Title

Eight Coordinate 1,2-bis(dimethylarsino) and 1,2-bis(dimethylphosphino)-benzene Complexes of Uranium Tetrachloride, $\text{UCl}_4[(1,2\text{-Me}_2\text{E})_2\text{C}_6\text{H}_4]_2$ where E is As or P.

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Dedication

This article is dedicated to M. L. H. Green on the occasion of his 80th birthday with the thanks for writing “Organometallic Compounds, Volume 2”, a book that shaped my (RAA) interests in and understanding of organometallic chemistry.

Graphical Abstract

The eight coordinate complexes $\text{UCl}_4[(1,2\text{-Me}_2\text{E})\text{C}_6\text{H}_4]_2$ (E = As, P) have a dodecahedral geometry in the solid state and exchange their bidentate chelating ligands slowly in solution.

Abstract.

The eight coordinate complexes of 1,2-bis(dimethylarsino)benzene, $MCl_4(diars)_2$ where M is Th or U, and 1,2-bis(dimethylphosphino)benzene, $UCl_4(diphos)_2$, are prepared and characterized. Both coordination complexes of uranium crystallize in the tetragonal crystal system in space group $I\bar{4}2m$, in which the geometry is a D_{2d} -dodecahedron. In solution the uranium complexes do not exchange with added free ligand on the NMR time scale but they undergo bidentate ligand exchange on the chemical time scale. The $^{31}P\{^1H\}$ NMR chemical shifts of $UI_4(diphos)_2$ and $UX_4(dmpe)_2$, X = Cl, Br, I range from 1500 to 2100 ppm and are strongly dependent on temperature.

Introduction

The first report of an eight coordinate complex of the first long period of the Periodic Table (Sc-Cu) was $TiCl_4(diars)_2$, where diars is 1,2-bis(dimethylarsino)benzene, also abbreviated das or pdma (orthophenylenebisdimethylarsine).¹ The complex crystallized in the tetragonal crystal system in space group $\bar{4}2m$, the geometry is dodecahedral (D_{2d}), and the stereochemistry is that referred to as the A-isomer by Kepert.² Several other eight coordinate complexes were prepared for M = Zr, Hf and V, all of which were shown to be isomorphous with the titanium complex.³ The neutral niobium complex, $NbCl_4(diars)_2$, was prepared later and it also crystallized in the $\bar{4}2m$ space group as did the cations $[MCl_4(diars)_2]^+$, M = Nb, Ta and Mo.⁴ The technetium cation is also a D_{2d} -dodecahedron but it crystallizes in the orthorhombic crystal system in space group $Fddd$.⁵ These are the only eight coordinate diars complexes in the literature, they all have a D_{2d} -dodecahedral geometry with the arsenic atom on the A-sites, the chlorides on the B-sites, and the metal on the $\bar{4}$ -site.⁶ Several examples of lower coordinate complexes have been prepared.⁷

The coordination chemistry of the analogous phosphorus complex, 1,2-bis(dimethylphosphino)benzene, diphos, has been extensively studied,⁸ but only one eight coordinate complex, $TiCl_4(diphos)_2$ isomorphous with the diars analogue, is known.⁹

In this article, we describe the synthesis of $MCl_4(diars)_2$, M = Th and U, and $UX_4(diphos)_2$, X = Cl, Br, I and the crystal structures of $UCl_4(diars)_2$ and $UCl_4(diphos)_2$. In a historical context it is important to note that the diars complexes of UCl_4 (or UBr_4) and $ThCl_4$ could not be isolated,^{3,10} however an insoluble complex of stoichiometry $UCl_4(diars)_2$ was

isolated and reported to have a “very similar” X-ray powder diffraction pattern as, but not isomorphous with, $\text{NbCl}_4(\text{diars})_2$.^{4b} As shown below, $\text{UCl}_4(\text{diars})_2$ prepared as outlined in the Experimental Section is isomorphous and isostructural with $\text{NbCl}_4(\text{diars})_2$.

Results and Discussion

Synthesis and Solution Properties $\text{MCl}_4(\text{diars})_2$, $\text{M} = \text{U, Th}$.

