(C_8H_8)_2Th_2(CO)_n$ structures into mononuclear $C_8H_8Th(CO)_m$ derivatives are predicted to be very large, in excess of 60 kcal/mol. The high energies for the dissociation of $(C_8H_8)_2Th_2(CO)_n$ into mononuclear $C_8H_8Th(CO)_m$

fragments appear to relate to the favorability of the central Th(η^4-μ-C_2O_2)Th, Th(η^4-μ-C_2O_2)(η^2-μ-CO)$_2$, and Th(η^2-μ-CO)$_4$Th units in the binuclear $(C_8H_8)_2Th_2(CO)_n$ derivatives. Furthermore, the dissociation energies for $(C_8H_8)_2Th_2(CO)_n$ into mononuclear fragments increase nearly monotonically with decreasing numbers of carbonyl groups. We therefore conclude that the mononuclear $C_8H_8Th(CO)_m$ fragments are not likely to play an important role in the chemistry of the binuclear $(C_8H_8)_2Th_2(CO)_n$ derivatives.

Table 9. Energies (kcal/mol) for the dissociation of $(C_8H_8)_2Th_2(CO)_n$ (n = 7 to 2) into mononuclear fragments $C_8H_8Th(CO)_m$ (m = 1 to 5).

		BP86	M06-L
$(C_8H_8)_2Th_2(CO)_7$ (**7S-1**)	→ $C_8H_8Th(CO)_4$ + $C_8H_8Th(CO)_3$	47.1	55.8
$(C_8H_8)_2Th_2(CO)_7$ (**7S-1**)	→ $C_8H_8Th(CO)_5$ + $C_8H_8Th(CO)_2$	62.5	71.7
$(C_8H_8)_2Th_2(CO)_6$ (**6S-1**)	→ $C_8H_8Th(CO)_4$ + $C_8H_8Th(CO)_2$	60.8	66.5
$(C_8H_8)_2Th_2(CO)_6$ (**6S-1**)	→ $2C_8H_8Th(CO)_3$	57.8	66.1
$(C_8H_8)_2Th_2(CO)_5$ (**5S-1**)	→ $C_8H_8Th(CO)_3$ + $C_8H_8Th(CO)_2$	69.6	77.0
$(C_8H_8)_2Th_2(CO)_5$ (**5S-1**)	→ $C_8H_8Th(CO)_4$ + $C_8H_8Th(CO)$	82.5	86.1
$(C_8H_8)_2Th_2(CO)_4$(**4S-1**)	→ $2C_8H_8Th(CO)_2$	82.9	94.4
$(C_8H_8)_2Th_2(CO)_4$ (**4S-1**)	→ $C_8H_8Th(CO)_3$ + $C_8H_8Th(CO)$	95.1	103.1
$(C_8H_8)_2Th_2(CO)_3$ (**3S-1**)	→ $C_8H_8Th(CO)_2$ + $C_8H_8Th(CO)$	98.1	102.0
$(C_8H_8)_2Th_2(CO)_3$ (**2S-1**)	→ $2C_8H_8Th(CO)$	133.8	113.5

3.5 Natural Bond Orbital Analysis of the $Cp_2Th_2(CO)_n$ Derivatives

In order to obtain more insight into the chemical bonding in the $Cp_2Th_2(CO)_n$ derivatives, the natural charges on the thorium atoms were determined from Weinhold Natural Bond Orbital (NBO) analyses[51] using the BP86 method (Table 10). In the $(C_8H_8)_2Th_2(CO)_n$ structures, addition of terminal CO groups to one thorium atom increases the negative charge on the thorium atom bearing the terminal CO groups with relatively little change of the positive charge on the other thorium atom. Thus in the series **2S-2**, **3S-1**, **4S-2**, and **5S-2**, all of which have a bridging μ-C_2O_2 ligand and 0, 1, 2, and 3 terminal CO groups, respectively, bonded to the same thorium atom, the formal charge on the thorium atom bearing the terminal CO group(s) decreases in the sequence ~1.7, ~1.2, ~0.6, and ~0, respectively. However, the natural charge on the thorium atom not bearing any CO groups in any of these structures remains nearly constant at ~1.7. In all of the $(C_8H_8)_2Th_2(CO)_n$ structures discussed in this paper, the Th···Th distances are 4.0 Å and greater, indicating the lack of direct Th-Th bonds.

