coupling of carbon monoxide. This discovery suggests that extension of the reaction chemistry to other ligand systems or to heteroligand coupling may be possible. The bis(trimethylsiloxy)ethyne ligand constitutes a new type of coordinated product derived from CO, and its formation here represents a novel synthetic route to an acetylene diether.[18] The generality of this reaction chemistry and the possibility of removing the alkyne moiety from the complex are currently being investigated.

Acknowledgment. This work was supported by a grant from the National Science Foundation (NSF-CHE-8542205). We also thank the M.I.T. Undergraduate Research Opportunities Program for partial financial support of M.P.E.

Supplementary Material Available: Atomic positional and thermal parameters for compound **3** (2 pages). Ordering information is given on any current masthead page.

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Synthesis and X-ray Structure of $(C_5Me_5)_2Th(\mu\text{-}PPh_2)_2Pt(PMe_3)$: A Complex with a Thorium–Platinum Bond

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In a recent paper,[1] we reported the synthesis of $Cp_2^*Th(PPh_2)_2$[2] (**1**), and the preparation (eq 1) of $Cp_2^*Th(\mu\text{-}PPh_2)_2Ni(CO)_2$ (**2**),

$$\underset{\mathbf{1}}{Cp_2^*Th(PPh_2)_2} + Ni(COD)_2 + 2CO \xrightarrow[48\text{ h, }25\text{ °C}]{THF} \underset{\mathbf{2}}{Cp_2^*Th(\mu\text{-}PPh_2)_2Ni(CO)_2} + 2COD \quad (1)$$

the first phosphido-bridged heterobimetallic complex incorporating an actinide element. The X-ray structure of **2** revealed distorted tetrahedral environments about both metal centers, as well as two unexpected features: (1) acute Th–P–Ni angles which average 76.2 [4]° and (2) a short thorium–nickel separation of 3.206 (2) Å. These data led us to postulate the existence of a direct, albeit weak, thorium–nickel interaction, one that could be formulated as a donor–acceptor bond from Ni(0) to the electron-deficient Th(IV) center. Because bonding interactions between actinides (An) and transition metals (M) were unprecedented in discrete complexes,[3] we sought additional experimental evidence for donor–acceptor bonding in $Cp_2^*An(\mu\text{-}PR_2)_2ML_n$ systems. Replacement of the $Ni(CO)_2$ fragment of **2** with an electron-rich transition-metal donor was a logical first step toward providing that evidence. Here we describe the synthesis, properties, and structure of a new thorium–platinum complex and provide some theoretical insight on the nature of the Th–Pt bond contained therein.

Toluene solutions of **1** react smoothly with 1 equiv of $Pt(COD)_2$[4] in the presence of trimethylphosphine (1–2 equiv) to provide red-brown, air-sensitive $Cp_2^*Th(\mu\text{-}PPh_2)_2Pt(PMe_3)$ (**3**) in ca. 50% isolated yield (eq 2).[5–7] The room temperature 200-MHz proton

$$\underset{\mathbf{1}}{Cp_2^*Th(PPh_2)_2} + Pt(COD)_2 + PMe_3 \xrightarrow[8\text{ h, }25\text{ °C}]{PhCH_3} \underset{\mathbf{3}}{Cp_2^*Th(\mu\text{-}PPh_2)_2Pt(PMe_3)} + 2COD \quad (2)$$

NMR spectrum of **3** in toluene-d_8 shows two methyl resonances at δ 1.86 (s, 30 H, Cp*) and 1.89 (s, 9 H, PMe_3). Cooling the sample to −90 °C had no significant effect on the appearance of the spectrum. The $^{31}P\{^1H\}$ NMR spectrum (81 MHz, 25 °C, toluene-d_8) consists of a doublet at δ +149.3 attributable to the μ-PPh_2 groups and a triplet at δ −3.3 due to the terminal PMe_3 ligand. The spin system is AX_2 with $^2J_{pp'}$ = 7 Hz. Each of the resonances is flanked by platinum-195 ($I = {}^1/_2$, 33.8% abundance) satellites. The $^{195}Pt-^{31}P$ coupling constants of 2459 Hz (μ-PPh_2) and 2556 Hz (PMe_3) are much lower than the values of 4438 and 4188 Hz observed in the $^{31}P\{^1H\}$ NMR spectra of $Pt(PPh_3)_3$[8] and $Pt(PEt_3)_3$,[9] respectively, and are taken as an indication of four-coordinate platinum(0).[10]

