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Preparation of Tetraalkyl Phosphine Complexes of the f-Block Metals. Crystal Structure of $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$ and $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$

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Reaction of 4 molar equiv of $PhCH_2Li$ with $MCl_4(Me_2PCH_2CH_2PMe_2)_2$ gives $M(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$, where M is Th or U. Reaction of a mixture of 3 molar equiv of $PhCH_2Li$ and 1 molar equiv of MeLi with $MCl_4(Me_2PCH_2CH_2PMe_2)_2$ gives the unsymmetrical alkyls $M(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$, where M is Th or U. The molecular structure of $Th(CH_2C_6H_5)_4(Me_2PCH_2CH_2PMe_2)$ and $U(CH_2C_6H_5)_3Me(Me_2PCH_2CH_2PMe_2)$ were determined by single-crystal X-ray diffraction methods. Crystals of $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$ are triclinic of space group $P\bar{1}$ with cell dimensions $a = 11.463$ (2) Å, $b = 16.151$ (3) Å, $c = 21.527$ (3) Å, $\alpha = 106.28$ (2)°, $\beta = 95.85$ (2)°, and $\gamma = 107.78$ (2)°; there are four molecules in the unit cell. Crystals of $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$ are monoclinic of space group $P2_1/c$ with cell dimensions $a = 13.035$ (2) Å, $b = 15.381$ (2) Å, $c = 14.540$ (2) Å, $\beta = 98.06$ (2)°; there are four molecules in the unit cell. In the Th complex there are two independent molecules in the unit cell. The Th atoms are each bonded to four benzyl groups and to two phosphorus atoms from the bis(dimethylphosphino)ethane ligand; the average Th–C distance is 2.55 (2) Å, and the average Th–P distance is 3.17 (3) Å. In the U complex the uranium atom is bonded to a methyl group, three benzyl groups, and the two phosphorus atoms of the bis(dimethylphosphino)ethane ligand. The U–C(methyl) distance is 2.41 (1) Å; the average U–C(benzyl) distance is 2.50 (4) Å.

Introduction

Binary σ-alkyls of the actinide metals are rare, doubtless due to their thermal instability.[1] The tetrabenzyls of thorium and uranium[2] and some anionic complexes of uranium[3] are the only known binary and ternary compounds that are thermally stable at room temperature. The thermal stability of σ-alkyls increases considerably when cyclopentadienyl or related ligands are present in the coordination sphere of the actinide metal atom.[4] The principal reason for the increased thermal stability is related to the increased coordination number of the complex, i.e., kinetic stabilization. As the steric congestion about the metal atom increases, the σ-bonded alkyl cannot get sufficiently close to the metal atom, in an inter- or intramolecular sense, to become activated and the decomposition pathway is therefore a high-energy process. This explanation assumes a homolytic rather than a heterolytic decomposition pathway; increased steric congestion could well increase thermal instability in heterolytic processes.[5] Thus, the principal function of the auxillary ligands is to occupy space about the metal center.[6]

The strategy of saturating the coordination sphere with "inert" ligands has been applied to the preparation of thermally stable d-block metal alkyls.[1,7a] In particular, the pioneering work of Chatt has shown that tertiary phosphine ligands impart considerable thermal stability to the metal–carbon bond in phosphine alkyls.[7b,c] Since we have described the preparation of phosphine complexes of the tetravalent actinides of the type $MX_4(Me_2PCH_2CH_2PMe_2)_2$, where M is uranium or thorium and X is halide or methyl,[8] it was of interest to extend the range of alkyls to the β-elimination-stabilized alkyls $PhCH_2$ etc.[9]

Addition of 4 molar equivalents of benzyllithium to $MCl_4(Me_2PCH_2CH_2PMe_2)_2$, where M is Th or U, gives the tetrabenzyls $M(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$, where M is Th or U. The complexes are thermally stable and melt with decomposition at ca. 85 °C. The ^1H NMR spectrum of the thorium complex at 29 °C in PhMe-d_8 has a singlet at δ 0.82 and a three-line pattern centered at δ 1.23 (the separation between the outermost lines, which are more intense than the centerline, is 10 Hz) due to the Me_2P and CH_2P, respectively, of the coordinated phosphine ligand. The resonances of the benzyl protons appear as a singlet at δ 1.48 and as a complex pattern between δ 7.17 and 6.38 due to the methylene and aryl protons, respectively. Lowering the temperature to −66 °C causes the resonances due to the methyl and methylene phosphine protons to approximate pseudotriplet structure and the methylene protons of the benzyl group to broaden into the base line. The aryl protons of the benzyl ligands do not change appreciably. Clearly some type of exchange process is occurring. The $^{31}P\{^1H\}$ NMR spectrum is rather informative. The spectrum at 27 °C shows a broad ($\nu_{1/2} = 86$ Hz) signal at δ −33.3. Cooling the sample to −51 °C yields a two-line spectrum, δ −23.6 and −47.9. The latter resonance is due to free phosphine as shown by addition of free phosphine

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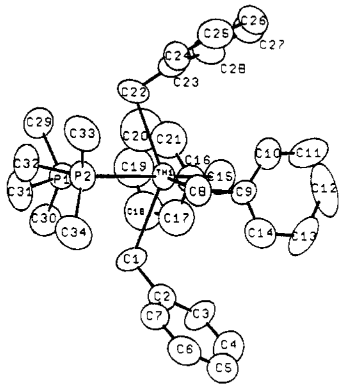

Figure 1. ORTEP drawing of molecule 1 in $Th(CH_2Ph)_4(Me_2PCH_2Ch_2PMe_2)$.