Table 10. Atomic charges and the Th-Th bond distances (in Å) for the $(C_8H_8)_2Th_2(CO)_n$ singlet structures predicted by the BP86 method.

	Natural charges on Th1/Th2	Th-Th distance (Å)	Number of η^2-μ-CO groups
$(C_8H_8)_2Th_2(CO)_5$ (**5S-1**)	+0.59/+1.15	4.844	2
$(C_8H_8)_2Th_2(CO)_5$ (**5S-2**)	-0.06/+1.69	4.855	2
$(C_8H_8)_2Th_2(CO)_5$ (**5S-3**)	+0.08/+1.04	4.542	4
$(C_8H_8)_2Th_2(CO)_4$ (**4S-1**)	+0.56/+0.93	4.477	4
$(C_8H_8)_2Th_2(CO)_4$ (**4S-2**)	+0.60/+1.68	4.850	2
$(C_8H_8)_2Th_2(CO)_4$ (**4S-3**)	+1.24/+1.23	4.945	2
$(C_8H_8)_2Th_2(CO)_4$ (**4S-4**)	+1.25/+1.18	4.898	2
$(C_8H_8)_2Th_2(CO)_3$ (**3S-1**)	+1.17/+1.69	4.797	2
$(C_8H_8)_2Th_2(CO)_3$ (**3S-2**)	+1.22/+1.72	4.886	2
$(C_8H_8)_2Th_2(CO)_2$ (**2S-1**)	+1.70/+1.70	4.830	2
$(C_8H_8)_2Th_2(CO)_2$ (**2S-2**)	+1.64/+1.68	4.709	2
$(C_8H_8)_2Th_2(CO)_2$ (**1S-2**)	+1.50/+1.57	4.013	1

3.6 Carbonyl Vibrational Frequencies

The ν(CO) frequencies of the terminal CO groups in the $(C_8H_8)_2Th_2(CO)_n$ structures are similar to the terminal ν(CO) frequencies of carbonyl derivatives of the d-block transition metals. Thus the terminal CO groups in the $(C_8H_8)_2Th_2(CO)_3$ structures **3S-1** and **3S-2** exhibit ν(CO) frequencies at ~1960 cm^1 (Table 11). However, the situation is very different for the ν(CO) frequencies for the bridging carbonyls in the central Th(η^2-μ-CO)$_4$Th and Th(η^4-C_2O_2)Th units in the $(C_8H_8)_2Th_2(CO)_n$ structures. The bridging μ-C_2O_2 groups found in many of the $(C_8H_8)_2Th_2(CO)_n$ structures discussed in this paper exhibit extremely low ν(CO) frequencies as exemplified by those at 984 and 1018 cm^{-1} for **2S-1** and at 892 and 1110 cm^{-1} for **2S-2**. Addition of terminal CO groups to these structures increases the ν(CO) frequencies assigned to the bridging μ-C_2O_2 group by competing for the extreme back bonding leading to the low ν(CO) frequencies of the latter. This effect is particularly apparent in the $(C_8H_8)_2Th_2(CO)_4$ structure **4S-2** with a bridging μ-C_2O_2 group and two terminal CO groups for which the ν(CO) frequencies of the μ-C_2O_2 ligand of 1117 and 1219 cm^{-1} are more than 100 cm^{-1} higher than those in **2S-2**. The four bridging η^2-μ-CO groups in the $(C_8H_8)_2Th_2(CO)_4$ structure **4S-1** exhibit ν(CO) frequencies at 1527, 1562, and 1600 cm^{-1}, which are approximately midway between those for terminal CO groups and those for the CO groups in the μ-C_2O_2 ligand.

Table 11. Vibrational frequencies (νCO), in cm^{-1}) and infrared intensities (in parentheses, in km/mol) for the some selected $(C_8H_8)_2Th_2(CO)_n$ derivatives.

