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### Title

The Bond Between CO and Cp<sup>3</sup>U in Cp<sup>3</sup>U(CO) involves Backbonding from the Cp<sup>3</sup>U Ligand-based Orbitals of  $\pi$ -Symmetry, where Cp' Represents a Substituted Cyclopentadienyl Ligand.

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## Abstract

The experimental CO stretching frequencies in the 1:1 adducts between (C<sub>5</sub>H<sub>5-n</sub>R<sub>n</sub>)<sub>3</sub>U and CO range from 1976 cm<sup>-1</sup> in (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U(CO) to 1900 cm<sup>-1</sup> in (C<sub>5</sub>HMe<sub>4</sub>)<sub>3</sub>U(CO). The origin of the large difference between the stretching frequencies in free (2143 cm<sup>-1</sup>) and coordinated CO and the large effect the substituents on the cyclopentadienyl ligands play in the difference is explored by DFT calculations with a small core effective core potential in which 32 electrons on uranium are explicitly treated. The results of these calculations, along with a NBO analysis, show that a σ-bond is formed between CO and an empty σ-orbital on the Cp'<sub>3</sub>U fragment composed of f<sub>σ</sub> and d<sub>σ</sub> parentage orbitals. The backbonding interaction, which results in lowering the CO stretching frequency, does not originate

from non-bonding metal-based orbitals but from the filled ligand-based orbitals of  $\pi$ -symmetry that are used for bonding in the  $\text{Cp}'_3\text{U}$  fragment. This model, which is different from the backbonding model used in the d-transition metal complexes, rationalizes the large substituent effect in the 5f-metal complexes.

## Introduction

The observation that a hexane solution of  $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}$  changes color from green to burgundy when exposed to an atmosphere of CO, along with the appearance of an absorption band in the infrared spectrum at  $1976\text{ cm}^{-1}$ , was interpreted as arising from a CO adduct with considerable backbonding from the  $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}$  fragment into the  $\pi^*$  orbitals on CO. The reaction is reversible in hexane solution and in the solid state where  $\nu_{\text{CO}}$  is  $1969\text{ cm}^{-1}$ .<sup>1</sup> The lowering of  $\nu_{\text{CO}}$  on coordination was a phenomenological observation that does not address the strength of the interaction nor the orbitals on the  $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}$  fragment used in the bonding. Although the complex was not isolated, the observations were the first indication that a  $\text{Cp}'_3\text{U}$  molecule could behave as a  $\pi$ -donor fragment. An early  $X_\alpha$  calculation concluded that backbonding was from the three electrons located in the  $5f_\pi$  orbitals which are largely uranium in character, “the bonding orbital is 14% C and 84% U in character with the uranium portion consisting of 96% f character”.<sup>2</sup> Although the  $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}(\text{CO})$  was not isolated and crystallographically characterized, Carmona and coworkers isolated  $(\text{C}_5\text{HMe}_4)_3\text{U}(\text{CO})$  and the crystal structure answered the important question of how CO was bound to the  $(\text{C}_5\text{HMe}_4)_3\text{U}$  fragment, viz., the CO is terminal and bound to the  $(\text{C}_5\text{HMe}_4)_3\text{U}$  fragment by way of the carbon atom even though  $\nu_{\text{CO}}$  is  $1900\text{ cm}^{-1}$  in petroleum ether solution;  $\nu_{\text{CO}}$  is  $1880\text{ cm}^{-1}$  in Nujol.<sup>3</sup> The crystal structure of  $(\text{C}_5\text{Me}_5)_3\text{U}(\text{CO})$ , where  $\nu_{\text{CO}}$  is  $1925\text{ cm}^{-1}$  in  $\text{C}_6\text{D}_6$  solution and  $1922\text{ cm}^{-1}$  in KBr, is similar to that of  $(\text{C}_5\text{HMe}_4)_3\text{U}(\text{CO})$  with the exception that the U-C(CO) distance of  $2.485(9)\text{ \AA}$  in the former is longer than that of  $2.383(6)\text{ \AA}$  in the latter complex. The averaged U-C(Cp') distances follows a similar pattern, viz., the averaged U-C distance in the  $\text{C}_5\text{HMe}_4$ -derivative is  $2.80(5)\text{ \AA}$  whereas the distance in the  $\text{C}_5\text{Me}_5$ -derivative is  $2.87(4)\text{ \AA}$ .<sup>4</sup> The strong dependence of  $\nu_{\text{CO}}$  in these three complexes is surprising since  $\nu_{\text{CO}}$  in CO complexes of the d-transition metal metallocenes display a small substituent effect. For example, the averaged  $\nu_{\text{CO}}$  values in the zirconocene dicarbonyls,  $\text{Cp}'_2\text{Zr}(\text{CO})_2$ , range from  $1932\text{ cm}^{-1}$  when Cp' is

$C_5H_5$ , to  $1899\text{ cm}^{-1}$  when  $Cp'$  is  $C_5Me_5$ , a spread of only  $33\text{ cm}^{-1}$ .<sup>5</sup> The averaged  $\nu_{CO}$  values for  $(C_5H_4SiMe_3)_2Zr(CO)_2$ ,  $(C_5HMe_4)_2Zr(CO)_2$ , and  $(C_5Me_5)_2Zr(CO)_2$  of  $1929\text{ cm}^{-1}$ ,  $1904\text{ cm}^{-1}$  and  $1899\text{ cm}^{-1}$ , respectively, are of interest with regards to the CO adducts described in this article. It is noteworthy that the difference in  $\nu_{CO}$  between the  $C_5HMe_4$  and  $C_5Me_5$ -derivatives is only  $5\text{ cm}^{-1}$ , whereas the difference in the  $Cp'_3U(CO)$  adducts is  $42\text{ cm}^{-1}$  and  $\Delta\nu_{CO}$  is larger when  $Cp'$  is  $C_5HMe_4$  than when it is  $C_5Me_5$ . The small effect on  $\nu_{CO}$  observed in the zirconocene case is due to the fact that the d-orbitals in the bent sandwich zirconocenes that are available for bonding to CO are non-bonding relative to the  $Cp'$  ligands and therefore the small substituent effect is expected.<sup>6</sup> Conversely, the larger substituent effect observed in the  $Cp'_3U(CO)$  adducts implicates the importance of the  $Cp'_3U$ -bonding orbitals in bonding to CO, a thesis that will be developed in this article.

