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Are the Carbon Monoxide Complexes of Cp_2M (M = Ca, Eu, or Yb) Carbon or Oxygen Bonded? An Answer from DFT Calculations

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The bonding in metal−CO adducts in which there is mimimal back-bonding is of considerable current calculational and experimental interest.[1] The CO adducts of Cp^*_2M (M = Ca, Sr, Eu, or Sm) are a member of this class since they show single CO stretching frequencies in their solution IR spectra that are shifted to higher energy than that of free CO (2136 cm^{-1}) in methylcyclohexane or toluene. The values of ν_{CO} are 2158 (M = Ca and Sr), 2150 (M = Eu), and 2153 cm^{-1} (M = Sm). On the other hand, the IR spectrum of Cp^*_2Yb contains two CO stretching frequencies, 2114 and 2072 cm^{-1}, both of which are lower in energy than that of free CO.[2,3] Studies of the equilibrium between $Cp_2{}^*Yb$ and CO as a function of CO pressure and temperature show that the 2114 cm^{-1} band is due to $Cp^*_2Yb(CO)$, while the 2072 cm^{-1} absorption is due to $Cp^*_2Yb(CO)_2$.[2b] The formation of the CO adducts is reversible and no structural information is available. Structural studies of the diisocyanide adducts of several ytterbocenes show that the geometries are unexceptional and solid-state and solution IR spectra of the metallocenes for Ca, Sr, Eu, and Yb show single absorption bands that are shifted to higher energy (+11 to +30 cm^{-1}) relative to that of free isocyanide depending upon the identity of the metal and the isocyanide.[2a,4] This paper reports DFT calculations on the model systems $Cp_2M(CO)_x$ for M = Ca, Eu (x = 1) and Yb (x = 1, 2) and $Cp_2Yb(CNMe)_2$.[5]

Table 1. Calculated and Experimentally Observed Values of the CO Stretching Frequencies (cm^{-1})

compd	calcd ν_{CO}	exptl
CO	2220	2136
$Cp_2Yb(CO)$	2232	$Cp^*_2Yb(CO)$ 2114[2a]
$Cp_2Yb(CO)_2$	2228, 2230	$Cp^*_2Yb(CO)_2$ 2072[2a]
$Cp_2Eu(CO)$	2238	$Cp^*_2Eu(CO)$ 2150[2b]
$Cp_2Ca(CO)$	2239	$Cp^*_2Ca(CO)$ 2158[3]
$Cp_2Yb(OC)$	2192	
$Cp_2Yb(OC)_2$	2188, 2190	
$Cp_2Eu(OC)$	2193	
$Cp_2Ca(OC)$	2195	
$Cp_2Yb(CO)(OC)$	2194, 2226	

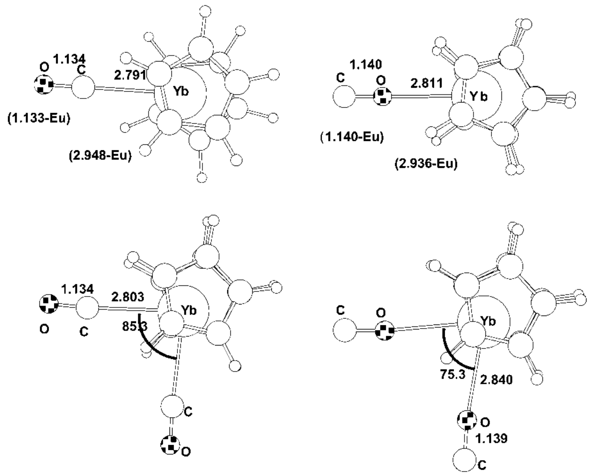

Figure 1. Optimized (B3PW91) structures (Å, deg) of $Cp_2Yb(CO)_{1,2}$. Values for $Cp_2Eu(CO)$ are given in parentheses.

The isocyanide adduct $Cp_2Yb(CNMe)_2$ was first examined to see if the calculated values of the CN stretching frequency and the geometry mirror the experimental system.[2a] The calculated CN stretching frequency of the 1:1 and 1:2 adducts increases by 18 and 15 cm^{-1}, respectively, relative to that of the calculated value for free MeNC. These values are in the range and direction observed, and more importantly, only one ν_{CN} is obtained for the isolated 1:2 adduct, which is in accord with the experimental results that were rationalized by the suggestion that coupling between the two vibrators is small. The calculated geometry of the 1:2 adduct is compared with that observed for $Cp^*_2Yb(CN\text{-}2,6\text{-}Me_2C_6H_5)_2$ (Supporting Information). The calculated geometry is in good agreement with the experimental result. This result is particularly important since the substituents are greatly simplified in the calculations. These results are extremely encouraging since they clearly imply that the calculations are reliable indicators of geometrical structure and ν_{CN} stretching frequencies and therefore the nature of the chemical bonds between the metallocene and the isocyanide ligands. We are therefore optimistic that the results for the carbonyl system will be trustworthy relative to ν_{CO} even though the experimental structures are unknown.