The uranium complex, $\text{UCl}_4(\text{diars})_2$, is prepared by stirring solid UCl_4 in a slight excess (2.5 eq) of 1,2-bis(dimethylarsino)benzene for three days, or heating at 90°C for a day. The complex is insoluble in aliphatic hydrocarbons and diethyl ether, slightly soluble in aromatic hydrocarbons and CH_2Cl_2 , from which it crystallizes. It dissolves in THF, but crystallizes from that solvent as $\text{UCl}_4(\text{diars})(\text{THF})_2$. The thorium complex is prepared by heating a suspension of ThCl_4 and diars at 90°C for one day. The thorium complex has similar solubility properties as its uranium analogue and is crystallized from CH_2Cl_2 .

The solution ^1H NMR spectrum of $\text{UCl}_4(\text{diars})_2$ in either C_7D_8 or CD_2Cl_2 at 30°C consists of a singlet at 1.73 due to Me_2As and a $\text{AA}'\text{BB}'$ pattern for the 1,2-disubstituted benzene hydrogens that appear as a pair of four-line patterns that are simulated with the following chemical shifts and coupling constants: $\delta_{\text{A}} = 1.02$, $\delta_{\text{B}} = -4.09$ and $^3J_{\text{AB}} = 8$ Hz, $^3J_{\text{BB}'} = 7$ Hz, $^4J_{\text{A}'\text{B}} = 1.2$ Hz, and $^5J_{\text{AA}'} = 0.5$ Hz, where A and B are the hydrogens on the 3,6 and 4,5 positions, respectively. The ^1H NMR spectrum of $\text{ThCl}_4(\text{diars})_2$ is similar; the Me_2As groups are a singlet at 1.59 and the $\text{AA}'\text{BB}'$ subspectrum is $\delta_{\text{A}} = 7.67$, $\delta_{\text{B}} = 7.00$ and $^3J_{\text{AB}} = 8$ Hz, $^3J_{\text{BB}'} = 7$ Hz, $^4J_{\text{A}'\text{B}} = 1.2$ Hz, and $^5J_{\text{AA}'} = 0.5$ Hz. The simulated values for free diars are: $\delta_{\text{A}} = \delta_{\text{A}'} = 7.67$, $\delta_{\text{B}} = \delta_{\text{B}'} = 7.00$ and $^3J_{\text{AB}} = 8$ Hz, $^3J_{\text{BB}'} = 7$ Hz, $^4J_{\text{A}'\text{B}} = 1.3$ Hz, and $^5J_{\text{AA}'} = 0.5$ Hz. The simulated coupling constants for the $\text{AA}'\text{BB}'$ subspectra for the free and coordinated ligands in the diamagnetic thorium complex and paramagnetic uranium complex have essentially identical values, but the difference between δ_{A} and δ_{B} , $\delta_{\text{A}} - \delta_{\text{B}}$, in the uranium and thorium complexes of 5.1 and 0.67 ppm, respectively alters the appearance of the individual spectra. The temperature dependence of the chemical shifts for $\text{UCl}_4(\text{diars})_2$ in toluene- d_8 are linear in $1/T$ from -80°C to + 110°C implying no temperature-dependant processes are presented over this temperature range, a plot of δ vs. $1/T$ is available in SI.

$\text{UX}_4(\text{diphos})_2$, $\text{X} = \text{Cl, Br, I}$.

The phosphorus analogues of the diars complexes are prepared in order to compare their chemical and physical properties. The diphos complex, $X = Cl$, is prepared by addition of 1,2-bis(dimethylphosphino)benzene to a solution of $UCl_4(tmed)_2$ in toluene. The complex is also prepared by refluxing a suspension of UCl_4 in excess (2.5 eq.) 1,2-bis(dimethylphosphino)benzene for 12 hours. The complex crystallizes as blue-green prisms from a large excess of toluene. The diphos complex is less soluble in toluene and CH_2Cl_2 than the diars complex, but the other halides, $X = Br$ and I are rather more soluble in these solvents. The experimental details for the synthesis of $UX_4(diphos)_2$, $X = Cl, Br, I$ are given in the Experimental Section, as are those for the 1,2-bis(dimethylphosphino)ethane complexes, $UX_4(dmpe)_2$.¹¹

