

Study of CO Adducts. A sample of $1a$ - ^{13}CO (25 mg) in CD_2Cl_2 (0.5 mL) was placed in an NMR tube (5 mm) fitted with a Teflon tap. Excess ^{13}CO was condensed into the liquid-nitrogen-cooled tube via a vacuum line, and the tap was closed. 1H , ^{13}C , and ^{31}P NMR spectra were recorded at variable temperatures between room temperature and $-90^\circ C$, the lowest temperature possible using CD_2Cl_2 solvent. Spectral parameters are given in the text, except for the ^{31}P NMR spectrum of $4a$ at $-90^\circ C$. $4a$: δ -14.8 [d, $^1J(PtP^a) = 3595$, $^3J(P^aP^c) = 165$, $^2J(P^aC) \approx 20$ Hz, P^a], -42.9 [s, $^1J(PtP^m) = 3440$, $^3J(P^mP^m) = 160$, $^2J(PtP^m) = 170$ Hz, P^m], -40.9 [d, $^1J(PtP^x) = 2246$, $^3J(P^aP^x) = 165$ Hz, P^x]. ^{31}P NMR spectra were also obtained on samples prepared from ^{12}CO in the same way.

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Registry No. $1a$, 99583-74-1; $1b$, 89189-79-7; $2a$, 106213-08-5; $2b$, 106213-09-6; $3a$, 106230-79-9; $4a$, 106230-78-8; $5a$ (X = Cl), 106213-10-9; $5a$ (X = Br), 106213-11-0; $5a$ (X = I), 106213-07-4; $5b$ (X = Cl), 106213-12-1; $5b$ (X = Br), 106213-13-2; $5b$ (X = I), 106213-14-3; CO, 630-08-0.

Unusual Th-C-C Angles in Bis(cyclopentadienyl)-Diethyl Complexes of Thorium

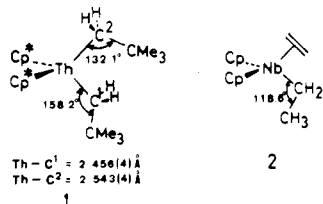
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Summary: Some $Cp_2Th(alkyl)_2$ complexes display an interesting structural deformation in which a Th-C-C(alkyl) angle opens up considerably. A molecular orbital analysis of $Cp_2Th(C_2H_5)_2$ traces the deformation to the characteristic shape of the d_σ fragment orbital of $Cp_2Th(C_2H_5)^+$. The potential energy curve for the ethyl pivoting was found to be very soft, with a shallow minimum at $\alpha \approx 160^\circ$. Nonrigidity of the ethyl orientation indicates that either an α -hydrogen or a β -hydrogen can come close to Th without a loss of Th-C bond strength.

In the rapidly growing area of organoactinide chemistry,¹ it remains a major challenge to construct logical frameworks that aid us to understand factors determining the properties characteristic of 5f-transition-metal complexes. The immediate impetus for this theoretical study was provided by the neutron-derived accurate structure of $Cp^*_2Th(CH_2CMe_3)_2$ (**1**),^{2,3} where one Th-C-C(neopentyl)



(1) See for example: (a) Marks, T. J., Fischer, R. D., Eds. *Organometallics of the f-Elements*; D. Reidel: Dordrecht, 1979; and references therein. (b) Marks, T. J., Fraga, I. L., Eds. *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; D. Reidel: Dordrecht, 1985, and references therein.

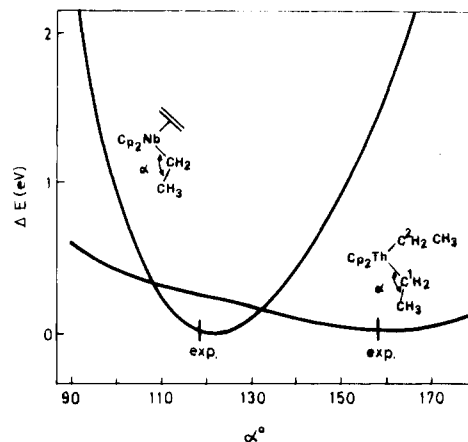


Figure 1. Potential energy curves of $Cp_2Th(C_2H_5)_2$ and $Cp_2Nb(H_2C=CH_2)(C_2H_5)$ as a function of M-C-C(ethyl) angle α . The experimentally observed angle α for $Cp^*_2Th(CH_2CMe_3)_2$ or $Cp_2Nb(H_2C=CH_2)(C_2H_5)$ is located by a mark "exp." in each corresponding curve.