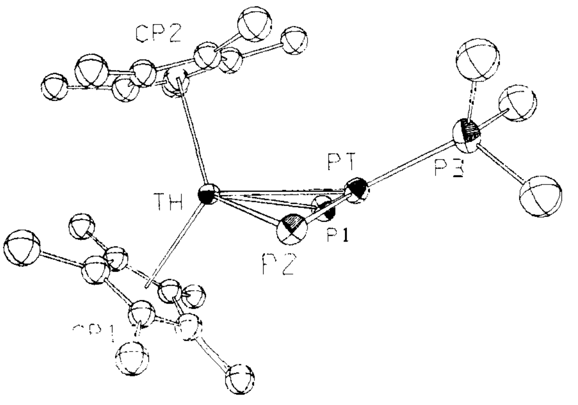

Figure 1. ORTEP II drawing of the $Cp_2^*Th(\mu\text{-}PPh_2)_2Pt(PMe_3)$ molecule. Hydrogen atoms and the phenyl groups on the μ-PPh_2 ligands have been omitted for clarity (30% thermal ellipsoids).

An X-ray diffraction study of **3** revealed that the molecule crystallizes in the monoclinic space group $P2_1/n$ with a = 16.394 (3) Å, b = 13.269 (5) Å, c = 24.319 (4) Å, β = 105.41 (1)°, V = 5100 Å^3, and ρ(calcd) = 1.49 g cm^{-3} for Z = 4.[11] Solution of the structure by direct methods and Fourier techniques was followed by full-matrix least-squares refinements[11] which converged to an unweighted R value of 0.056 (Figure 1).

The most salient feature of the present structure is the Th–Pt distance of 2.984 (1) Å. An early estimate of the covalent single bond radius of Pt(0), viz., 1.31 Å,[12] has been revised to 1.38 Å by Otsuka and co-workers.[13] The latter value is consistent with the 2.77-Å separation in platinum metal,[14] the 2.765 (1)-Å Pt–Pt

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[2] Abbreviations used in the text: Cp* = η^5-$C_5(CH_3)_5$, Ph = phenyl, R = alkyl or aryl, COD = 1,5-cyclooctadiene, dmpe = 1,2-bis(dimethylphosphino)ethane, Cy = cyclohexyl, Et = ethyl.

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[5] No $Cp_2^*Th(\mu\text{-}PPh_2)_2Pt(PMe_3)_2$ was isolated from reaction mixtures containing excess PMe_3. In addition, **3** does not exchange with free PMe_3 in toluene solution at 25 °C on the phosphorus NMR time scale.

[6] Anal. Calcd for $C_{47}H_{59}P_3PtTh$: C, 49.34; H, 5.20; P, 8.12. Found: C, 49.95; H, 5.26; P, 7.31.

[7] Similar $Cp_2M(\mu\text{-}PR_2)_2Pt(PR_3')$ complexes (M = Zn, Hf; R = Ph, Cy, Et; R′ = Me, Ph, Cy) have been prepared by Baker using this route. Baker, R. T., personal communication.

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[10] (a) $^1J_{Pt-P}$ values in parentheses. Compare $Pt(PPh_3)_3$ (4438 Hz) with $Pt(PPh_3)_3(CO)$ (3537 Hz) and $Pt(PPh_3)_2(CO)_2$ (3232 Hz) and $Pt(PEt_3)_3$ (4188 Hz) with $Pt(PEt_3)_4$ (3723 Hz). (b) The $Cp_2M(\mu\text{-}Pr_2)_2Pt(PR'_3)$ complexes of Baker,[7] which contain Zr– and Hf–Pt single bonds also exhibit characteristically low J_{Pt-PR_2} (2200–2733 Hz) and J_{Pt-PR_3} (3700–3987 Hz) coupling constants.