Carbon monoxide adducts have been postulated in several reactions between CO and uranium compounds. For example, a CO adduct is postulated to precede methyl migration in the conversion of  $Cp'_3UR$  to  $Cp'_3U(COR)$ .<sup>7</sup> Recently, Cloke and co-workers have shown that CO can be cyclotrimerized or tetramerized by complexes of the general type  $(C_8H_8)U(Cp')$  and these reaction presumably begin by adduct formation.<sup>8</sup> More recently, these authors have calculated that the value of  $\nu_{CO}$  in the hypothetical adduct  $(C_8H_8)U(C_5H_5)(CO)$  is lowered by  $243\text{ cm}^{-1}$ , a value identical to that observed in  $(C_5HMe_4)_3U(CO)$ .<sup>9</sup> Thus, the specific model developed in this article for binding of CO to the  $Cp'_3U$  fragment is of general applicability and interest.

### Computational Details

Although the electronic structures of these U(III) complexes are best described by a multiconfigurational method, DFT calculations with hybrid functionals such as B3PW91 and B3LYP have been validated by comparison with CCSD(T) or CASSCF calculations for various uranium complexes.<sup>10</sup> In addition, the calculated distances between the actinide atom and the ligands vary little with the electronic state of the complex<sup>10b,11</sup> and vibrational frequencies calculated by DFT methods agree well with those calculated with other methods as well as with experimental values.<sup>12</sup> For these reasons, DFT calculations are used in this article.

The Stuttgart-Dresden-Bonn small core quasi-Relativistic Effective Core Potential (RECP) has been used to represent the 60 core electrons of U, leaving 32 electrons in the 5s, 5p, 5d, 6s, 6p, 5f, 6d, and 7s orbitals outside of the core which are represented with the associated basis set, including up to g functions.<sup>13</sup> This ECP will be referred as the 32 electron ECP. This ECP is associated with a large basis 12s11p10d8f1g contracted in 8s7p6d4f1g. Carbon and oxygen of the CO ligand have been represented with an all-electron 6-311G\* basis set.<sup>14a</sup> Carbon and hydrogen of the Cp' rings have been represented by an all-electron 6-31G(d, p) basis set.<sup>14b</sup> Silicon has been treated with a large core RECP and the adapted 4s3p1d basis set,<sup>15</sup> augmented by a polarization d function ( $\exp = 0.284$ ). Calculations have been carried out at the DFT(B3PW91) level<sup>16</sup> at the unrestricted Kohn-Sham (UKH) level with Gaussian 03.<sup>17</sup> Optimization of geometry was carried out in  $C_1$  symmetry without any constraint and the nature of the extrema as minima was verified with analytical calculations of frequencies. There was no spin contamination as shown by the value of  $\langle S^2 \rangle$  which is calculated to be 3.7502 for the base-free complexes and the CO adducts, equal to the ideal eigenvalue of  $15/4$  ( $s(s+1)$  for  $s = 3/2$ ) for U(III) complexes with 3 unpaired electrons. As will be discussed later, these 3 unpaired electrons are in essentially pure 5f orbitals. Spin-orbit coupling corrections were not introduced because they are unlikely to influence the structures and vibrational frequencies in the present systems.<sup>10i,j</sup> The calculated unscaled CO frequencies are given in the Supporting Information and only the differences in the values relative to free CO are reported. The population analysis was carried out with the NBO methodology,<sup>18a</sup> which has been found appropriate in various uranium complexes<sup>10c,18b</sup> even if some modifications have been suggested.<sup>18c</sup> Additional restricted SCF calculations were carried out with an 11 electron ECP<sup>19</sup> in which the 5f orbitals are part of the effective core potential.

## Results

The results of the calculated geometries of the base-free Cp'<sub>3</sub>U compounds are presented followed by the geometries of the CO adducts. The calculated change in  $\nu_{\text{CO}}$  for the various adducts and the NBO analysis of the charges follows. The structure for the base-free complexes, (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>U, (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U, (C<sub>5</sub>HMe<sub>4</sub>)<sub>3</sub>U, (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U, and the corresponding CO complexes (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>U(CO), (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U(CO), (C<sub>5</sub>HMe<sub>4</sub>)<sub>3</sub>U(CO), (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U(CO), have been optimized with

the 32 electron ECP for uranium and relevant distances and angles are shown in Tables 1 and 2 for the base-free complexes and the CO adducts, respectively.

### The Cp'<sub>3</sub>U Fragments

In the four base-free complexes, the uranium atom is located at the vertex formed by intersection of the lines defined by the centroid of the Cp'-rings so that the geometry is trigonal planar and the idealized symmetry is  $D_{3h}$ . The basal plane of the Cp'<sub>3</sub>U fragment is the plane defined by the centroids of the three Cp' ligands. The cyclopentadienyl rings are essentially planar with a slight envelope distortion as indicated by the unequal U-C distances to each of the cyclopentadienyl rings. However, these distortions are small and uranium is most reasonably described as being surrounded by three regular pentagonal rings perpendicular to the basal plane, as shown in Figure 1 for (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>U. The calculations are carried out without symmetry constraints and the range in the resulting U-C distances is indicated by the average deviation from the mean (value in parentheses); the averaged U-C and U-ring centroid (U-C<sub>n</sub>) distances are listed in Table 1. Comparison with the X-ray crystal structures is good to excellent for all of the derivatives except that of C<sub>5</sub>H<sub>5</sub>, whose crystal structure is unknown. The calculated distance between uranium and the cyclopentadienyl ligand increases slightly in the order C<sub>5</sub>H<sub>5</sub> < C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub> < C<sub>5</sub>HMe<sub>4</sub> < C<sub>5</sub>Me<sub>5</sub> and the experimental distances follow a similar order.

| Ligand  |                   | U-C <sub>ave</sub> <sup>a</sup> | U-C <sub>n</sub> <sub>ave</sub> <sup>b</sup> |
|---|-------------------|---------------------------------|--|
|   |                   | Å                               | Å  |
| C <sub>5</sub> H <sub>5</sub>                   | calc              | 2.77(1)                         | 2.49   |
|   | exp               | NA <sup>c</sup>                 | NA <sup>c</sup>                              |
| C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> | calc              | 2.78(2)                         | 2.50   |
|   | exp <sup>20</sup> | 2.78(4)                         | 2.51   |
| C <sub>5</sub> HMe <sub>4</sub>                 | calc              | 2.83(5)                         | 2.56   |
|   | exp <sup>3b</sup> | 2.79(5) <sup>d</sup>            | 2.52   |
| C <sub>5</sub> Me <sub>5</sub>                  | calc              | 2.87(3)                         | 2.60   |
|   | exp <sup>21</sup> | 2.84(4) <sup>e</sup>            | 2.58   |