Table I. Distances (Å) in $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$

Th(1)-C(1)	2.54 (2)	Th(2)-C(35)	2.56 (2)
Th(1)-C(8)	2.53 (2)	Th(2)-C(42)	2.53 (2)
Th(1)-C(15)	2.54 (2)	Th(2)-C(49)	2.59 (2)
Th(1)-C(22)	2.57 (2)	Th(2)-C(56)	2.57 (2)
Th(1)-C(9)	2.86 (2)	Th(2)-C(43)	2.90 (2)
Th(1)-P(1)	3.16 (1)	Th(2)-P(3)	3.21 (1)
Th(1)-P(2)	3.15 (1)	Th(2)-P(4)	3.15 (1)
P(1)-C(29)	1.82 (2)	P(3)-C(63)	1.85 (2)
P(1)-C(30)	1.83 (2)	P(3)-C(64)	1.89 (2)
P(1)-C(31)	1.83 (2)	P(3)-C(65)	1.89 (2)
P(2)-C(32)	1.76 (2)	P(4)-C(66)	1.85 (2)
P(2)-C(33)	1.83 (2)	P(4)-C(67)	1.85 (2)
P(2)-C(34)-	1.83 (2)	P(4)-C(68)	1.88 (2)

to the sample. Hence the coordination chemical shift at –51 °C is 24.3 ppm. The $^{31}P\{^1H\}$ NMR experiment shows that the phosphine ligand is dissociating at room temperature on the NMR time scale and thus accounts for lack of coupling information and the apparent chemical equivalence of the methylene groups of the benzyl ligand in the ^1H NMR spectrum.

The ^1H NMR spectrum of the paramagnetic uranium complex at 25 °C in PhMe-d_8 consists of four singlets at δ 51.3, 5.83, –2.07, and –13.4 in area ratio 4:12:20:8. At –60 °C, 13 single resonances are observed which are spread from δ +84.6 to –78.7; see Experimental Section for peak positions. The complex spectrum is impossible to interpret with confidence, and a crystal structure determination is warranted. Since the thorium complex crystallizes better than the uranium complex, we have carried out a single-crystal X-ray analysis of the thorium complex.

The $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$ crystallizes in space group $P\bar{1}$ with two independent molecules in the asymmetric unit. ORTEP drawings are shown in Figures 1 and 2, and some bond lengths and bond angles are listed in Tables I and II. Crystal data are shown in Table V. The structure contains two independent molecules whose essential features are identical. Although Figures 1 and 2 show the two independent molecules as enantiomers, the center of symmetry operation on one will produce a molecule of the same chirality as the other.

Ignoring for the moment the short Th(1)–C(9) and Th(2)–C(42) contacts, the geometry of the complex is based upon that of an octahedron with two benzyl groups trans to the chelating phosphine ligand and two benzyl groups trans to each other. The averaged thorium–carbon bond distance of 2.55 ± 0.02 Å is similar to that found in the related benzyl derivative $Th(Me_5C_5)(CH_2Ph)_3$ of 2.58 ± 0.02 Å.[10] The averaged thorium–phosphorus bond distance is 3.17 ± 0.03 Å and the normalized bite of the phosphine ligand is 1.08 for both molecules.[11]

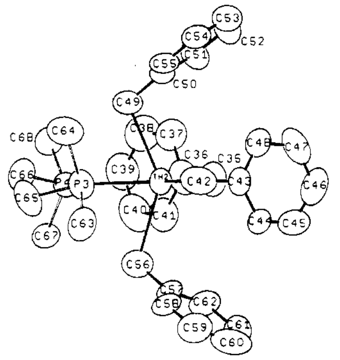

Figure 2. ORTEP drawing of molecule 2 in $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$.

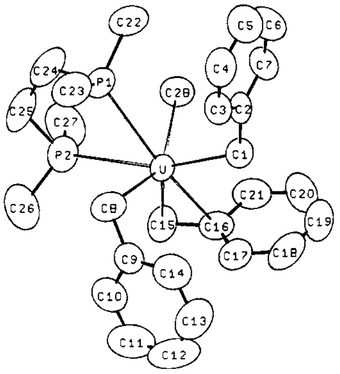

Figure 3. ORTEP drawing of $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$.

An interesting feature of the molecular structure is the unusual geometry exhibited by the benzyl group defined by C(8–14) in molecule 1 and C(42–48) in molecule 2. The Th(1)–C(1)–C(2), Th(1)–C(15)–C(16), Th(1)–C(22)–C(23), Th(2)–C(35)–C(36), Th(2)–C(49)–C(50), and Th(2)–C(56)–C(57) bond angles are 114 (1)°, 105 (1)°, 103 (1)°, 105 (1)°, 103 (1)°, and 109 (1)°, respectively, whereas the Th(1)–C(8)–C(9) and Th(2)–C(42)–C(43) bond angles are 88 (1)° and 90 (1)°, respectively. As a consequence of the smaller Th(1)–C(8)–C(9) and Th(2)–C(42)–C(43) bond angles, the Th(1)–C(8) and Th(2)–C(42) distances are 2.86 (2) and 2.90 (2) Å; the comparable Th–C distances in the other benzyl groups are all greater than 3.2 Å. Thus, three benzyl groups may be described as "normal" and the other as "abnormal". The abnormality is discussed below.