[11] Crystal data are presented as supplementary material.

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[13] Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

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distance in the unbridged d^{10}-d^{10} dimer [Pt(*t*-$Bu_2PCH_2CH_2CH_2P$-*t*-Bu_2)]$_2$,[15] and the Pt-Pt bond lengths of 2.65-2.79 Å in several carbonyl cluster compounds, e.g., $Pt_3(\mu$-$CO)_3(PCy_3)_3$.[16] An appropriate covalent radius for Th(IV) is, of course, more difficult to judge. We consider 1.8-2.0 Å a reasonable estimate, based on the 3.59-Å separation in thorium metal,[17] the 3.8-4.1-Å Th-Th distances in two binary hydrides,[18] and the 4.007 (1)-Å distance in $[Cp_2{}^*ThH]_2(\mu$-$H)_2$.[19] These data suggest a covalent Th-Pt bonding distance of ca. 3.2 Å. The Th-Pt separation in **3** is significantly shorter than this value, ca. 0.2 Å *less* than the Th-Ni distance in **2**, and comparable to the shortest Th-Pt distance (2.99 Å) in the alloy ThPt.[3b]

In addition to the short metal-metal separation, the acute Th-P-Pt angles of 69.1 (1)° and 67.8 (2)° also argue for the presence of a metal-metal bond in **3**. For phosphido-bridged transition-metal systems, M-P-M angles in the range 70-85° have invariably been associated with some degree of metal-metal bonding. One such example is $(CO)_3Fe(\mu$-$PPh_2)_2Fe(CO)_3$.[20] Here the Fe-Fe distance is 2.623 (2) Å and the Fe-P-Fe angles average 72.0 [1]°. A metal-metal single bond is required to satisfy the 18-electron rule and Fenske-Hall MO calculations[21] indicate that the HOMO of this complex has appreciable Fe-Fe bonding character. In the context of this discussion it is important to emphasize that μ-PR_2 ligands are also known to span nonbonding M-M distances as long as 4.3 Å with M-P-M angles as large as 116°.[20,22]

Another exceptional feature of solid-state **3** is the dihedral angle (ϕ) of 45.2° between the P(1)-Th-P(2) and P(1)-Pt-P(2) planes. Puckering of the $Th(\mu$-$P)_2Pt$ core could be due to an arrested distortion of the now four-coordinate Pt center toward a tetrahedral geometry. This explanation, however, is mitigated by the fact that the PtP_3 unit is nearly planar. The sum of the P-Pt-P angles is 359.9° and Pt is only 0.04 Å above the least-squares P(1)P(2)P(3) plane. In fact, the PtP_3 fragment of **3** is very similar to the PtP_3 core of trigonal-planar $Pt(PPh_3)_3$.[23] In the absence of metal-centered stereochemical preferences, the barrier to interconverting the puckered and planar $Th(\mu$-$P)_2Pt$ conformations should be small. Our observation of a single Cp* proton NMR resonance in solution, from -90 to +25 °C (vide supra), is consistent with this hypothesis. We are therefore inclined to ascribe the 45.2° dihedral angle to crystal packing forces.

The Th-P(1) and Th-P(2) distances, 2.891 (6) and 2.953 (6) Å, respectively, are slightly asymmetric but compare favorably with the values found for mononuclear **1** (2.87 [2] Å)[1,24] and binuclear **2** (2.88 [2] Å).[1] These bond lengths are significantly shorter than the thorium(IV)-*phosphine* distance of 3.17 [3] Å recently established for $Th(CH_2Ph)_4(dmpe)$.[25] The remaining metrical parameters about the Th center are also similar to those observed in **1** and **2**. The largest deviations are found for the P-Th-P angles, which are 88.3 (2)°, 83.7 (1)°, and 92.0 (2)° in **3**, **2**, and **1**, respectively. The Pt-P distances are comparable to those found in $Pt(PPh_3)_3$.[23]