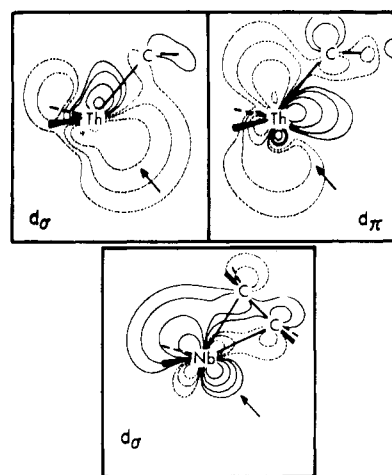


Figure 2. Contour plots of the two frontier orbitals d_σ and d_π of a $Cp_2Th(C_2H_2CH_3)^+$ fragment (top), and the frontier d_σ orbital of $Cp_2Nb(H_2C=CH_2)^+$ (bottom). The orbitals are shown in the xy plane. The contour levels of each diagram are ± 0.025 , ± 0.05 , ± 0.1 , and ± 0.2 . The arrows indicate the direction from which the incoming ligand $C_2H_5^-$ approaches.

angle, at C^1 in **1**, is remarkably obtuse while coordination of the other neopentyl ligand is slightly distorted as well. The steric congestion around Th may have something to do with the distortion. However, what we find impressive about **1**, and what we wish to understand in terms of its electronic origin, is that the Th atom is capable of holding tightly the extensively distorted neopentyl ligand. The observed Th-C¹ bond is short, even shorter than the Th-C² distance.

The model compound for **1** is $Cp_2Th(C_2H_5)_2$ in our extended Hückel calculations.^{4,5} Figure 1 presents the po-

(2) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650-6667. (b) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *Ibid.* **1986**, *108*, 40-56.

(3) There are three homologues of **1**: $Cp^*_2Th(CH_2CMe_3)(CH_2SiMe_3)$, $Cp^*_2Th(CH_2SiMe_3)_2$, and $(CH_3)_2Si[(CH_3)_4C_6H_5]Th(CH_2SiMe_3)_2$. Each molecule is also characterized by one large Th-C-Si angle ($\sim 150^\circ$) and simultaneous Th-C bond shortening (2.46-2.48 Å). See ref 2b and: (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, *250*, 237-246. (b) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819-821.

tential energy curve for bending of an ethyl group ($\text{Th-C}^1\text{-C} = \alpha$) in $\text{Cp}_2\text{Th}(\text{C}_2\text{H}_5)_2$, with the $\text{Th-C}^2\text{-C}$ angle being fixed at 132.1° . Superimposed on it, for comparison, is the energy of an ethyl ligand so bent in a d-transition-metal congener, $\text{Cp}_2\text{Nb}(\text{H}_2\text{C}=\text{CH}_2)(\text{C}_2\text{H}_5)$ (2). For the Nb complex, the theoretically optimized angle of $\alpha = 121^\circ$ and the corresponding experimental value of $\alpha = 118.6^\circ$ (7)⁶ may well represent a "normal" mode of alkyl coordination to a metal center. On the other hand, the Th complex exhibits a very soft energy curve with a shallow minimum at about $\alpha = 160^\circ$. Nonrigidity of the alkyl orientation at a Th center was suggested also by the NMR data for 1.² Thus the optimum angle α may be varied by small electronic and/or steric perturbations, but nevertheless it is encouraging to find that the computed $\text{Th-C}^1\text{-C}$ angle fits satisfactorily to the geometry of 1.

From an orbital analysis, to be presented in detail elsewhere, we noticed that the $\text{Cp}_2\text{Th}(\text{C}^2\text{H}_2\text{CH}_3)^+$ fragment carried two low-lying vacant levels right above the f-block orbitals, namely "d_σ" and "d_π".⁷ The contour plots of these orbitals are shown in Figure 2. When the $\text{C}^1\text{H}_2\text{CH}_3$ ligand adopts a normal coordination mode ($\alpha = 120\text{--}130^\circ$), it is bound to Th mostly through an interaction with d_σ. Distortion weakens this interaction, but only slightly, because the main lobe of d_σ exhibits a large spatial extension toward the incoming ligand so that even at large α 's the ethyl donor orbital can overlap well with d_σ. This is the most striking aspect of the $\text{Cp}_2\text{Th}(\text{C}^2\text{H}_2\text{CH}_3)^+$ fragment and is a crucial factor that allows the Th atom to maintain a strong bond with the highly distorted ethyl. At the same time, d_π starts to participate in the Th-C^1 bonding to a certain degree, which may also assist the ethyl to distort.⁸ The presence of an analogous low-lying vacant d_π in d⁰ $\text{Cp}_2\text{M}(\text{C}_2\text{H}_5)_2$ (M = Ti, Zr, or Hf) may cause a similar ethyl distortion, but the deformation, if any, would not be as large as the Th case due to a smaller size of d_σ.

The evolution of the overlap populations supports the above view. The Th-C^1 overlap population $P(\text{Th-C}^1)$ stays large over the wide range of α , and at $120^\circ \leq \alpha \leq 160^\circ$ it is even larger than the $P(\text{Th-C}^2)$. As the angle α opens up, a new interaction turns on between Th and the α -hydrogen atoms on C¹ (3). Although the calculated $P(\text{Th-H}_\alpha)$ is not particularly great, e.g., 0.042 at $\alpha = 160^\circ$, the agostic interaction helps the $\text{C}^1\text{H}_2\text{CH}_3$ group to deform, and perhaps it is another reason behind the Th-C^1 bond shrinkage in 1. Thus the $\text{Th-(C}^1\text{H}_2\text{CH}_3)$ group overlap population (GOP), defined as a sum of all the Th-C and Th-H overlap populations associated with the ethyl ligand, is notably larger than the $\text{Th-(C}^2\text{H}_2\text{CH}_3)$ GOP, i.e., 0.554 and 0.437, respectively, at $\alpha = 160^\circ$.