The solution 1H NMR spectrum of $UCl_4(diphos)_2$ in C_7D_8 at $30^\circ C$ is similar to that of the diars complex, the Me_2P resonance is a singlet at 2.42 and the $AA'BB'$ subspectrum appears as a pair of four line patterns with simulated values of: $\delta_A = 0.92$ and $\delta_B = -4.23$ and $^3J_{AB}$ and $^3J_{A'B'} \approx 3$ Hz. The 1H resonances are slightly broadened and the small values of $^2J_{HP}$ are not resolved in any of the uranium-phosphine complexes reported here and those in $UCl_4(dmpe)_2$.¹² The chemical shifts are linear in $1/T$ over the temperature range $-80^\circ C$ to $+110^\circ C$, a plot is available in SI.

Neither $UCl_4(diars)_2$ nor $UCl_4(diphos)_2$ exchange with added diars nor diphos, respectively, on the NMR time scale up to temperatures of $110^\circ C$ in C_7D_8 , since plots of δ vs. $1/T$ for the paramagnetic resonances are identical to those for the complexes without and with added Lewis base. However, mixing solutions of $UCl_4(diars)_2$ and $UCl_4(diphos)_2$ in a 1.3 to 1.0 ratio in C_7D_8 and monitoring the spectra as a function of time at $30^\circ C$ shows that intermolecular exchange of the bidentate ligand occurs slowly. After 4 hours, new resonances begin to appear that increase in intensity at the expense of the resonances in the homo-complexes. The new resonances have their EMe_2 resonances at 1.47 and 2.57 and their $AA'BB'$ resonances are centered at 0.60, -5.14 and 1.04, -3.19, which are assigned to the hetero-complex $UCl_4(diars)(diphos)$ in C_{2v} symmetry. After 24 hours at $30^\circ C$ the ratio is constant and does not change over an additional 24 hour period. The ratio of $UCl_4(diars)_2:UCl_4(diphos)_2:UCl_4(diars)(diphos)$ is approximately 1:1:2 after adjusting the ratios for the different concentrations of the initial complexes. In addition, a variable temperature study of the equilibrium mixture shows that the methyl resonances for each of the compounds in

the mixture are linear in $1/T$ over the temperature range of 30°C to 110°C. These results show that, although intermolecular exchange is slow on the NMR time scale, the phosphine and arsine ligands exchange on the chemical time scale. The statistical distribution between the homo- and hetero-bidentate ligand complexes shows that the U-P and U-As bond enthalpies are essentially the same, although the rate at which equilibrium is reached is slow.

The paramagnetic uranium phosphine complexes give $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Table 1 shows the chemical shifts for those complexes that are sufficiently soluble in C_7D_8 to give quality spectra in reasonable time frames. Two features are immediately apparent, (i) the down field chemical shifts are very large and (ii) they have a strong dependence on the halide bond to uranium. The large chemical shifts are presumably the reason why these resonances were not detected in an earlier study of $\text{UCl}_4(\text{dmpe})_2$ in either CD_2Cl_2 or $(\text{CD}_3)_2\text{SO}$.¹² What is not apparent from data in Table 1 is the large temperature dependence of the chemical shift. The relatively low solubility in non-interacting solvents renders a variable temperature study problematic for all the compounds listed except $\text{UI}_4(\text{dmpe})_2$ in which the chemical shift varies from 3560 ppm at -82°C to 1700 ppm at 100°C; a plot of δ vs. $1/T$ is available in SI.

Table 1. $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts.

Compound	$^{31}\text{P}\{^1\text{H}\}$ ^(a)	ν ^b
$\text{UCl}_4(\text{dmpe})_2$	1506	135
$\text{UBr}_4(\text{dmpe})_2$	1773	115
$\text{UI}_4(\text{dmpe})_2$	2053	150
$\text{UBr}_4(\text{diphos})_2$	1749	170
$\text{UI}_4(\text{diphos})_2$	2100	240

^a δ values in C_7D_8 at 30°C, relative to the external 85 % H_3PO_4 ; positive values are downfield.

^b full width at half-height in Hz.