**Table 1:** Calculated and experimental bond lengths in (C<sub>5</sub>H<sub>n</sub>R<sub>5-n</sub>)<sub>3</sub>U. a) The averaged values are followed by the average deviation from the mean in parentheses. b) C<sub>n</sub> is

the cyclopentadienyl-ring centroid. c) Not available. d) The averaged U-C distance is different from that quoted in ref 3b, 2.77(5) Å, since six U-C distances are not reported in the Table of bond distances in the CCDC; however all 15 U-C distances are available from the cif in the CCDC. The range of U-C distances in (C<sub>5</sub>HMe<sub>4</sub>)<sub>3</sub>U is 2.772 Å to 2.861 Å. e) The range of U-C distances in (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U is 2.813(4) Å to 2.920(3) Å where the values in parentheses are the estimated standard deviation.

| Ligand  |                   | U-C <sub>ave</sub><br>(Å) <sup>a</sup> | U-Cn <sub>ave</sub><br>(Å) <sup>b</sup> | U-C(CO)<br>(Å) <sup>c</sup> | d<br>(Å) <sup>d</sup> | α <sub>ave</sub><br>(°) | Δν(CO) <sup>e</sup><br>cm <sup>-1</sup> | ΔE <sup>f</sup><br>kcal mol <sup>-1</sup> |
|---|-------------------|--|---|-----------------------------|-----------------------|-------------------------|---|---|
| C <sub>5</sub> H <sub>5</sub>                   | calc              | 2.77(1)                                | 2.49                                    | 2.38                        | 0.18                  | 94                      | -180                                    | 21.6                                      |
|   | exp               | NA <sup>h</sup>                        |   |                             |                       |                         |   |   |
| C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> | calc              | 2.78(2)                                | 2.50                                    | 2.41                        | 0.17                  | 94                      | -195                                    | 14.3                                      |
|   | exp <sup>3b</sup> | NA <sup>h</sup>                        | NA <sup>h</sup>                         | NA <sup>h</sup>             | NA <sup>h</sup>       | NA <sup>h</sup>         | -167                                    | 10 <sup>g</sup>                           |
| C <sub>5</sub> HMe <sub>4</sub>                 | calc              | 2.82(6)                                | 2.55                                    | 2.34                        | 0.12                  | 92                      | -241                                    | 17.7                                      |
|   | exp <sup>3</sup>  | 2.80(5) <sup>i</sup>                   | 2.53                                    | 2.383(6)                    | NA <sup>h</sup>       | 91.1                    | -243                                    | NA <sup>h</sup>                           |
| C <sub>5</sub> Me <sub>5</sub>                  | calc              | 2.87(2)                                | 2.60                                    | 2.34                        | 0.06                  | 91                      | -221                                    | 22.3                                      |
|   | exp <sup>4</sup>  | 2.87(4) <sup>j</sup>                   | 2.59                                    | 2.485(9)                    | NA <sup>h</sup>       | 90.0                    | -218                                    | NA <sup>h</sup>                           |

**Table 2:** Calculated and experimental bond lengths and stretching frequencies for (C<sub>5</sub>H<sub>n</sub>R<sub>5-n</sub>)<sub>3</sub>U(CO). a) The averaged values are followed by the average deviation from the mean in parentheses. b) Cn is the cyclopentadienyl-ring centroid. c) Values in parentheses are the estimated standard deviation d) Distance of the uranium atom from the plane defined by the three Cn's. e) Difference between the free and coordinated CO stretching frequencies in solution; free ν<sub>CO</sub> is 2143 cm<sup>-1</sup> (exp, gas phase) and 2175 cm<sup>-1</sup> (calc). f) Bond dissociation energy of CO from (C<sub>5</sub>H<sub>n</sub>R<sub>5-n</sub>)<sub>3</sub>U(CO). g) Experimental CO dissociation enthalpy at 25°C.<sup>22</sup> h) Not available. i) The averaged U-C distance is different from that quoted in ref 3b, 2.772(6) Å, since four U-C distances are not reported in the Table of bond distances in the Supporting Information; however all 15 U-C distances are available from the cif in the CCDC. The range of U-C(Cp) distances in (C<sub>5</sub>HMe<sub>4</sub>)<sub>3</sub>U(CO) is 2.711(6) to 2.890 Å where the value in parentheses is the estimated standard deviation. j) The range of U-C(Cp) distances in (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U(CO) is 2.821(2) to 2.927(3) Å where the values in parentheses are the estimated standard deviations.

## The CO Adducts

A small structural change results when the CO adduct forms. The metal moves only slightly out of the basal plane towards the CO ligand and the complexes have idealized  $C_{3v}$  symmetry. For ease of description, any atom or group of atoms proximal to CO is said to be above the basal plane and therefore any atom or group of atoms distal from CO is below the basal plane.

In  $(C_5H_5)_3U(CO)$ , the metal is 0.18 Å above the basal plane and each cyclopentadienyl ligand is almost perpendicular to the basal plane (Figure 1). The metal is equidistant from the centers of the three cyclopentadienyl rings at 2.49 Å, and the U-C average distance is 2.77 Å. However, the U-C distance to the carbons below the basal plane are slightly shorter, 2.74 Å, than those above the basal plane, 2.78 Å. Accordingly, the carbon atoms in the cyclopentadienyl rings below the plane are slightly tilted inwards. The U-C(CO) distance is 2.376 Å and the CO distance is 1.155 Å.

In  $(C_5H_4SiMe_3)_3U(CO)$ , the three rings are also almost perpendicular to the basal plane with two  $SiMe_3$ -groups below and one above the basal plane (Figures showing the geometry for this and related structures are available as Supporting Information). The  $Me_3Si$ -substituted carbon atom is further away from uranium than are the unsubstituted carbons. Consequently, the inward tilt of the cyclopentadienyl rings below the basal plane is seen only for the ring in which the  $SiMe_3$ -group is above the plane. The average distance between uranium and Cn is 2.50 Å. The metal is 0.17 Å above the basal plane and 2.5 Å from the center of each of the cyclopentadienyl rings. The  $SiMe_3$ -group is bent slightly away from uranium with an average Cn-C-Si angle of  $166^\circ$ . The U-C(CO) distance is 2.408 Å and the CO distance is 1.154 Å. The U-C-O angle is  $175^\circ$  and the CO ligand is directed away from the proximal  $SiMe_3$ -group.