1S-1	**1045**(*176*)
2S-1	**984**(*117*), **1018**(*0*)
2S-2	**892***(35)*, **1110***(51)*
3S-1	**939***(6)*, **1104***(56)* , **1959***(368)*
3S-2	**1039***(105)*, **1161***(69)* , **1969***(556)*
4S-1	**1527***(448)*, **1527***(448)* , **1562***(0)*， **1660***(208)*
4S-2	**1117***(30)*, **1219***(563)* , **1964***(527)*， **1981***(267)*

4. Discussion

The previously studied[20] $(C_5H_5)_2Th_2(CO)_n$ ($n = 3, 4, 5$) derivatives containing the monoanionic cyclopentadienide ligands, $C_5H_5^-$, were predicted to have Th$\cdots$Th distances ranging from ~3.7 to ~4.4 Å suggested to correspond to weak Th-Th bonding at best. This is consistent with the thorium atoms being in the favored +4 oxidation state, which arises if the bridging η^2-μ-CO and η^4-μ-C_2O_2 ligands are interpreted as dianions derived from double deprotonation of hydroxycarbene, :C(H)(OH), and ethynediol, HOC≡COH, respectively. Only the dicarbonyl structures $(C_5H_5)_2Th_2(\eta^2\text{-}\mu\text{-}CO)_2$ with much shorter Th–Th distances of ~3.3 to 3.4 Å and corresponding Wiberg bond indices of ~0.8 approaching unity can be regarded as having formal Th–Th single bonds. This corresponds to the +3 thorium oxidation state arising from considering the two η^2-μ-CO ligands as dianions.

All of the $(C_8H_8)_2Th_2(CO)_n$ structures found in this work have Th$\cdots$Th distances of at least 4.0 Å, clearly suggesting the absence of formal Th-Th bonds. The NBO analysis of natural atomic charges suggests accumulation of negative charges on the oxygen atoms of the CO groups consistent with strong back bonding from the thorium atoms to the CO ligands (Figure 2). However, the dianionic $C_8H_8^{2-}$ ligands in the $(C_8H_8)_2Th_2(CO)_n$ structures means that less highly charged CO and C_2O_2 anions are required to give the thorium atoms the favored +4 oxidation state compared with related $(C_5H_5)_2Th_2(CO)_n$ structures with monoanionic $C_5H_5^-$ ligands. Thus consider the analogous $(C_5H_5)_2Th_2(CO)_4$ and $(C_8H_8)_2Th_2(CO)_4$ structures with four separate bridging η^2-μ-CO groups as an example (**4T-3** in ref. 20 and **4S-1** in Figure 7, respectively). The NBO charges on CO for the $(C_8H_8)_2Th_2(CO)_4$ structure **4S-1** of 0.342 and –0.485 for the carbon and oxygen atoms, respectively, are significantly less negative than those for the $(C_5H_5)_2Th_2(CO)_4$ structure **4T-3** (ref. 20) of 0.178 and –0.536 for the carbon and oxygen atoms, respectively. This relates to ν(CO) frequencies for the $(C_5H_5)_2Th_2(CO)_4$ structure approximately 100 cm^{-1} lower than those in the corresponding $(C_8H_8)_2Th_2(CO)_4$ structure. This suggests that less electron density is transferred to CO in $(C_8H_8)_2Th_2(CO)_n$ structures relative to corresponding $(C_5H_5)_2Th_2(CO)_n$ structures. This difference in charge distribution in $(C_8H_8)_2Th_2(CO)_n$ structures relative to corresponding $(C_5H_5)_2Th_2(CO)_n$ structures suggests that coupling of two CO groups to form the $C_2O_2^{2-}$ dianion ligand is likely to be less favorable in the $(C_8H_8)_2Th_2(CO)_n$ structures relative to $(C_5H_5)_2Th_2(CO)_n$ structures. This is consistent with the coupling of two CO groups to give the $C_2O_2^{2-}$ ligand in the lower energy $(C_5H_5)_2Th_2(CO)_4$ structure **4S-1** relative to **4T-3** with four separate CO groups (ref. 20).