Reaction of $MCl_4(Me_2PCH_2CH_2PMe_2)_2$ with a mixture of benzyllithium and methyllithium in a 3:1 molar ratio in diethyl ether gives the unsymmetrical alkyls $M(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$, where M is thorium or uranium. The alkyls are thermally stable at room temperature and melt with decomposition at ca. 80 °C. The ^1H NMR spectrum of the thorium complex at 27 °C in PhMe-d_8 shows the resonance due to the Me_2P groups as a pseudotriplet centered at δ 1.01, the separation of the outermost lines is 2.4 Hz, and the CH_2P protons as a widely spaced pseudodoublet centered at δ 1.39 with a separation of 13 Hz. The benzylic methylene groups and methyl group appear as single resonances at δ 1.65 and –0.05, respectively. The aryl protons appear as a complex set of resonances between δ 7.38 and 6.46. The ^1H NMR spectrum of the uranium alkyl at –60 °C in PhMe-d_8 contains 21 single resonances from δ 10 to –114. Again, as in U-

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[11] The normalized bite of a chelating ligand is defined as the phosphorus–phosphorus distance divided by the metal–phosphorus distance; cf.: Kepert, D. L. *Prog. Inorg. Chem.* **1978**, *24*, 179.

Table II. Angles (Deg) in $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$

C(1)-Th(1)-C(22)	137.9 (6)	C(49)-Th(2)-C(56)	139.7 (6)
C(1)-Th(1)-C(8)	96.9 (5)	C(49)-Th(2)-C(42)	105.3 (6)
C(1)-Th(1)-C(15)	96.5 (6)	C(49)-Th(2)-C(35)	97.3 (6)
C(1)-Th(1)-P(1)	67.5 (4)	C(49)-Th(2)-P(4)	68.3 (5)
C(1)-Th(1)-P(2)	80.4 (4)	C(49)-Th(2)-P(3)	78.9 (5)
C(8)-Th(1)-C(22)	107.9 (6)	C(42)-Th(2)-C(56)	101.4 (6)
C(8)-Th(1)-C(15)	117.1 (6)	C(42)-Th(2)-C(35)	115.1 (7)
C(8)-Th(1)-P(1)	135.2 (4)	C(42)-Th(2)-P(4)	140.6 (5)
C(8)-Th(1)-P(2)	70.8 (4)	C(42)-Th(2)-P(3)	75.6 (5)
C(15)-Th(1)-C(22)	101.3 (6)	C(35)-Th(2)-C(56)	98.2 (6)
C(15)-Th(1)-P(1)	106.5 (5)	C(35)-Th(2)-P(4)	104.4 (4)
C(15)-Th(1)-P(2)	171.9 (5)	C(35)-Th(2)-P(3)	169.4 (4)
C(22)-Th(1)-P(1)	71.0 (4)	C(56)-Th(2)-P(4)	71.9 (5)
C((22)-Th(1)-P(2)	76.7 (4)	C(56)-Th(2)-P(3)	79.1 (5)
P(1)-Th(1)-P(2)	65.4 (2)	P(3)-Th(2)-P(4)	65.0 (2)

Table III. Distances (Å) and Angles (Deg) in $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$

		Bond Distances			
U-C(1)	2.46 (1)	U-P(2)	3.010 (2)	P(1)-C(23)	1.81 (1)
U-C(8)	2.51 (1)	U-C(2)	3.43 (1)	P(1)-C(24)	1.82 (1)
U-C(15)	2.54 (1)	U-C(9)	3.06 (1)	P(2)-C(25)	1.84 (1)
U-C(28)	2.41 (1)	U-C(16)	2.76 (1)	P(2)-C(26)	1.81 (1)
U-P(1)	3.020 (2)	P(1)-C(22)	1.81 (1)	P(2)-C(27)	1.82 (1)
		Bond Angles			
C(1)-U-C(8)	98.6 (3)	C(8)-U-C(28)	145.1 (3)	C(28)-U-P(1)	71.9 (2)
C(1)-U-C(15)	121.6 (3)	C(8)-U-P(1)	73.5 (2)	C(28)-U-P(2)	78.6 (3)
C(1)-U-C(28)	90.2 (3)	C(8)-U-P(2)	83.5 (2)	P(1)-U-P(2)	67.0 (1)
C(1)-U-P(1)	96.6 (2)	C(15)-U-C(28)	92.3 (3)	U-C(1)-C(2)	119.6 (4)
C(1)-U-P(2)	162.2 (2)	C(15)-U-P(1)	139.2 (2)	U-C(8)-C(9)	97.7 (4)
C(8)-U-C(15)	110.9)3)	C(15)-U-P(2)	73.1 (2)	U-C(15)-C(16)	83.0 (4)

$(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$ the complex nature of the spectrum precludes a definitive assignment and a crystal structure determination is required to deduce the solid state structure.

An ORTEP drawing of $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$ is shown in Figure 3. Some selected bond lengths and bond angles are shown in Table III. Carbon–carbon bond lengths are unremarkable and are presented in the supplementary material. Crystal data are shown in Table V.