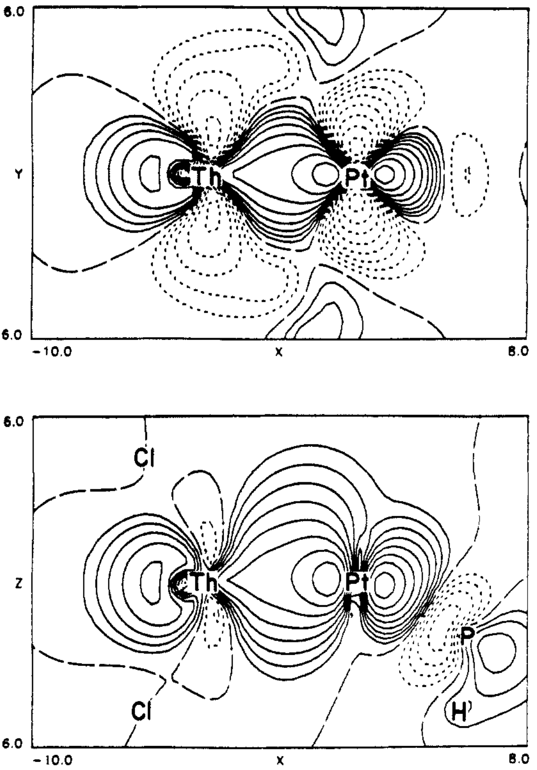

Figure 2. Contour plots of the metal-metal bonding HOMO of $Cl_2Th(\mu$-$PH_2)_2Pt(PH_3)$ in the *xy* (top) and *xz* planes. Positive, negative, and nodal contours are represented by solid, short dash, and long dash lines, respectively.

On the basis of the ^{31}P NMR data, structural parameters, and comparisons with **2** and other heterobimetallic complexes, *we conclude that* **3** *contains a direct thorium-platinum bond.* The nature of this metal-metal bond has been explored through ab initio calculations[26] on the model compound $Cl_2Th(\mu$-$PH_2)_2Pt(PH_3)$, using effective core potentials[27] to replace the inner electrons on all non-hydrogen atoms and employing the experimental geometry.[28] The metal-metal bonding orbital (HOMO), which was qualitatively similar in both Hartree-Fock and generalized valence bond calculations,[29] is formed from the $5d_{x^2-y^2}$ orbital on Pt and the $6d_{x^2-y^2}$ orbital on Th,[30] with a larger fraction of the electron density located on the platinum center (Figure 2). A Mulliken population analysis of all occupied orbitals revealed the following charge densities: Cl -0.30, Th +1.48, μ-PH_2 -0.43, Pt 0.00, and PH_3 0.00. The orbital populations on Th were 6p(6.00), 7s(0.35), 7p(0.35), 6d(1.61), and 5f(0.22); those on Pt were 6s(0.77), 6p(0.00), and 5d(9.21). Overall, the Th-Pt bond can be regarded as a formal donor-acceptor or dative bond from the "filled" d^{10} shell of Pt into the "empty" d shell of Th.

In summary, the data presented here demonstrate, quite convincingly, the existence of a Th-Pt bond in **3**. We intend to use the $Pt(PMe_3)$ fragment to prepare other early actinide analogues of **3** and explore the question of metal-metal bonding as a function of the size and 5f-electron configuration of the actinide. The observation of Th-Pt bonding in **3** naturally raises the question

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(29) Full computational details will be provided in the full paper.

(30) The $(\sigma)^1(\sigma^*)^1$ triplet excited state was calculated to lie 2.71 (Hartree-Fock) and 3.12 eV (GVB) above the σ^2 ground state.

of whether *unsupported* actinide–transition-metal bonds can be synthesized. This goal has been achieved recently by Marks and co-workers.[31]

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy and, in part, under the auspices of the Division of Chemical Energy Sciences, Office of Basic Energy Sciences, Department of Energy. We are grateful to Professor T. J. Marks (Northwestern) and Dr. R. T. Baker (Du Pont) for preprints of their work on heterobimetallic chemistry and for many helpful discussions.