Solid State Crystal Structure of $\text{UCl}_4(\text{diars})_2$ and $\text{UCl}_4(\text{diphos})_2$.

An ORTEP of $\text{UCl}_4(\text{diars})_2$ is shown in Figure 1. Crystal data are given in the Experimental Section and SI. Bond lengths and bond angles are given for $\text{UCl}_4(\text{diars})_2$, $\text{UCl}_4(\text{diphos})_2$, and $\text{UCl}_4(\text{dmpe})_2$ ¹² in Table 2.

Table 2. Bond distances (Å) and angles (deg) in $\text{UCl}_4(\text{L-L})_2$.

	diars	Diphos	dmpe ^(a)
U-Cl	2.627(1)	2.625(1)	2.648±0.007
U-As/P	3.041(3)	2.984(2)	2.994±0.008
C _(bridge) -As/P	1.942(3)	1.826(5)	1.832±0.011
C _(Me) -As/P	1.953(3)	1.836(5)	
Cl-U-Cl	94.47(1)	94.15(3)	89.89±0.75
	147.57(4)	148.8(1)	148.54±0.40
As/P-U-As/P	66.75(1)	66.25(3)	66.23±0.21
	134.22(1)	134.53(5)	140.74±1.03
U-As/P-C _(bridge)	116.54±0.15	115.6±0.5	113.1±0.6

^a the average value for the three independent molecules in the unit cell, $\pm$ values are the average deviation from mean.¹²

The diars and diphos complexes crystallize in the tetragonal crystal system in space group $\text{I}\bar{4}2\text{m}$. The dmpe complex crystallizes in the orthorhombic crystal system in space group $\text{P}2_12_12_1$ and it is isomorphous with $\text{UCl}_4(\text{tmed})_2$.¹³

The U-Cl distances in the diars and diphos complexes are identical but the U-As distance is only 0.057 Å longer than that of the U-P distance in these isomorphous and isostructural complexes. The As-C distances for As-C(sp²) and As-C(sp³) are 0.116 Å and 0.117 Å longer than the equivalent P-C distances, documented by the average E-C distances between X₂As-C(sp²) and X₂AsC(sp³) relative to the equivalent P-C distances as tabulated by Allen and co-workers.¹⁴ Since the U-Cl distances are equal in the two structures, the difference between the U-As and U-P distance of only 0.057 Å is approximately 0.055 Å shorter than expected from the difference in the As/P radii. A possible explanation for the shorter U-As distance is that the electron density at arsenic is more polarizable than at phosphorus, resulting in a shorter U-As bond distance and greater sharing of the electron density between the uranium and arsenic atoms.

The geometry of the four halide complexes and that of $\text{U}(\text{OPh})_4(\text{dmpe})_2$ ¹¹ are based on a D_{2d} dodecahedron, as shown by their nearly identical shape parameters listed in Table 3.

Table 3 Shape parameters in eight coordination.

Compound	δ' (deg) ^a	Φ (deg) ^b	Normalized bite ^c
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UCl ₄ (diars) ₂	24.1	0	1.10
UCl ₄ (diphos) ₂	26.1	0	1.10
UCl ₄ (dmpe) ₂	26.0, 24.8, 25.1, 28.0	-	1.10
UCl ₄ (tmed) ₂	20.4, 21.9, 38.7, 39.6	1.6	1.09
U(OPh) ₄ (dmpe)	13.0, 15.5, 8.3, 11.1	1.7	-
D _{2d} dodecahedron	29.5	0	-

^a The δ values are the set of angles between the pairs of faces intersecting along the edges connecting the atoms on the B-sites.¹⁵

^b Φ is the dihedral angle between the two orthogonal trapezoids.²

^c the normalized bite distance is L...L/M-L (Å)

Figure 1. ORTEP of UCl₄(diars)₂, 100 K. 50 % thermal ellipsoids, the non-hydrogen atoms are refined anisotropically and the hydrogen atoms are located in the Fourier map and refined isotropically. The ORTEP of UCl₄(diphos)₂ is given available in SI; the same atom numbering scheme is used.

Experimental Section.