The geometry of the molecule, ignoring the short U–C(16) contact, is based upon that of an octahedron with two benzyl groups trans to the bidentate phosphine ligand and the remaining benzyl group trans to a methyl group. The averaged uranium–carbon (benzyl) bond length of 2.50 ± 0.03 Å is significantly longer than the uranium–methyl bond length of 2.41 (1) Å. At first glance, this is surprising since all of the carbon atoms in the benzyl and methyl groups are formally sp^3 hybridized. This type of disparity has been observed previously. The uranium–carbon (benzyl) bond length in $UCp_3CH_2(p\text{-tolyl})$ is 2.51 (2) Å, and the uranium–carbon (alkyl) bond length in $UCp_3(n\text{-butyl})$ is 2.43(2) Å.[12] A rationalization for this difference in $U–C(sp^3)$ bond lengths is to note that the benzylic carbanion is resonance stabilized due to the electron-withdrawing effect of a phenyl group relative to that of hydrogen or an alkyl group. If one views the bonding in these actinide molecules as primarily electrostatic, then the longest bond length should be associated with the carbanion that has the least amount of electron density at the sp^3-hybridized carbon atom, viz., the benzylic carbon atom, as observed. The bond length pattern does not prove that the bonding in these compounds is electrostatic since steric and covalency effects will also rationalize the trends. The relative importance of these effects is impossible to define though we believe that the bonding is primarily electrostatic. It is interesting to note, in this regard, that the uranium–carbon (sp^3) bond length in UCp_3(2-methylallyl) is 2.48 (3) Å.[13] This bond length is consistent with the above argument since an allyl group is more electron withdrawing than that of a hydrogen atom or an alkyl group. We do not wish to overemphasize the bond length trends since the error limits are rather large.

The averaged uranium–phosphorus bond length in the unsymmetrical alkyl is 3.015 ± 0.005 Å. This is close to that found in $U(OPh)_4(Me_2PCH_2CH_2PMe_2)_2$ of 3.104 ± 0.006 Å.[8] The uranium–phosphorus distance in $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$ is 0.14 Å shorter than that in $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$. This difference is in the direction expected since uranium(IV) is smaller than thorium(IV), in a given coordination number, by 0.05 Å.[14] The normalized bite of the bidentate phosphine is 1.10.[11]

As noted earlier, the benzyl groups in $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$ are not identical. This can be seen most readily by comparing the U–C–C bond angles. The U–C(1)–C(2), U–C(8)–C(9), and U–C(15)–C(16) bond angles are 119.6 (4)°, 97.7 (4)°, and 83.0 (4)°, respectively. The acute nature of the latter two bond angles requires that several uranium–carbon contacts are short. The benzyl group associated with C(1) has a U–C(2) contact of 3.429 (5) Å, and the U–C(3,7) contact is >3.5 Å. The benzyl group associated with C(8) has a U–C(9) contact of 3.061 (6) Å, and the U–C(10,14) distances are >3.5 Å. The benzyl group associated with C(15) has U–C(16,17,21) contacts of 2.758 (5), 3.089 (6), and 3.450 (7) Å, respectively.

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Table IV. Bond Lengths in Benzylmetal Compounds

compound	$MC_1 - MCH_2$[a]	$MC_0 - MCH_2$[b]	$MC_{0'} - MCH_2$[c]	Δ[d]	Δ'[e]	ref
$CoCH_2Ph[P(OMe)_3]_3$	0.081	0.37		0.29	large	15a
$MoCH_2PhCp(CO)_2$	0.095	0.21	1.04	0.12	0.95	15b
$RhCH_2C_6Me_5[P(O\text{-}i\text{-}Pr)_3)]_2$	0.12	0.33		0.21	large	15c
$PdCPh_3(acac)$	0.049	0.095	1.03	0.046	0.98	15d
$PtCPh_3(acac)$	0.032	0.060	0.993	0.028	0.96	15d
$Fe_2C_{18}H_{14}(CO)_5$	0.053	0.12		0.067	large	15e
$Ru_2C_{18}H_{14}(CO)_5$	0.086	0.11		0.019	large	15e
$LiCH_2Ph(C_6H_{12}N_2)_2$	0.18	0.38		0.20	large	15f
$Th(CH_2Ph)_3(Me_5C_5)$ (shortest contacts)	0.29	0.77	1.00	0.48	0.71	4b
$Th(CH_2Ph)_4(dmpe)$ (shortest contacts)	0.35	0.78	0.39	0.43	0.58	this work
$U(CH_2Ph)_3Me(dmpe)$ (shortest contacts)	0.22	0.55	0.91	0.33	0.69	this work

[a] Metal to ipso carbon bond length minus metal to methylene carbon bond length. [b] Metal to shorter ortho carbon bond length minus metal to methylene carbon bond length. [c] Metal to longer ortho carbon bond length minus metal to methylene carbon bond length. [d] $[MC_0 - MCH_2] - [MC_i - MCH_2]$. [e] $[MC_{0'} - MCH_2] - [MC_i - MCH_2]$.

Hence, two benzyl groups are "normal" and one is peculiar, similar to that found in $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$.