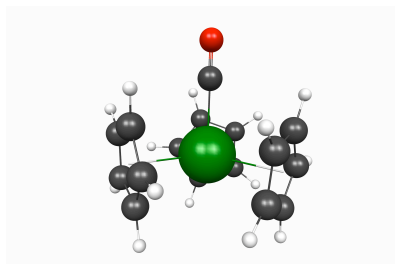
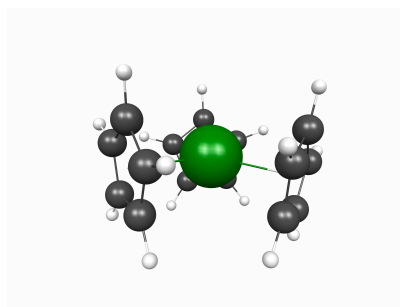




Figure 1. Optimized structures for  $(C_5H_5)_3U$  and  $(C_5H_5)_3U(CO)$

In  $(C_5HMe_4)_3U(CO)$ , the three  $C_5HMe_5$  rings are arranged such that one ring has the CH bond in the basal plane and the other two have their CH bonds below that plane. The relative orientation of the CH bonds does not correspond to that found in the crystal structure, where the three CH bond are related to each other by a  $C_3$  symmetry axis. The distances from uranium to the carbon atoms bonded to a methyl group are longer than those to the carbon atom of the CH group. In addition, the U-C distance is shorter to the carbons below the basal plane (2.76 to 2.80 Å) than to the carbons above the plane (2.80 to 2.90 Å). The average distance between uranium and Cn is 2.55 Å; uranium is 0.12 Å above the basal plane, the U-C(CO) distance is 2.34 Å and the CO distance is 1.16 Å.

In  $(C_5Me_5)_3U(CO)$ , the three rings are perpendicular to the basal plane. The U-C distance of 2.60 Å is the longest in all of the complexes studied, as is the average U-C distance of 2.87 Å. As in the other complexes, the carbon atoms below the basal plane are slightly closer to uranium than those above the basal plane (2.82 Å vs. 2.89 Å). The uranium atom is only 0.06 Å above the basal plane; the U-C(CO) distance is 2.34 Å and the CO distance is 1.16 Å.

Comparison between the calculated structures and the crystal structures is limited to the  $C_5HMe_4$  and  $C_5Me_5$ -derivatives. The calculations reproduce the experimental trend that the  $C_5HMe_4$  rings are closer to uranium than those in the  $C_5Me_5$  structure and the calculated distances are in reasonable agreement with the experimental values. The calculated U-C(CO) distances for  $C_5HMe_4$  and  $C_5Me_5$  are equal, which contrasts with the experimental values where CO is about 0.1 Å closer to uranium in the  $C_5HMe_4$ -derivative. The calculations show that the U-C(CO) bond lies in a shallow potential energy well resulting in a rather large spread in the U-C(CO) distances.

In all of the complexes, the coordination of CO only weakly perturbs the geometry of the  $Cp'_3U$  fragment. The average distance between the rings and uranium is not changed on coordination of CO. The tendency of the cyclopentadienyl rings to move slightly closer to uranium for atoms below the basal plane and away from uranium atom for those carbons above the basal plane is very slight and decreases when the hydrogen atom on the carbon below the plane is substituted by a Me group. The tendency for uranium to move out of the basal plane is larger for  $C_5H_5$  and

C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub> since the C<sub>5</sub>H<sub>5</sub> and C<sub>5</sub>H<sub>4</sub>R rings have more rotational degrees of freedom than the more heavily substituted cyclopentadienyl rings.

### The CO Stretching Frequencies

The differences between the calculated, unscaled CO stretching frequencies for the adducts and free CO are shown in Table 3; the calculated, unscaled CO stretching frequencies for all of the adducts are given in the Supporting Information. In all systems, the calculated  $\nu_{\text{CO}}$  is less than that of free  $\nu_{\text{CO}}$  and the trend is in good agreement with the experimental values. Setting aside the case of C<sub>5</sub>H<sub>5</sub>, for which experimental information is not available, the  $\nu_{\text{CO}}$  frequencies decrease from C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub> to C<sub>5</sub>Me<sub>5</sub> and to C<sub>5</sub>HMe<sub>4</sub>. The experimental values range from -167 cm<sup>-1</sup> for C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub> to -243 cm<sup>-1</sup> for C<sub>5</sub>HMe<sub>4</sub>, while the calculated values range from -194 cm<sup>-1</sup> to -241 cm<sup>-1</sup>. Thus, the agreement between experimental and calculated values is good to excellent as is the trend. The C<sub>5</sub>H<sub>5</sub> complex gives the smallest lowering of  $\nu_{\text{CO}}$  relative to that of free CO.

The bond dissociation energies of CO in these Cp'<sub>3</sub>U(CO) complexes are given in Table 2. It is somewhat paradoxical that the largest lowering in the CO stretching frequencies is not associated with the largest bond dissociation energy but calculation of accurate bond dissociation requires, most probably, a higher level of calculation.<sup>23</sup> The calculations show that the binding energy of CO to these uranium complexes ranges from 15 to 20 kcal mol<sup>-1</sup> which is in fair agreement with an estimation of 10 kcal mol<sup>-1</sup> for the bond dissociation enthalpy in (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U(CO).<sup>22</sup>

In order to identify the role played by the 5f electrons in the lowering of  $\nu_{\text{CO}}$ , calculations were carried out with the large core 11 electron effective core potential in which the 5f orbitals are included in the core. These results are shown in Table 3. Geometry optimization with 11 electron ECP gives complexes with the same overall geometry but the uranium-ligand distances are too long. The distance from uranium to C<sub>n</sub> increases by up to 0.4 Å in the case of C<sub>5</sub>Me<sub>5</sub>. However the trends found with the 32 electron ECP of an increase in the U-C(Cp') distance from C<sub>5</sub>H<sub>5</sub> to C<sub>5</sub>Me<sub>5</sub> is also found with the 11 electron ECP. The U-C(CO) distance is also longer by up to 0.2 Å with the 11 electron ECP. The metal-ligand interaction is thus significantly less with the 11 electron ECP than with the 32 electron ECP, showing that the 5f electrons are