All reactions were carried out in an atmosphere of dinitrogen in Schlenk tubes or a drybox. Elemental analyses were done at the microanalytical laboratory at UC Berkeley. All NMR

spectra were recorded using a JEOL-FX90Q spectrometer operated at 89.86 MHz for proton and 36.37 MHz for phosphorus in either C₆D₆, C₇D₈ or CD₂Cl₂ at 30°C, unless otherwise specified. The chemical shifts are reported in δ-units, relative to Me₄Si (for ¹H) and 85% H₃PO₄ (for ³¹P). The ligands were prepared as described in the literature, 1,2-bis(dimethylarsino)benzene,¹⁶ 1,2-bis(dimethylphosphino)benzene¹⁷ and 1,2-bis(dimethylphosphino)ethane.¹⁸

UCl₄[(1,2-Me₂As)₂C₆H₄]₂: A slurry of UCl₄ (0.84g, 2.2 mmol) in 1,2-bis(dimethylarsino)benzene (2.0 g, 7.0 mmol) was stirred for 24 h at 90 °C. The blue-grey suspension was extracted with dichloromethane (5 x 20 mL) and the combined extracts were concentrated to ca. 50 mL and cooled to -80 °C. The blue-violet powder was collected, washed with hexane (2 x 10 mL) and dried under reduced pressure. Crystals suitable for an X-ray diffraction study were obtained by layering a saturated CH₂Cl₂ solution with diethyl ether at 20°C. Yield: 1.6 g, 75%. mp 160 °C (dec.) {powder does not melt up to 350 °C}. ¹H NMR (toluene-*d*₈, 30 °C): δ 1.73 (s, Me₂As, 24 H), 0.68 (m, aryl-H, 4 H), -4.19 (m, aryl-H, 4 H). IR (Nujol, CsI): 3160(w), 1303(w), 1270(m), 1247(w), 1236(w), 1210(w), 1168(m), 1147(m), 1121(m), 1090(m), 1028(m), 970 (m, br.), 902(s), 871(s), 846(m), 757(s), 723(s), 602(s), 445(s), and 257(s) cm⁻¹. Anal. Calcd for C₂₀H₃₂As₄Cl₄U: C, 25.2; H, 3.36; Cl, 14.9. Found: C, 24.5; H, 3.34; Cl, 14.8.

ThCl₄[(1,2-Me₂As)₂C₆H₄]₂: Thorium tetrachloride (1.0g, 0.0027 mol) and the diarsine (1.9g, 0.0066 mol) were mixed and the mixture was heated to 90°C for 3d. The pale grey suspension was cooled to room temperature and extracted with dichloromethane (5 x 20 mL). The combined extracts were concentrated to ca. 50 mL and cooled (-20°C). The colorless prisms (1.9g, 76% yield) were collected and dried under reduced pressure. The complex decomposed at ca. 200°C without melting. Anal. Calc. for C₂₀H₃₂As₄Cl₄Th: C, 25.4; H, 3.41; Cl, 15.0. Found: C, 25.7; H, 3.44; Cl, 14.4. The infrared spectrum is essentially identical to that of its uranium analogue.

UCl₄[(1,2-Me₂P)₂C₆H₄]₂: A solution of UCl₄(tmed)₂¹⁹ (0.95 g, 1.6 mmol) in toluene (40 mL) was treated with 1,2-bis(dimethylphosphino)benzene (0.62 g, 3.1 mmol). After stirring for 12 h at room temperature the light purple solid was isolated by cold (0°C) filtration, washed with hexane (2 x 10 mL), and dried under reduced pressure. The resulting solid is slightly soluble in toluene and dichloromethane. Yield: 0.86 g, 72%. The complex does not melt up to 350 °C. ¹H

NMR (toluene-*d*₈, 30 °C): δ 2.42 (s, Me₂P, 12 H), 1.12 (m, aryl-H, 2 H), -3.84 (m, aryl-H, 2 H). IR (Nujol, KBr): 1572(m), 1290(m), 1275(m), 1241(m), 1208(m), 1170(m), 1159(m), 1136(m), 1118(m), 1114(m), 1084(m), 1037(m), 871(m), 836(w), and 683(m) cm⁻¹. Anal. Calcd for C₂₀H₃₂P₄Cl₄U: C, 30.94; H, 4.15. Found: C, 31.62; H, 4.20.