Several benzyl derivatives of the metals are known in which there is an interaction of the metal atom with the ortho carbon of the aryl group. Generally only one of the carbon atoms (not both) has a short metal–carbon distance which is longer than the metal–ipso carbon distance. Thus, the bond length trend is M–CH_2 < M–C(ipso) < M–C(ortho) < M–C(ortho′). Table IV lists the crystallographically known benzyl compounds that have short ortho carbon to metal distances. In an attempt to quantify the bond length differences we have defined two parameters Δ and Δ', where $\Delta = [MC_0 - MCH_2] - [MCi - MCH_2]$ and $\Delta' = [MC_{0'} - MCH_2] - [MCi - MCH_2]$ and where MC_0 is the shorter metal to ortho carbon contact and $MC_{0'}$ is the longer metal to ortho carbon contact etc. For the transition-metal series, Δ ranges from ca. 0.03 to 0.30 and Δ' (which is calculated when sufficient information is reported) is ca. 1.0. The larger difference between Δ and Δ' is indicative of a η^3-benzyl ligand to metal interaction, as pointed out in the papers (Table IV). For the f-block metals the Δ and Δ' values are of similar magnitude, suggesting that the benzylic groups in the f-metal complexes are best viewed as η^4-benzyl groups. In this context, the binary tetrabenzyls of the group 4A (Ti, Zr, Hf) metals have been shown to have very acute M–C–C angles.[16] These organotransition-metal compounds are not listed in Table IV since they were published in preliminary form and the relevant data for calculation of Δ and Δ' are not listed.

The tendency for η^4 bonding in the organoactinide compounds may be rationalized in the following way. Hückel theory shows that the contribution to the charges in a benzyl radical has $^4/_7$th of the charge on the CH_2 group, $^1/_7$ of the change on each of the ortho and para carbon atoms and zero on each of the ipso and meta carbon atoms.[17] Consequently, in the bonding of an actinide metal atom to a benzyl group the primary interaction is by way of the methylene carbon atom. The coordination number of the actinide metal in, for example, $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$, in which the benzyl groups are only σ bonded, is only six and the metal atom is coordinatively unsaturated. The metal can increase its coordination number in a number of ways, viz., coordination to an additional phosphine or solvent ligand, formation of associated (oligomeric) species,[18] or an intramolecular interaction with the available electron density in the aryl group by bending the $ThCH_2Ph$ angle. Clearly the thorium and uranium species described in this paper prefer the latter interaction. The thorium and uranium compounds described in this paper, and those in Table IV, show short metal to ipso carbon distances even though this carbon atom carries a trivial amount of electron density. This is expected. The four-carbon fragment of the η^4-benzyl group in each of the compounds is essentially planar. In order for the ortho carbon atoms to get close to the metal atom, the ipso carbon atom must get close to the metal center and the M–CH_2Ph angle will bend until the intramolecular repulsions become unacceptable.

We have attempted to make other examples of phosphine actinide, β-elimination-stabilized alkyls with Me_3CCH_2, Me_2PhCCH_2, and Me_3SiCH_2 ligands. In all cases we have isolated materials that are thermally unstable at 0 °C in the solid state or in solution. Hence, reliable analytical and spectroscopic data were not obtained.

Experimental Section

All manipulation of the compounds was performed under argon. Elemental analyses were done by the microanalytical laboratory of this department. Proton and phosphous nuclear magnetic resonance spectra were recorded on a JEOL FX90 Q instrument operating at 89.56 and 36.25 MHz, respectively. Infrared spectra were obtained as Nujol mulls.

Tetrabenzyluranium 1,2-Bis(dimethylphosphino)ethane. To a cold (−70 °C) suspension of uranium tetrachloride–bis-[1,2-bis(dimethylphosphino)ethane][8] (0.60 g, 0.90 mmol) in diethyl ether (50 mL) was added benzyllithium[19] (3.2 mL of a 1.1 M solution in diethyl ether, 3.5 mmol) dropwise with stirring. The brown-red solution was warmed to 10 °C over 2 h and stirred at that temperature for 1 h. The volatile material was evaporated, the red residue was extracted with toluene (3 × 20 mL) and filtered, and the filtrate was concentrated to ca. 20 mL. Pentane (ca. 15 mL) was added until the solution appeared to become turbid. Cooling the solution (−20 °C) afforded brown prisms that were collected, washed with pentane (2 × 2 mL), and dried under reduced pressure: yield 0.4 g (60%); mp 85 °C dec. The complex

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[16] Davies, G. R.; Jarvis, J. A.; Kilbourn, B. T.; Pioli, A. J. P. *J. Chem. Soc., Chem. Commun.* 1971, 677. (b) Davies, J. R.; Jarvis, J. A.; Kilbourn, B. T. *Ibid.* 1971, 1511. (c) Bassi, I. W.; Allegra, G.; Scordamaglia, R.; Chioccola, G. *J. Am. Chem. Soc.* 1971, *93*, 3787.

[17] (a) McWeeny, R. "Coulson's Valence", 3rd ed.; Oxford University Press: London, 1979; p 248. (b) Stucky, G. D. In "Polyamine-Chelated Alkali Metal Compounds"; Langer, A. W., Ed., American Chemical Society: Washington, D.C., 1974; *Adv. Chem. Ser. No. 130*, p 56. (c) At this level of approximation the benzyl radical and the benzyl anion will give similar charge density results.

[18] As in $Al_2(CH_2Ph)_6$: Rahman, A. F. M. M.; Siddiqui, K. F.; Oliver, J. P. *Organometallics* 1982, *1*, 881.

[19] Seyferth, D.; Suzuki, R.; Murphy, C. J.; Sabet, C. R. *J. Organomet. Chem.* 1964, *2*, 431.