Supplementary Material Available: Crystal data, tables of distances and angles, positional and thermal parameters, observed and calculated structure factors, and selected theoretical results (25 pages). Ordering information is given on any current masthead page.

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Cation-Directed Photochemistry of an Anthraceno-Crown Ether

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We report on a system, bis(anthraceno)-crown ether I, designed to direct intramolecular photophysics and photochemistry by complexation with cations.

The interplay between ion complexation and spectroscopic properties of chromophores has aroused considerable interest. Vögtle[1] recently reviewed the topic with emphasis on molecules called "chromoionophores" showing ion-specific color changes resulting from the perturbation of electronic absorption spectra by cation insertion into a neutral ligand cavity. *Luminescence is also susceptible to such effects.*[2a–j]

Relationships between photoreactivity and complexation have been examined from two standpoints: (i) the modification of complexing ability as a result of a photochemical reaction; (ii) the change of photochemistry as a result of cation complexation. The first of these has been well illustrated by Shinkai's photoresponsive[3] systems based on cis–trans isomerization of the azobenzene chromophore as well as by related molecules,[4a–e] such as the "photoresponsive molecular tweezers".[4e] Cation complexation with crown ethers has often been reported to enhance the rates of photochemical reactions[5a–e] and, in one case, to favor the photochemical reaction of one excited state at the expense of another state.[5f]

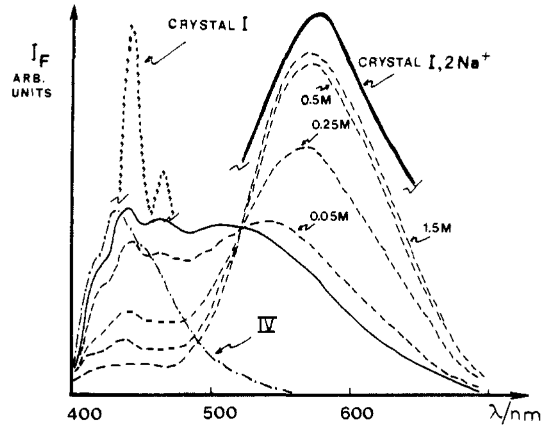

Figure 1. Corrected fluorescence spectra (λ_{exc} = 380 nm, room temperature, degassed solutions) of I (5×10^{-6} M): (i) in methanol (—), (ii) in methanol + $NaClO_4$ 0.05, 0.25, 0.5, 1.5 M (---), and of IV in methanol (-·-). Fluorescence spectra (λ_{exc} = 366 nm) of microcrystals of I (···) and of I,2Na$^+$ (—), represented, in part, at a different scale.

We sought a system with the potential to give a highly sensitive response to variations in conformations which arise from cation complexation. A good candidate was the anthracene ring because of its dual (monomer/excimer) fluorescence *and* its versatile photoreactivity. Therefore we designed new bisanthracenic anthracenophanes such as I; their synthesis has already been described.[6]

In this paper, we will demonstrate that important alterations of conformations of 1,4,7,10,13,28,31,34,37,40-decaoxa[13.13](9,10)-anthracenophane (I) are induced by metal cation complexation and these greatly affect fluorescence emission and photochemical regioselectivity. (Part of this study was presented at the 7th Symposium on Macrocyclic Compounds, Provo, UT, Aug 1983, and at the 10th IUPAC Symposium on Photochemistry, Interlaken, Switzerland, July 1984.)

Electronic absorption spectra[7] *of the bichromophore I were examined in order to elucidate intramolecular ground-state interactions.*[8] A comparison of the UV absorption spectra in methanol between I and the monochromophoric reference compound IV (9,10-bis[(1-methoxy-3,6-dioxaoctyl)oxy]anthracene) shows hypochromism for the first transition (^1L_a)[9] and intensity redistribution for the second transition (^1B_b).[9] These features are an indication of some weak interactions between the two rings; strong interactions are known to produce pronounced red shifts.[10]

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[‡] Laboratoire de Cristallographie.

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