essential to reproduce the bond distances. A surprising result of the calculations with the 11 electron ECP is that the  $\nu_{\text{CO}}$  values are calculated to be lower than that of free CO for all of the complexes;  $\Delta\nu_{\text{CO}}$  ranges from -25 to -83  $\text{cm}^{-1}$  for  $\text{C}_5\text{H}_5$  and  $\text{C}_5\text{Me}_5$ , respectively. The trend is similar to that calculated with the 32 electron ECP with  $\text{C}_5\text{H}_5$  giving the smallest lowering in  $\nu_{\text{CO}}$  and the methylated cyclopentadienyl complexes giving the highest values. However,  $\nu_{\text{CO}}$  for  $\text{C}_5\text{HMe}_4$  and  $\text{C}_5\text{Me}_5$  are not ordered in the same manner by the two ECPs; a greater lowering for  $\text{C}_5\text{HMe}_4$  relative to  $\text{C}_5\text{Me}_5$  is found with the 32 electron ECP, which is also in agreement with the experimental observation, is not obtained with the 11 electron ECP. Because of the significant difference in geometries between the 32 electron and the 11 electron ECP results, the  $\nu_{\text{CO}}$  stretching frequency was also calculated with the 11 electron ECP at the geometry optimized with the 32 electron ECP. In principle, frequencies should only be calculated at the stationary point where the first derivative of the energy is zero. However, calculation of the frequencies at the 32 electron geometry gives exclusively positive frequencies, which suggests that the potential energy surface associated with the U-C(CO) distance is flat.<sup>24</sup> Under these circumstances, the calculated frequencies are only qualitatively correct. The shortening of the U-C(CO) distance lowers  $\nu_{\text{CO}}$ ; the values are close to those obtained with the 32 electron ECP but with an order reversal for  $\text{C}_5\text{H}_5$  and  $\text{C}_5\text{H}_4\text{SiMe}_3$ . While the 11 electron ECP is clearly not appropriate for accurate calculation of frequencies, the small core ECP with a large number of explicitly treated electrons is needed for quantitative reproduction of experimental parameters, these calculations clearly show that the 5f orbitals are not solely responsible for the lowering of  $\nu_{\text{CO}}$  in these adducts.

| Ligand                              | $\Delta\nu_{\text{CO}}^{\text{a}}$<br>$\text{cm}^{-1}$ | $\Delta\nu_{\text{CO}}^{\text{b}}$<br>$\text{cm}^{-1}$ | $\Delta\nu_{\text{CO}}^{\text{c}}$<br>$\text{cm}^{-1}$ | U-C $n_{\text{ave}}^{\text{d}}$<br>(Å) | U-C(CO) <sup>d</sup><br>(Å) | $d^{\text{d}}$<br>(Å) | $\alpha_{\text{ave}}^{\text{d}}$<br>(°) |
|-------------------------------------|--|--|--|--|-----------------------------|-----------------------|---|
| $\text{C}_5\text{H}_5$              | -180   | -170   | -25  | 2.57                                   | 2.67                        | 0.24                  | 95                                      |
| $\text{C}_5\text{H}_4\text{SiMe}_3$ | -195   | -169   | -48  | 2.60                                   | 2.59                        | 0.09                  | 91                                      |
| $\text{C}_5\text{HMe}_4$            | -241   | -230   | -81  | 2.67                                   | 2.53                        | 0.06                  | 90                                      |
| $\text{C}_5\text{Me}_5$             | -221   | -224   | -83  | 3.00                                   | 2.55                        | 0.11                  | 91                                      |

**Table 3:** Calculated difference between free and coordinated CO stretching frequencies and bond distances and angles in  $(\text{C}_5\text{H}_n\text{R}_{5-n})_3\text{U}(\text{CO})$  using 32 or 11

electron ECPs on uranium. a) Difference for the geometry optimized with 32 explicitly treated electrons. b) Same geometry as in a), but obtained with 11 electrons treated explicitly. c) Difference for the geometry optimized with 11 explicitly treated electrons. d) Optimized bond distances and angles found with 11 explicitly treated electrons. The symbols and abbreviations are as defined in Table 1.

### The NBO analysis

The charges on atoms and groups obtained from an NBO analysis are given in Table 4. In the base-free complexes, the calculations show that the negative charge accumulated on the cyclopentadienyl rings increases from  $C_5H_5$  to  $C_5Me_5$ , hence the more substituted cyclopentadienyl ligand carries more electron density. The positive charge on the uranium atom varies in the same direction. Upon coordination of CO, electron density accumulates on CO at the expense of a decrease of electron density on the cyclopentadienyl ring. The charge on the metal becomes less positive but changes little relative to that in the base-free  $Cp'_3U$  compounds. The largest change in electron density on uranium is in the  $(C_5H_4SiMe_3)_3U$  fragment,  $0.09 e^-$ , and the smallest changes,  $0.04$  and  $0.05 e^-$ , are found in the  $(C_5HMe_4)_3U$  and  $(C_5Me_5)_3U$  fragments. The key result that emerges from the NBO analysis is that significant electron density is transferred from the cyclopentadienyl ligands to the CO ligand. In the  $C_5HMe_4$  case, the cyclopentadienyl ligands lose  $0.31 e^-$ ,  $0.27$  of which are acquired by CO and the remainder is localized on the uranium atom. Somewhat smaller, but still significant, transfer of electron density is found for the  $C_5H_5$ -derivative where  $0.27 e^-$  is lost by the ligands,  $0.19$  of which is acquired by CO. The highest amount of density on CO is obtained with the methylated cyclopentadienyl rings and this is associated with the greatest lowering of  $\nu_{CO}$  as the density is located in the  $2 \pi^*$  orbitals of CO. However, the relation between electron density acquired by CO and  $\nu_{CO}$  stretching frequency is not monotonous since the density on CO is higher in  $(C_5H_4SiMe_3)_3U(CO)$  than in  $(C_5H_5)_3U(CO)$  (Table 4) but  $\nu_{CO}$  is higher for the former (Table 3). Thus, the extent of the lowering of  $\nu_{CO}$  is not a simple function of the increase of electron density on the CO ligand but is a reflection on the nature of the U-CO bond that is composed of  $\sigma$ -donor and  $\pi$ -acceptor components as well as an electrostatic interaction. Since these components change  $\nu_{CO}$  in opposite directions,  $\nu_{CO}$  does not depend only on the change in density on CO.<sup>25</sup>

| Ligand         | $(C_5H_nR_{5-n})_3U$ |         | $(C_5H_nR_{5-n})_3U(CO)$ |         |            |
|----------------|----------------------|---------|--------------------------|---------|------------|
|                | $q_L^a$              | $q_U^b$ | $q_L^a$                  | $q_U^b$ | $q_{CO}^c$ |
| $C_5H_5$       | -2.24                | 2.24    | -1.97                    | 2.16    | -0.19      |
| $C_5H_4SiMe_3$ | -2.28                | 2.28    | -2.03                    | 2.19    | -0.16      |
| $C_5HMe_4$     | -2.30                | 2.30    | -1.99                    | 2.26    | -0.27      |
| $C_5Me_5$      | -2.35                | 2.35    | -2.04                    | 2.30    | -0.26      |

**Table 4** : NBO charges on  $(C_5H_nR_{5-n})_3U$  and  $(C_5H_nR_{5-n})_3U(CO)$ . a) Charge on the three  $C_5H_nR_{5-n}$  ligands. b) Charge on the uranium atom. c) Charge on the CO ligand.