Table V. Data Collection Details and Results for $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$ and $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$

	Th	U
space group	$P\overline{1}$	$P2_1/c$
a, Å	11.463 (3)	13.035 (3)
b, Å	16.151 (4)	15.381 (4)
c, Å	21.527 (4)	14.540 (4)
α, deg	106.28 (2)	90.00
β, deg	95.85 (2)	98.06 (2)
γ, deg	107.78 (2)	90.00
Z	4	4
color	yellow	brown-red
μ, cm^{-1}	44.3	54.5
cryst dimens, mm	0.20 × 0.25 × 0.35	0.12 × 0.20 × 0.25
range of abs correctn	1.87-2.58	1.80-2.77
cryst decay	5%	13%
2θ range	$3 < 2\theta < 45°$	
hkl range	$+h, \pm k, \pm l$	$+h, +k, \pm l$
no. of reflctns measd	7261	3029
no of independent reflctns, $I > \sigma(I)$	7033	2891
R^a	4.70	2.37
$R_w{}^a$	8.43	2.42

^{a} $R = \Sigma||F_o| - F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

is sparingly soluble in pentane and very soluble in toluene and tetrahydrofuran. Anal. Calcd for $C_{34}H_{44}P_2U$: C, 54.3; H, 5.85; P, 8.24. Found: C, 54.8; H, 6.02; P, 7.95. The ^1H NMR (PhMe-d_8, −60 °C) spectrum consists of the following single resonances whose approximate relative intensities are given in parentheses: δ 84.6 (4), 39.5 (2), 23.0 (2), 13.4 (2), 0.86 (4), −3.40 (6), −4.73 (6), −7.18 (3), −19.1 (3), −20.8 (3), −54.7 (3), −78.7 (4). The infrared spectrum is virtually identical with that of its thorium analogue, given below.

Tetrabenzylthorium 1,2-Bis(dimethylphosphino)ethane. The thorium complex was prepared, in 60% yield after crystallization as yellow needles from toluene, in a manner similar to that of its uranium analogue, mp 90 °C dec; IR 1587 (s), 1554 (w), 1298 (m), 1280 (m), 1259 (m), 1206 (s), 1172 (m), 1150 (w), 1138 (w), 1088 (m br), 1020 (m), 927 (s), 899 (s br), 858 (m), 843 (w), 825 (w), 809 (m), 789 (s), 736 (s), 724 (s), 690 (s), 638 (w), 543 (m), 512 (m), 468 (m), and 340 (m br) cm^{-1}. Anal. Calcd for $C_{34}H_{44}P_2Th$: C, 54.7, H, 5.90; P, 8.31. Found: C, 54.7; H, 5.65; P, 8.61.

Tribenzylmethyluranium 1,2-Bis(dimethylphosphino)ethane. To a cold (−70 °C) suspension of uranium tetrachloride–bis[1,2-bis(dimethylphosphino)ethane] (1.0 g, 1.5 mmol) in diethyl ether (50 mL) was added a mixture of benzyllithium (7.9 mL of a 0.56 M solution in diethyl ether, 4.5 mmol) and methyllithium (1.3 mL of a 1.1 M solution in diethyl ether, 1.5 mmol). The red suspension was allowed to warm slowly (2 h) to 10 °C, and the solution was stirred at that temperature for 1 h. The volatile material was evaporated to dryness, and the brown residue was extracted with toluene (3 × 10 mL) and filtered, and the filtrate was concentrated to ca. 10 mL. Pentane (ca. 5 mL) was added, and the solution was cooled (−20 °C). The brown-red needles were collected, washed with pentane (2 × 2 mL), and dried under reduced pressure: yield 0.6 g (60%); mp 80 °C dec. The compound is soluble in toluene and tetrahydrofuran and sparingly soluble in diethyl ether and pentane. Significant amounts of decomposition of solutions of the alkyl can be observed at room temperature over periods of 1 h: IR 1588 (s), 1292 (w), 1278 (w), 1257 (w), 1217 (m), 1174 (w), 1150 (w), 1137 (w), 1083 (m br), 966 (w), 945 (m), 924 (m), 889 (m), 861 (w), 852 (w), 805 (m), 790 (s), 737 (s), 724 (m), 704 (w), 693 (s), 627 (w), 540 (w), 523 (m), 468 (w), 355 (m br), 322 (w) cm^{-1}. Anal. Calcd for $C_{28}H_{40}P_2U$: C,