Due to the size of the systems the calculations of $Cp_2Eu(CO)$ with small effective core potential (ECP) could not be carried out but test calculations on smaller systems show the absence of back-donation from the f orbitals.[6] The calculated ν_{CO} for the CO adduct is 18 cm^{-1} higher in energy than that in free CO (calcd). This is in the correct direction for the value found for $Cp^*_2Eu(CO)$ and also for $Cp_2Ca(CO)$ (Table 1). The calculated geometry is shown in Figure 1.

The CO adducts of Cp_2Yb are treated similarly to the Cp_2Eu adducts described above. The net result is also similar in that back-donation is very small[6] and the calculated CO stretching frequencies for carbon-bound mono- and di-adducts are +12 and +9 cm^{-1}

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higher than that of free CO (calcd) as shown in Table 1. These calculated values are clearly in contradiction to the observed values of ν_{CO} in the 1:1 and 1:2 adducts of Cp^*_2Yb, which decrease upon coordination. It is important to note that only a single ν_{CO} is calculated for the 1:2 adduct as is found in the calculation for the isocyanide adducts.[7] The calculated geometry of the two carbon bound adducts is shown in Figure 1. The calculations clearly and unequivocally show that Cp_2Yb and Cp_2Eu should behave similarly toward CO, and this is *not the* experimental result for the Cp^*_2M adducts. What is wrong with the calculations? In search of an answer, the energies of several other structural isomers were calculated with the shocking result that the isomer with the oxygen bound CO is only slightly higher in energy (3 kcal.mol^{-1}) than that of the carbon-bound isomer for both the 1:1 and 1:2 adducts. The geometries are shown in Figure 1. More importantly the counterintuitive structures predict that ν_{CO} will decrease in energy for both adducts; the calculated ν_{CO} values for the 1:1 and 1:2 adducts are lower than that of free CO (calcd) by 28 and 31 cm^{-1}, respectively. Further, a single stretching frequency for the 1:2 adduct is calculated. These values are in agreement with the direction of the experimental values in the equilibrium reaction between Cp^*_2-Yb and CO which are reduced by 22 and 64 cm^{-1} relative to free CO (exptl). The calculated and observed magnitude of the shifts are in good agreement for the 1:1 adduct but rather less good for the 1:2 adduct. The calculated CO stretching frequencies for the hypothetical mixed isomer, $Cp_2Yb(CO)(OC)$, should have two absorptions, one of which is at a lower energy (26 cm^{-1}) and the other at a higher energy (6 cm^{-1}) relative to that of free CO (calcd). Since the theoretical calculations show that oxygen-bound CO results in ν_{CO} values that are in the right direction, a calculation was done on Cp_2Eu with oxygen-bound CO. The calculated ν_{CO} is lower than that in free CO (calc) by 20 cm^{-1} (Table 1). The energy difference between the carbon and oxygen bound isomers is only 2.9 kcal•mol^{-1} in favor of the carbon-bound isomer in which ν_{CO} increases upon coordination. Similar results are obtained for Cp_2-Ca(OC) which is 4.4 kcal•mol^{-1} less stable than $Cp_2Ca(CO)$. This is in accord with the lowering of ν_{CO} in O-bonded CO adducts of gas-phase naked alkali cations[8,9] and other metal cations.[1] Furthermore, the difference in energy between the C- and O-bound isomers decreases as each column is descended.[8]

The calculated stretching frequencies and geometries for the isocyanide adducts, $Cp_2Yb(CNMe)_2$, are in accord with the experimental results for $Cp^*_2Yb(CNR)_2$, thus the calculated results reproduce faithfully the experimental ones. A similar conclusion is reached for the $Cp_2Eu(CO)$ system in that the calculated ν_{CO} reproduce faithfully the experimental values for $Cp^*_2Eu(CO)$. This is clearly not the case for the ytterbocene adducts with CO. An alternative postulate is that the CO adducts are oxygen bound, rather than carbon bound as in the europium adduct. A physical model that fits the experimental result may be traced to the fact that Yb-(II) has a closed shell 4f^{14} electronic configuration while that of Eu(II) is 4f^{7}. Thus, binding CO by way of the carbon atom increases the negative charge on the Cp_2M fragment, which is more repulsive in the case of Yb than in Eu. Since neither metal can engage in back-bonding to remove the increased electronic density (coherent with the single stretching frequency in the 1:2 adduct), the Cp_2M fragment relieves the repulsion by binding to the more electronegative (O) end of CO where the repulsion is the highest (Yb).

The general theoretical principle that emerges from these calculations is that the bivalent lanthanide metallocenes cannot use their 4f electrons for charge transfer to their ligands, which means that back-bonding cannot be the reason for reduction in the values of ν_{CO} in the CO adducts of Cp^*_2Yb. The calculations show that the only structures that reproduce the experimental ν_{CO} values are ones in which CO is O rather than C bonded.

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Supporting Information Available: Optimized geometry (□, deg) of $Cp_2Yb(CNMe)_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Calculated ν_{CO} with small ECP and large ECP of $H_2M(CO)$ differ by only 8 (Eu) and 7 cm^{-1} (Yb) with the lower energy for the small ECP.

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