## Discussion

### *General*

The quality of the calculations described in this article is judged by how well the calculated change in  $\nu_{CO}$ ,  $\Delta\nu_{CO}$  is the difference between the stretching frequency of free CO and that of CO in  $Cp'_3U(CO)$ , reproduce the experimental values. The agreement is good to excellent, Table 2, for all the  $Cp'_3U(CO)$  complexes when uranium is calculated with a small core quasi-relativistic effective core potential in which 32 electrons in the 5s, 5p, 5d, 6s, 6p, 5f, 6d, and 7s orbitals are explicitly treated. The long computer time spent in getting closer agreement with experiment is therefore justified. In addition, the calculated trends in geometrical parameters associated with the  $Cp'_3U$  fragments are also reproduced well with an ECP where 32 electrons are explicitly treated, when the statistical variation in the individual U-C distances, expressed as the average deviation from the mean, are taken into account. The calculated U-C(CO) distances, however, are shorter than the experimental values in the two examples known.

The NBO charges, and how they change on going from the base-free compounds to the CO adducts, are more important than the bond length and angles changes, since the model that is proposed addresses how charge density is redistributed on adduct formation. In the base-free compounds, the negative charge on the three  $Cp'$ -rings, which is equal to the positive charge on the uranium atoms,

becomes less negative on CO coordination by 0.26 to 0.31  $e^-$ . Concomitant with the loss of charge density from the  $\text{Cp}'_3\text{U}$  fragment is the increase in charge density in the CO group of 0.16 to 0.27  $e^-$ . The charge transfer, reflected by  $\Delta\nu_{\text{CO}}$ , is reproduced by the change in NBO charges on the CO adducts with the exception of the  $\text{C}_5\text{H}_4\text{SiMe}_3$ -derivative. In the latter complex, the increase in charge density on the CO ligand is larger than for the  $\text{C}_5\text{H}_5$ -derivative but  $\nu_{\text{CO}}$  is lower in the  $\text{C}_5\text{H}_5$  system. The change in charge density also shows that the charge on the uranium atom becomes less positive in the adducts by a smaller amount, 0.04 to 0.08  $e^-$ , showing that the largest charge redistribution occurs between the cyclopentadienyl ligands and the CO ligand. These calculated NBO charges are qualitative guides of the charge redistribution on adduct formation but, as mentioned earlier, their relation with  $\nu_{\text{CO}}$  is not a simple function. The NBO charges therefore reflect the charge density that is transferred into the two  $\pi^*$  orbitals on CO from  $\pi$ -symmetry orbitals on the  $\text{Cp}'_3\text{U}$  fragment and the only  $\pi$ -symmetry orbitals that are available are those used to construct the U-Cp' bonds. The non-bonding 5f orbitals on the  $\text{Cp}'_3\text{U}$  fragment of  $f_\sigma$ ,  $f_\delta$  and  $f_\phi$  symmetry cannot mix with  $\pi^*_{\text{CO}}$  orbitals by symmetry and therefore are not involved in  $\pi$ -backbonding.

### The Model

The symmetry orbitals used to construct the  $\text{Cp}_3\text{U}$  molecule have been given by Tatsumi<sup>26</sup> and Bursten in  $D_{3h}$  symmetry.<sup>27</sup> Since the maximum symmetry in the CO adduct is  $C_{3v}$ , the  $C_{3v}$  symmetry labels for the 15  $p_\pi$  orbitals for the planar  $\text{C}_5\text{H}_5$ -ligand symmetry adapted linear combinations (SALC's) are factored into  $\pi_1$  and  $\pi_2$  sets. The  $\pi_1$  set, not shown in Figure 2, comprises the  $a_1 + e$  combinations that are localized on the Cp-orbitals, are non-bonding with respect to the uranium atomic orbitals and are occupied by 6 electrons. The  $\pi_2$  set comprises the  $a_1 + a_2 + 2e$  irreducible representations that are involved in making the U-Cp bonds. The  $\pi_2$  set can overlap with the s, d and f uranium atomic orbitals of  $\pi$ -symmetry. In axial symmetry, they are the  $7s_\sigma$ ,  $5f_\phi$ ,  $5f_\pi$  and  $6d_\pi$  orbitals, which are color-coded as green, black and red, respectively, in Figure 2. These orbitals are filled with 12 paired electrons and the remaining three electrons enter the four non-bonding f-orbitals of  $5f_\sigma$ ,  $5f_\delta$  and  $5f_\phi$  symmetry, which are color-coded as green, blue and black, respectively. The electron configuration for the  $\text{Cp}'_3\text{U}$  compounds is thus  $5f^3$ ,

consistent with experimental magnetic susceptibility data for trivalent uranium compounds.<sup>28</sup>

When CO interacts with the Cp'<sub>3</sub>U fragment, the 5σ lone pair of CO forms the σ-U(CO) bond with f<sub>σ</sub>, d<sub>σ</sub>, s<sub>σ</sub> uranium hybrid orbitals; in C<sub>3v</sub> symmetry, each of these orbitals transform as an a<sub>1</sub> representation. This interaction results in charge transfer from CO to the Cp'<sub>3</sub>U fragment, which increases ν<sub>CO</sub>.<sup>25</sup> The π\* orbitals on CO are involved in charge-transfer from the Cp'<sub>3</sub>U fragment orbitals of π-symmetry and these are the filled π-symmetry orbitals used to build the U-Cp' bonds. The two f<sub>δ</sub> and a single f<sub>φ</sub> orbitals, which are non-bonding relative to the U-Cp' bonds, cannot be used in backbonding, due to their symmetry, and therefore these f-orbitals are just locations for the three unpaired electrons.

The calculated ν<sub>CO</sub> values with the 11 electron ECP can be understood with this model. The interaction diagram in Figure 3 shows the importance of f<sub>σ</sub> in establishing the U-C(CO) σ-bond. When the 5f electrons are in the core, the U-C(CO) bond can only be made from the interaction of the 5σ CO orbital with the 6d<sub>z</sub><sup>2</sup> and 7s orbitals. Both of these orbitals are energetically far removed from the 5σ orbital, so they cannot interact strongly. Backbonding uses the filled π-symmetry orbitals of the Cp'<sub>3</sub>U fragment, which are largely ligand-based orbitals. These ligand-based orbitals exist even when the 5f orbitals are in the core; their metal contribution is now built from the 6d<sub>π</sub> set. Transfer of electron density to the π\* orbitals on CO is therefore possible, resulting in lowering of ν<sub>CO</sub> when the 11 electron ECP is used. Calculations of the CO stretching frequencies, at the 32 electron ECP geometry, shortens all of the uranium to ligand distances, which allows more transfer of electron density to the π\* of CO due to greater overlap and also qualitatively rationalizes why Δν<sub>CO</sub> is greater in the CO complexes of (C<sub>5</sub>HMe<sub>4</sub>)U than (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U.