The high energies required for CO dissociation (Table 7) and disproportionation (Table 8) suggest that the $(C_8H_8)_2Th_2(CO)_2$ structures **2S-1** and **2S-2**, in which the two CO ligands have coupled to form η^2-μ-C_2O_2 ligands with *trans* and *cis* stereochemistries, respectively, are the favorable structures in the $(C_8H_8)_2Th_2(CO)_n$ system. In fact, most of the carbonyl richer $(C_8H_8)_2Th_2(CO)_n$ (n = 3, 4, 5) structures can be generated from **2S-2** by adding one or more terminal CO groups. In order for the thorium atoms in **2S-1** and **2S-2** to have the favored +4 oxidation state, the bridging μ-C_2O_2 ligand must be a tetraanion. Such a tetraanion could at least formally be generated from ethenediol (1,2-dihydroxyethylene, HOCH=CHOH) by removal of four protons. The extremely low ν(CO) frequencies of the μ-C_2O_2 ligands in **2S-1** and **2S-2** around 1000 cm^{-1} (Table 11) imply a low formal C-O bond order consistent with a chelating diolate dianion.

The experimental work on CO coupling in organouranium systems of Cloke and coworkers[7,8,9,10,12] results in not only the coupling of two CO units to give $C_2O_2^{2-}$ ligands but also coupling of three and four CO units to give $C_3O_3^{2-}$ (deltate) and $C_4O_4^{2-}$ (squarate) ligands, respectively. The $(C_8H_8)_2Th_2(CO)_4$ structure **4S-3** determined by the M06-L method has a bridging μ-C_3O_3 ligand formed by linear coupling of three CO ligands (Figure 7). Organouranium derivatives with similar bridging μ-C_3O_3 ligands might undergo ring closure to form the deltate complex $[(\eta^8\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)\text{-}(\eta^5\text{-}Me_5C_5)U]_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_3O_3)$ reported by Cloke and co-workers.[7]

The other $(C_8H_8)_2Th_2(CO)_n$ structure without a bridging μ-C_2O_2 ligand is the lowest energy $(C_8H_8)_2Th_2(CO)_4$ structure **4S-1** exhibiting C_{4v} symmetry with four equivalent separate bridging η^2-μ-CO ligands. Each η^2-μ-CO ligand must be a monoanion to give the thorium atoms the favored +4 oxidation state. Since a η^2-μ-CO^-

monoanion has an odd number of electrons, spin pairing must occur in the central Th(η^2-μ-CO)$_4$Th unit to lead to a singlet spin state structure.

A characteristic of d-block transition metal chemistry, particularly that involving strong field ligands such as CO and olefins, is the stability of complexes with the favored 18-electron configuration.[52,53,54,55,56] It is not clear what would be a realistic analogue of the 18-electron rule for f-block elements if any, indeed, exists. A 32-electron rule has been suggested corresponding to a filled sp^{3}d^{5}f^7 16-orbital manifold.[57,58,59] However, such a rule would lead to completely unreasonable coordination numbers for most ligands and thus does not appear applicable to most organometallic and/or coordination chemistry of the f-block elements. Our examination of the structures of the mononuclear carbonyl derivatives (η^8-C_8H_8)Th(CO)$_n$ (n = 5, 4, 3, 2, 1), undertaken to obtain thermochemical data on the dissociation of the dimeric species (η^8-C_8H_8)$_2$Th$_2$(CO)$_n$ into monomeric units, provides some insight into this matter from the CO dissociation energies of the (η^8-C_8H_8)Th(CO)$_n$ species. Thus the predicted CO dissociation energy from the pentacarbonyl (η^8-C_8H_8)Th(CO)$_5$ with a 22-electron thorium atom to give the tetracarbonyl (η^8-C_8H_8)Th(CO)$_4$ with a 20-electron thorium atom is relatively low at ~5 kcal/mol. However, the dissociation energy of the tetracarbonyl (η^8-C_8H_8)Th(CO)$_4$ to give the tricarbonyl (η^8-C_8H_8)Th(CO)$_3$ with an 18-electron thorium atom is much higher at ~20 kcal/mol. This clearly indicates that an 18-electron configuration for a thorium atom is not a preferred configuration, unlike the situation for the d-block transition metals. Note that the apparently preferred 20-electron complex (η^8-C_8H_8)Th(CO)$_4$ can be derived from the experimentally known "thorocene" (η^8-C_8H_8)$_2$Th by replacement of one of the octahapto η^8-C_8H_8 rings with four CO groups.