(4) The extended Hückel parameters for Th are the followings. Orbital exponent: 7s and 7p, 1.834; 6d, 2.461 (0.7612) + 1.165 (0.4071); 5f, 4.477 (0.7682) + 1.837 (0.4267); 6p, 3.806. H_{ii} : 7s and 7p, -5.39 eV; 6d, -10.11 eV; 5f, -9.64 eV; 6p, -27.83 eV. The H_{ij} values for 6d and 5f were determined by charge-iterative calculations on $\text{Cp}_2\text{Th}(\text{butadiene})$, and the details will be presented elsewhere. The off-diagonal elements H_{ij} were calculated by a weighted Wolfsberg-Helmholtz formula with the standard K value of 1.75. See, for example: Tatsumi, K.; Nakamura, A.; Hoffmann, P.; Hoffmann, R.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* 1986, 108, 4467-4476.

(5) The Nb parameters were taken from: Tatsumi, K.; Hoffmann, R. *J. Am. Chem. Soc.* 1981, 103, 3328-3341.

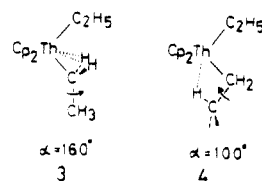
(6) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* 1974, 96, 5420-5427.

(7) These fragment orbitals are locally σ - and π -types with respect to an incoming ligand, $\text{C}^1\text{H}_2\text{CH}_3^-$ in this case. Tatsumi, K.; Nakamura, A.; Hoffmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1985, 107, 4440-4451.

(8) An effect similar to this d_π participation was emphasized in assessing the electronic origin of the deformation of carbene ligands in some Ta complexes and methyl tilting in Ti complexes. (a) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* 1980, 102, 7667-7676. (b) Eisenstein, O.; Jean, Y. *Ibid.*, 1985, 107, 1177-1186.

In the case of $\text{Cp}_2\text{Nb}(\text{H}_2\text{C}=\text{CH}_2)(\text{C}_2\text{H}_5)$, the computed Nb-C(ethyl) and the Nb-(C₂H₅) GOP both follow the trend of the energy curve in Figure 1. The Nb-ethyl bonding interaction is maximized at around $\alpha = 120^\circ$. This is traced to the optimum overlap again between the C_2H_5^- donor orbital and the vacant d_σ of $\text{Cp}_2\text{Nb}(\text{H}_2\text{C}=\text{CH}_2)^+$ shown in Figure 2. The Nb d_σ lobe is, however, much more compact in size than the Th d_σ lobe, and the ethyl ligand in the Nb complex does not have much freedom to choose various orientations. The good Nb-C interaction is achieved only in a narrow range of α around 120° . The vacant d_π orbital is absent in this case, for it is used up in the interaction with $\text{H}_2\text{C}=\text{CH}_2 \pi^*$.

We have emphasized the characteristic shape of $\text{Cp}_2\text{Th}(\text{C}_2\text{H}_5)^+ d_\sigma$, which allows the $\text{Th-C}^1\text{-C}$ angle to open up (3) without a loss of Th-C^1 bond strength. Pivoting the ethyl in the direction opposite to 3 is not a costly



deformation as well. For instance, the geometry 4 ($\alpha = 100^\circ$) is less stable than 3 by only 0.18 eV. A β -hydrogen comes close to Th in this case, and the calculated $P(\text{Th-H}_\beta)$ is weakly positive (0.036). The versatile ethyl coordination mode means hydrogen atoms (or C-H bonding electrons) in either the α - or the β -position can approach Th *without difficulty*. The same would be true for γ -hydrogens when present. This argument should provide a theoretical basis for understanding important aspects of C-H activation or cyclometalation chemistry involving actinide centers.⁹

Acknowledgment. We thank Prof. Tobin J. Marks for informing us of his experimental results prior to publication and helpful comments.

(9) (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* 1982, 104, 7357-7360. (b) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Ibid.* 1979, 101, 7728-7729; *Inorg. Chem.* 1981, 20, 2991-2995. (c) See ref 2b and references therein.

Preparation and Structure of $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCH}_2$, an Analogue of a Vinylidene Cluster Complex: Reduction of the Unique Carbonyl of $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCO}$

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Summary: The reaction of $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCO}$ with BH_3 in THF results in the reduction of the unique carbonyl to form a methylene group, giving a triosmium borylidene carbonyl, $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCH}_2$, which is an electronic and structural analogue of the triosmium vinylidene cluster $\text{H}_2(\text{CO})_9\text{Os}_3\text{CCH}_2$.

The unique carbonyl of $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCO}$ (I) is bound to a boron atom that caps an equilateral triangle of osmium atoms.¹ A recent calculation² indicates that the oxygen

(1) Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L. *J. Am. Chem. Soc.* 1983, 105, 5923.