The bond model advanced in this article is thus very different from that elaborated by Bursten and coworkers for Cp<sub>3</sub>U(CO) since their model involves backbonding from the non-bonding f-parentage orbitals.<sup>2</sup> In this model, the observed ν<sub>CO</sub> values should be affected only slightly by the substituents on the cyclopentadienyl ligands although ν<sub>CO</sub> is not calculated. Further, the X<sub>α</sub> calculations show that the three 5f electrons are in a doubly degenerate orbital, resulting in a Jahn-Teller active low-spin complex.

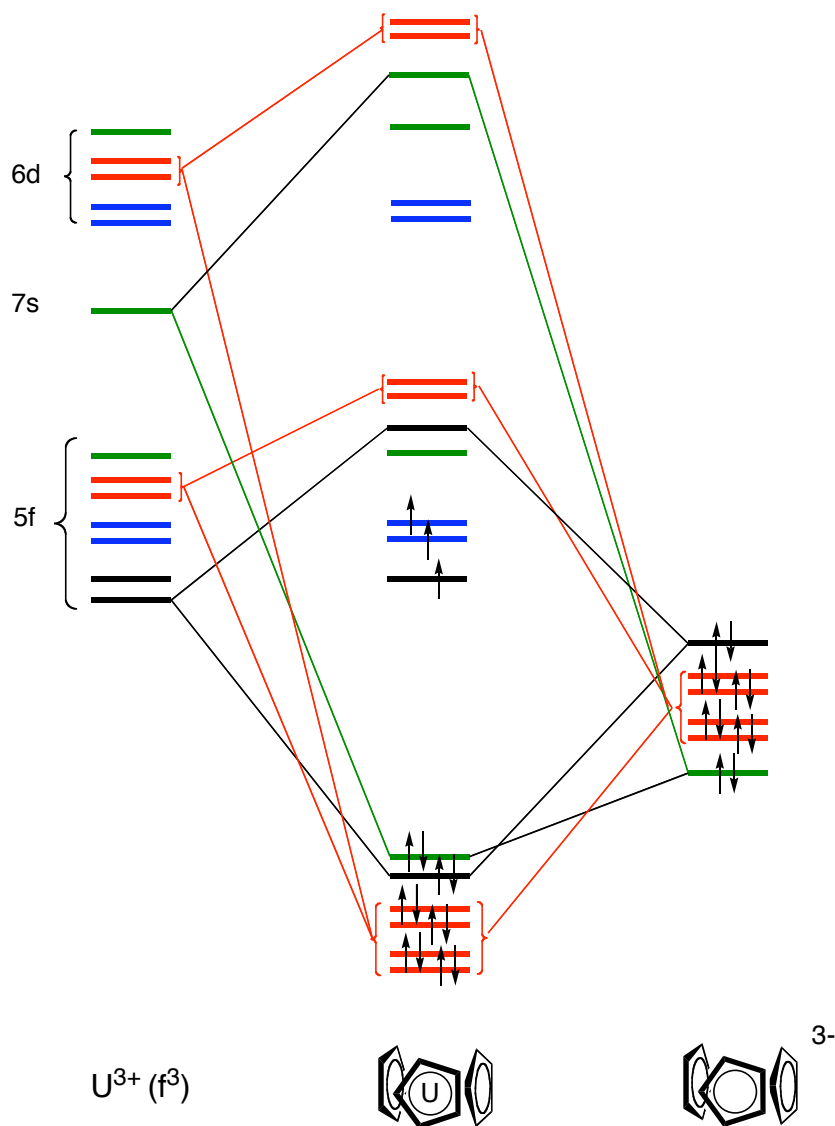
The bond model developed in this article provides a rationalization for the substantial effect that the substituents on the cyclopentadienyl rings have on the observed CO stretching frequency. The model can be extended to rationalize the lack of CO bonding to the tri-cyclopentadienyl lanthanide compounds  $(C_5H_4SiMe_3)_3M$  where M is Ce or Nd, an inference based upon the lack of an observed CO stretching frequency at room temperature,<sup>29</sup> and where the  $\pi_2$ -set of cyclopentadienyl  $p_\pi$ -ligand orbitals interact less well with the 4f and 5d symmetry orbitals than with the 5f and 6d symmetry orbitals on uranium compounds due to the smaller radial extension of the former,<sup>30</sup> and therefore the  $4f_\pi/5d_\pi$  set of orbitals in the  $Cp'_3M$  lanthanide complexes do not engage in transfer of  $\pi$ -electron density to the  $\pi^*$  orbitals of CO. This conjecture predicts that if the  $5f_\pi/6d_\pi$  orbitals are stabilized more than they are in the  $Cp'_3U$  fragment, the backbonding interaction with CO will be either weak or non-existent for other  $L_3U$  compounds. This is perhaps why  $U[N(SiMe_2)]_3$  does not bind CO.<sup>31</sup> Some quantitative information on the relative energies of the uranium-ligand orbitals energies is available from photoelectronic spectroscopy studies that supports, in a general way, these deductions.<sup>32</sup> The bond model advanced in this article also may be used to rationalize the increase in the calculated and observed  $\Delta\nu_{CO}$  for  $NdF_3(CO)$  of  $55\text{ cm}^{-1}$  and  $40\text{ cm}^{-1}$ , respectively<sup>33</sup> and the calculated value for  $UF_3(CO)$  of  $-151\text{ cm}^{-1}$ .<sup>33a</sup>

The model also accounts for the weak bond dissociation enthalpy of the U-C(CO) bonds. The only measured value of  $10\text{ kcal mol}^{-1}$  is for  $(C_5H_4SiMe_3)_3U(CO)$ ,<sup>22</sup> close to the calculated value of  $14\text{ kcal mol}^{-1}$ . Thus the U-C(CO) bond is weaker than those found in d-transition metallocene carbonyl derivatives; the measured CO bond dissociation enthalpy for  $(C_5Me_5)_2Zr(CO)_2$  and  $(C_5H_5)_2Ti(CO)$  are approximately  $40\text{ kcal mol}^{-1}$  even though the change in  $\nu_{CO}$  is greater in the f-metals.<sup>34</sup> The bond dissociation energy is not directly related to the change in  $\Delta\nu_{CO}$  which is a measure of the extent to which the  $\pi^*$  orbitals of CO are populated and does not address directly the sigma component of the bond. The bond strength is determined by the  $\sigma$  and  $\pi$ - interactions and therefore not susceptible to a simple physical picture.<sup>25</sup>