Table VI. Positional Parameters in $Th(CH_2Ph)_4(Me_2PCH_2CH_2Me_2)$

molecule 1				molecule 2			
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Th(1)	0.19407 (5)	0.25030 (4)	0.42154 (3)	Th(2)	0.19889 (5)	0.31012 (4)	0.82878 (3)
P(1)	0.1240 (4)	0.08570 (29)	0.28749 (21)	P(3)	0.2867 (4)	0.5171 (3)	0.12915 (22)
P(2)	0.4251 (4)	0.2092 (3)	0.37024 (22)	P(4)	0.0006 (4)	0.35497 (29)	0.11121 (20)
C(1)	0.1868 (14)	0.3028 (10)	0.3212 (8)	C(35)	0.0910 (16)	0.1416 (12)	−0.0433 (9)
C(2)	0.2253 (15)	0.4030 (11)	0.3364 (7)	C(36)	−0.0338 (19)	0.1162 (11)	−0.0290 (10)
C(3)	0.1417 (15)	0.4513 (11)	0.3518 (9)	C(37)	−0.1395 (18)	0.1208 (12)	−0.0696 (10)
C(4)	0.1820 (18)	0.5438 (15)	0.3697 (10)	C(38)	−0.2578 (23)	0.0981 (14)	−0.0548 (13)
C(5)	0.3020 (19)	0.5970 (12)	0.3710 (8)	C(39)	−0.2785 (20)	0.0758 (15)	0.0019 (13)
C(6)	0.3855 (16)	0.5490 (14)	0.3546 (9)	C(40)	−0.1757 (27)	0.0684 (14)	0.0407 (11)
C(7)	0.3491 (16)	0.4551 (12)	0.3377 (8)	C(41)	−0.0589 (18)	0.0906 (12)	0.0262 (10)
C(8)	0.3933 (14)	0.3777 (12)	0.4903 (8)	C(42)	0.4181 (15)	0.3860 (13)	0.0138 (9)
C(9)	0.3172 (14)	0.4192 (9)	0.5283 (7)	C(43)	0.4126 (14)	0.3028 (12)	−0.0308 (19)
C(10)	0.2623 (15)	0.3901 (12)	0.5760 (8)	C(44)	0.4536 (28)	0.2439 (16)	−0.0084 (10)
C(11)	0.1814 (20)	0.4223 (15)	0.6102 (10)	C(45)	0.439 (3)	0.1669 (26)	−0.0460 (16)
C(12)	0.1455 (19)	0.4855 (14)	0.5904 (10)	C(46)	0.3746 (28)	0.1278 (16)	−0.1110 (17)
C(13)	0.1937 (18)	0.5175 (13)	0.5416 (10)	C(47)	0.3307 (22)	0.1831 (19)	−0.1369 (10)
C(14)	0.2794 (15)	0.4835 (11)	0.5112 (8)	C(48)	0.3452 (17)	0.2708 (14)	−0.0970 (10)
C(15)	−0.0108 (16)	0.2651 (13)	0.4483 (10)	C(49)	0.0594 (16)	0.3771 (11)	−0.0293 (8)
C(16)	−0.1054 (14)	0.1972 (10)	0.3944 (7)	C(50)	0.1101 (15)	0.3816 (11)	−0.0893 (8)
C(17)	−0.1545 (19)	0.2101 (14)	0.3383 (9)	C(51)	0.0587 (16)	0.3071 (12)	−0 1494 (8)
C(18)	−0.2452 (21)	0.1379 (14)	0.2870 (11)	C(52)	0.1081 (20)	0.3125 (15)	−0.2053 (9)
C(19)	−0.2899 (24)	0.0516 (16)	0.2904 (13)	C(53)	0.2046 (20)	0.3897 (17)	−0.2031 (11)
C(20)	−0.2385 (24)	0.0293 (17)	0.3408 (12)	C(54)	0.2562 (16)	0.4600 (13)	−0.1448 (10)
C(21)	−0.1495 (20)	0.1048 (12)	0.3887 (11)	C(55)	0.2087 (15)	0.4558 (11)	−0.0899 (8)
C(22)	0.1871 (18)	0.1032 (12)	0.4474 (8)	C(56)	0.2450 (17)	0.2847 (13)	0.1400 (9)
C(23)	0.2123 (16)	0.1339 (11)	0.5171 (8)	C(57)	0.3586 (15)	0.2649 (12)	0.1452 (8)
C(24)	0.3313 (19)	0.1661 (13)	0.5530 (9)	C(58)	0.4731 (17)	0.3323 (13)	0.1758 (9)
C(25)	0.3593 (19)	0.2021 (14)	0.6212 (11)	C(59)	0.5768 (24)	0.3220 (18)	0.1808 (13)
C(26)	0.2619 (24)	0.2067 (15)	0.6569 (9)	C(60)	0.5776 (17)	0.2363 (25)	0.1564 (12)
C(27)	0.1452 (21)	0.1748 (14)	0.6226 (11)	C(61)	0.4659 (22)	0.1589 (15)	0.1230 (10)
C(28)	0.1181 (17)	0.1378 (13)	0.5531 (9)	C(62)	0.3519 (15)	0.1781 (14)	0.1178 (9)
C(29)	0.0548 (23)	−0.0331 (12)	0.2853 (10)	C(63)	0.4416 (17)	0.5703 (13)	0.1861 (10)
C(30)	0.0212 (19)	0.0835 (13)	0.2156 (9)	C(64)	0.2849 (18)	0.6118 (13)	0.0942 (10)
C(31)	0.2654 (20)	0.0890 (14)	0.2540 (10)	C(65)	0.1741 (20)	0.5274 (14)	0.1868 (9)
C(32)	0.3760 (19)	0.0992 (14)	0.3031 (10)	C(66)	0.0434 (15)	0.4798 (12)	0.1544 (9)
C(33)	0.5385 (18)	0.1930 (17)	0.4227 (10)	C(67)	−0.0341 (16)	0.3058 (13)	0.1780 (8)
C(34)	0.5159 (18)	0.2933 (15)	0.3356 (10)	C(68)	−0.1615 (14)	0.3319 (12)	0.0663 (9)