None of the (C_8H_8)Th(CO)$_n$ or (C_8H_8)$_2$Th$_2$(CO)$_n$ species discussed in this paper has yet been synthesized. However, the experimentally known species (η^8-C_8H_8)ThX$_2$ (X = Cl, BH$_4$) (Figure 4)[60,61] are potential precursors for the synthesis of (C_8H_8)Th(CO)$_n$ and/or (C_8H_8)$_2$Th$_2$(CO)$_n$ derivatives using reductive carbonylation reactions with strong reducing agents such as sodium naphthalide or potassium on graphite. The thermochemistry of these systems suggest (C_8H_8)Th(CO)$_4$ and (C_8H_8)$_2$Th$_2$(CO)$_n$ (n = 2, 4) to be the most promising synthetic objectives.

5. Conclusions

The systems (C_8H_8)Th(CO)$_n$ (n = 1 to 5) and (C_8H_8)$_2$Th$_2$(CO)$_n$ (n = 2 to 7) related to the known "thorocene," (η^8-C_8H_8)$_2$Th have been explored using density functional theory. All of the binuclear (C_8H_8)$_2$Th$_2$(CO)$_n$ structures found in this work have long

Th···Th distances ranging from 4.4 to 5.0 Å suggesting the absence of direct Th-Th bonds. Two $(C_8H_8)_2Th_2(CO)_2$ isomers of similar energies in which the two CO groups have coupled to form *tran*s and *cis* isomers of a bridging η^4-μ-C_2O_2 ligand are low energy structures. These bridging η^4-μ-C_2O_2 ligands exhibit ultralow ν(CO) frequencies around 1000 cm^{-1} indicating strong back donation of thorium d and f electrons into C-O antibonding orbitals. Most of the carbonyl richer $(C_8H_8)_2Th_2(CO)_n$ (n = 3 to 7) structures are derived from one of these basic $(C_8H_8)_2Th_2(CO)_2$ structures by addition of terminal CO groups. An exception is the lowest energy $(C_8H_8)_2Th_2(CO)_4$ structure which has C_{4v} symmetry with four equivalent separate η^2-μ-CO groups bridging the thorium atoms. The thermochemistry of these systems suggest $(C_8H_8)Th(CO)_4$ and $(C_8H_8)_2Th_2(CO)_n$ (n = 2, 4) to be the most promising synthetic objectives.

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Supporting Information. Tables S1 to S16: Optimized coordinates of the reported $(C_8H_8)_2Th_2(CO)_n$ (n = 2 to 7) structures; Tables S17 to S32: Harmonic vibrational frequencies and infrared intensities (in for the $(C_8H_8)_2Th_2(CO)_n$ (n = 2 to 7) structures; Complete Gaussian09 reference (Reference 47)

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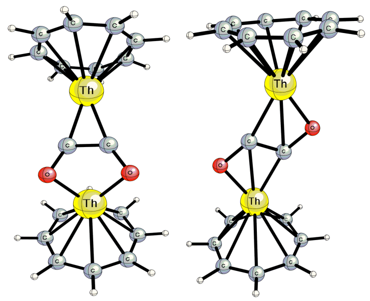
Table of Contents Synopsis

Modeling Intermediates in Carbon Monoxide Coupling Reactions Using Cyclooctatetraene Thorium Derivatives

Huidong Li, Hao Feng, Weiguo Sun, Qunchao Fan, R. Bruce King, and Henry F. Schaefer III

Density functional studies on $(C_8H_8)_2Th_2(CO)_n$ (n = 2 to 7) derivatives are used to model intermediates in CO coupling reactions in organoactinides related to those found by Cloke and coworkers.



$(\eta^8\text{-}C_8H_8)_2Th_2(\eta^4\text{-}\mu\text{-}C_2O_2)$