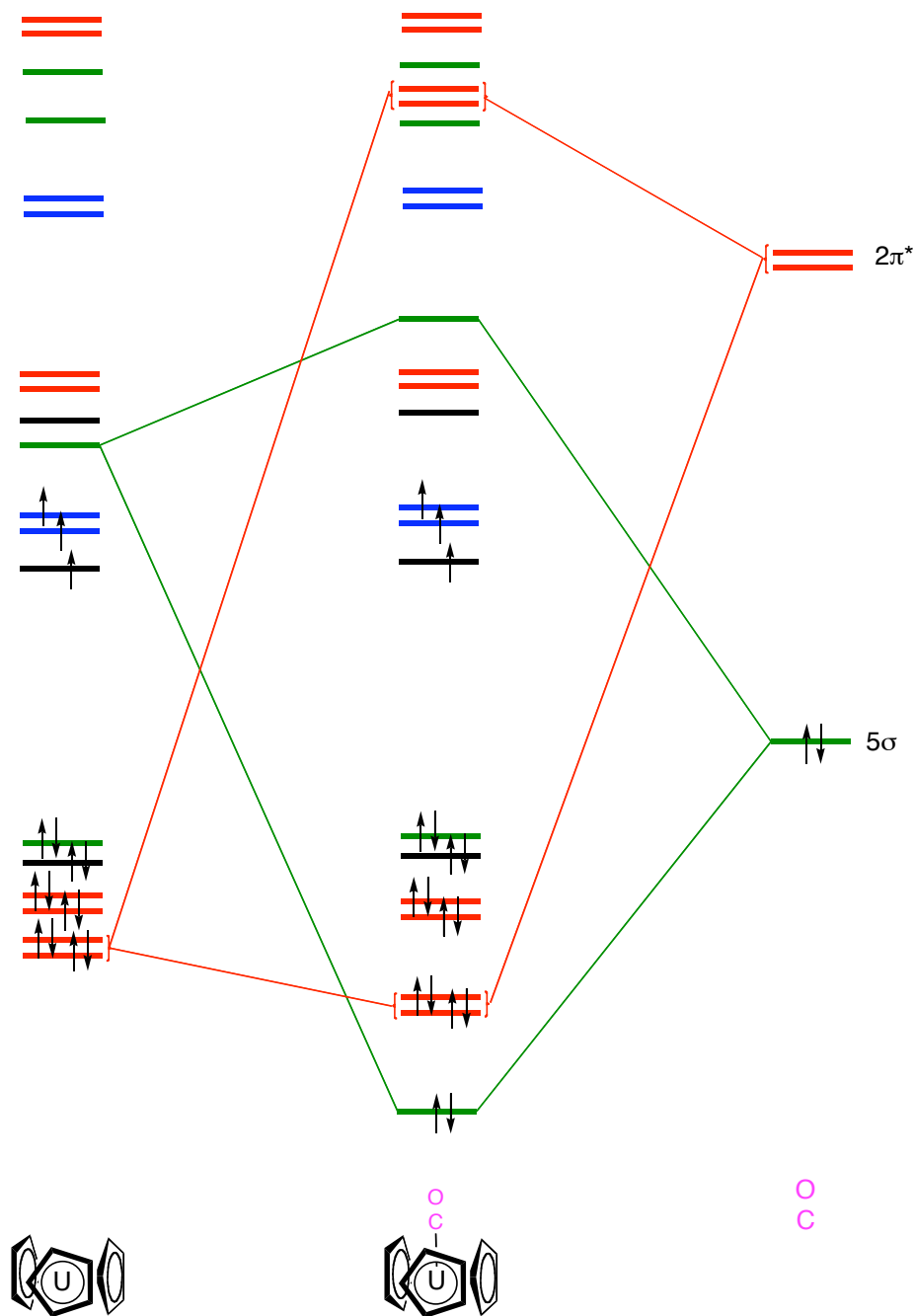
## Conclusion



The model advocated in this article for the lowered  $\nu_{\text{CO}}$ 's in  $\text{Cp}'_3\text{U}(\text{CO})$  complexes is distinctively different from that used to account for lowered  $\nu_{\text{CO}}$ 's in d-transition metal complexes. Although in each case, the  $\pi^*$  orbitals of CO are populated, in  $\text{Cp}'_3\text{U}(\text{CO})$  the electron density originates from the  $f_\pi$  and  $d_\pi$ -symmetry orbitals that are  $\text{Cp}'$ -U bonding, whereas in  $\text{Cp}'_2\text{M}(\text{CO})_x$  complexes of the d-transition metals the electron density is located in the  $\text{Cp}'_2\text{M}$  non-bonding d-orbitals. Although the model rationalizes the substituent effects on the value of  $\nu_{\text{CO}}$ , it provides only a qualitative physical picture as to how or why the order of  $\nu_{\text{CO}}$  lies in the order  $\text{C}_5\text{HMe}_4 > \text{C}_5\text{Me}_5 > \text{C}_5\text{H}_4\text{SiMe}_3$ . The model advocated in this article can be used to rationalize why the corresponding lanthanide complexes do not bind CO and why the actinide complexes with ligands whose filled U-L  $\pi$ -orbitals are stabilized relative to those in cyclopentadienyl ligands do not bind CO. Thus, the new model provides an adequate explanation for several chemical facts that were a mystery.



**Figure 2:** Qualitative symmetry orbital diagram for  $\text{Cp}_3\text{U}$  constructed from the uranium atomic orbitals and SALC  $p_\pi$ -orbitals of the  $\text{Cp}_3$  ligand orbitals derived from filled, degenerate  $\pi_2$  orbitals ( $\pi_1$  set is omitted). The color code: green are  $\sigma$ , red are  $\pi$ , blue are  $\delta$  and black are  $\phi$  orbitals. The bonding and antibonding interactions are indicated by connecting lines between fragment orbitals; the non-bonding uranium atomic orbitals do not have connecting lines.



**Figure 3.** Qualitative symmetry orbital diagram for the interaction of  $\text{Cp}_3\text{U}$  and  $\text{CO}$ . Only one set of  $\pi$ -symmetry SALC's is used in the back-bonding; as described in the text these orbitals have a mixed parentage as shown in Figure 2. The color code is identical to that used in Figure 2. The bonding and antibonding interactions are indicated by connecting lines between fragment orbitals, the non-bonding uranium orbitals do not have connecting lines.

**Supporting information:** List of x, y, z coordinates for all calculated structures with 32 electron ECP and 11 electron ECP, calculated unscaled CO frequencies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**BRIEFS** The backbonding from  $\text{Cp}'_3\text{U}$  to CO involves electrons in the U-Cp  $\pi$ -bonding orbitals of the  $d_\pi$  and  $f_\pi$ -parentage.

### TOC