Table VII. Positional Parameters in $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$

atom	*x*	*y*	*z*
U	0.25876 (1)	0.10863 (1)	0.25003 (1)
P(1)	0.37923 (13)	0.27693 (11)	0.26872 (12)
P(2)	0.12666 (13)	0.26367 (13)	0.28032 (14)
C(1)	0.3997 (5)	0.0174 (4)	0.2080 (6)
C(2)	0.4992 (4)	0.0575 (4)	0.1957 (4)
C(3)	0.5743 (5)	0.0798 (4)	0.2702 (4)
C(4)	0.6657 (5)	0.1161 (5)	0.2548 (5)
C(5)	0.6870 (5)	0.1338 (5)	0.1670 (5)
C(6)	0.6132 (5)	0.1119 (5)	0.0938 (5)
C(7)	0.5215 (4)	0.0770 (4)	0.1081 (4)
C(8)	0.3233 (7)	0.1269 (5)	0.4194 (5)
C(9)	0.2854 (5)	0.0448 (5)	0.4513 (4)
C(10)	0.1863 (6)	0.0364 (6)	0.4765 (5)
C(11)	0.1481 (7)	−0.0425 (8)	0.4982 (6)
C(12)	0.2039 (8)	−0.1153 (8)	0.4958 (6)
C(13)	0.3021 (8)	−0.1096 (6)	0.4727 (6)
C(14)	0.3435 (6)	−0.0303 (6)	0.4506 (5)
C(15)	0.0718 (5)	0.0572 (6)	0.2255 (7)
C(16)	0.1151 (4)	−0.0165 (4)	0.1851 (4)
C(17)	0.1734 (5)	−0.0790 (4)	0.2404 (4)
C(18)	0.2242 (5)	−0.1448 (5)	0.1995 (7)
C(19)	0.2220 (7)	−0.1516 (6)	0.1076 (9)
C(20)	0.1675 (7)	−0.0904 (7)	0.0527 (6)
C(21)	0.1155 (5)	−0.0239 (5)	0.0889 (5)
C(22)	0.4562 (6)	0.3053 (5)	0.1785 (5)
C(23)	0.4709 (6)	0.2989 (5)	0.3716 (5)
C(24)	0.2914 (7)	0.3697 (5)	0.2627 (7)
C(25)	0.2059 (7)	0.3603 (5)	0.3146 (7)
C(26)	0.0436 (6)	0.2615 (6)	0.3702 (5)
C(27)	0.0385 (6)	0.3004 (6)	0.1794 (6)
C(28)	0.2409 (7)	0.1769 (7)	0.0998 (5)

49.7; H, 5.92; P, 9.17. Found: C, 49.8; H, 5.67; P, 8.96.

Tribenzylmethylthorium 1,2-Bis(dimethylphosphino)ethane. This alkyl was prepared by a procedure similar to that used to prepare its uranium analogue. The yellow prisms were crystallized from toluene–pentane mixtures in 55% yield: mp 80 °C dec. The infrared spectrum is virtually identical with that of the uranium analogue. Anal. Calcd for $C_{28}H_{40}P_2Th$: C, 50.1; H, 5.97; P, 9.25. Found: C, 49.9; H, 5.78; P, 9.03.

X-ray Crystallography. The crystals, because of their air sensitivity, were sealed inside thin-walled quartz capillaries and mounted on a CAD4 automatic diffractometer equipped with a Mo Kα X-ray tube (λ (Kα_1) = 0.70930 Å) and a highly oriented graphite monochromator (2θ(monochromator) = 12.2°). A set of θ–2θ scan data were collected and corrected for crystal decay, absorption (analytical method),[20] and Lorentz and polarization effects. Details of the data collection and results are shown in Table V.

The Th and U atoms were located with the use of three-dimensional Patterson maps, and subsequent least-squares and electron density maps revealed the locations of all the non-hydrogen atoms. The structures were refined by full-matrix least squares using anisotropic thermal parameters on all of the non-hydrogen atoms, with the exception of the phenyl carbon atoms C(16) through C(21) in the thorium compound, which when refined with anisotropic thermal parameters resulted in excessively large and distorted thermal ellipsoids. Some of the positional parameters in the phenyl group C(9) through C(14) did not converge readily, and the difference electron density maps indicated some disorder. The positional parameters of both phenyl groups, represented by C(9)–C(14) and C(16)–C(21), were refined with imposed interatomic distance restraints.[21] Hydrogen atoms were included in their calculated positions but not refined. The thorium cell contains two crystallographically independent molecules, and the large number of parameters resulted in a matrix larger than our computer could handle; therefore the two molecules were alternately refined with the parameters of one molecule remaining fixed while the parameters of other molecules was allowed to change. Atomic scattering factors of Doyle and Turner[22] were used, and anomalous scattering[23] corrections were applied. No extinction corrections were indicated. Table V gives the resulting *R* factors. A list of positional parameters is given in Table VI and VII. Figures 1 through 3 show ORTEP drawings of the molecules with the numbering scheme used in the tables.

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Registry No. $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$, 88035-42-1; $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$, 88035-41-0; $U(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$, 88035-43-2; $Th(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$, 88035-44-3; $UCl_4(Me_3PCH_2CH_2PMe_2)_2$, 80290-55-7; $ThCl_4(Me_2PCH_2CH_2PMe_2)_2$, 80290-59-1; benzyllithium, 766-04-1; methyllithium, 917-54-4.

Supplementary Material Available: Listings of thermal parameters, hydrogen positional parameters, C–C bond lengths, and observed structure factors (46 pages). Ordering information is given on any current masthead page.

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