UBr₄[(1,2-Me₂P)₂C₆H₄]₂: This compound was prepared in a similar manner to that of UBr₄(dmpe)₂, see below, using longer reaction times of ca. 15 h. The complex did not crystallize readily from toluene or dichloromethane or other solvents, a product of sufficient purity was obtained by the removal of all volatile materials from the reaction mixture and washing the light green solid with two portions of hexane. The product was soluble in dichloromethane, slightly soluble in toluene and insoluble in aliphatic hydrocarbons and diethyl ether. Yield: 0.93 g (from 0.60 g of UCl₄(tmed)₂), 89%. The complex does not melt up to 350 °C. ¹H NMR (toluene-*d*₈, 30°C): δ 3.60 (s, Me₂P, 12 H), 2.90 (m, aryl-H, 2 H), -1.18 (m, aryl-H, 2 H). ³¹P{¹H} NMR (toluene-*d*₈, 30°C): δ 1749 (*v*_{1/2} = 167 Hz). IR (Nujol, CsI): 1295(m), 1280(w), 1263(m), 1122(br m), 1096(br m), 1043(br m), 1030(br m), 950(m), 912(m), 878(w), 804(br m), 760(m), 729(m), 685(w), and 468(w) cm⁻¹. Anal. Calcd for C₂₀H₃₂Br₄P₄U: C, 25.18; H, 3.38. Found: C, 25.83; H, 3.68.

UI₄[(1,2-Me₂P)₂C₆H₄]₂: The procedure for the synthesis of this compound was similar to that of UI₄(dmpe)₂ with longer reaction times of ca. 15 h. The orange solid was purified by recrystallization from a saturated toluene solution. The solubility of UI₄(diphos)₂ was greater than that of the 1,2-bis(dimethylphosphino)benzene adducts of UBr₄ or UCl₄. Yield: 1.12 g (from 0.60 g of UCl₄(tmed)₂), 74%. The complex decomposes slowly above 300°C without melting to 350 °C. ¹H NMR (toluene-*d*₈, 30°C): δ 5.12 (s, Me₂P, 12 H), 5.82 (m, aryl-H, 2 H), 3.40 (m, aryl-H, 2 H). ³¹P{¹H} NMR (toluene-*d*₈, 30°C): δ 2101 (*v*_{1/2} = 240 Hz). IR (Nujol, CsI): 1296(m), 1280(w), 1263(w), 1172(w), 1138(w), 1122(br m), 1095(br m), 1044(br m), 1030(br m), 948(m), 912(m), 873(w), 840(vw), 804(br m), 768(m), 723(m), 683(w), and 467(w) cm⁻¹. Anal. Calcd for C₂₀H₃₂I₄P₄U: C, 21.03; H, 2.82. Found: C, 20.97; H, 2.84.

UCl₄[(1,2-Me₂P)₂C₂H₄]₂: To a suspension of UCl₄(tmed)₂¹⁹ (3.06 g; 5.0 mmol) in dichloromethane (50 mL) was added 1,2-bis(dimethylphosphino)ethane (1.84 mL, 11 mmol). The solution was stirred for 12 h, filtered and concentrated to saturation, ca. 10 mL. Cooling at -20°C gave the product as blue-violet crystals. A second crop of crystals was obtained on further concentration and cooling of the supernatant. Yield: 2.38 g, 70%. The complex does not

melt up to 350°C. ^1H NMR (toluene- d_8 , 26°C): δ 2.09 (s, Me_2P , 12 H), -19.6 (s, CH_2 , 4 H). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8 , 30°C): δ 1506 ($\nu_{1/2}$ = 135 Hz). IR (Nujol, CsI): 1295(m), 1278(m), 1260(w), 1133(w), 1088(br w), 1020(br w), 996(w), 949(s), 93 l(s), 896(w), 867(w), 832(w), 800(w), 737(m), 704(m), 648(w), and 245(s) cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{32}\text{Cl}_4\text{P}_4\text{U}$: C, 21.2; H, 4.71; Cl, 20.88. Found: C, 21.6; H, 4.77; Cl, 22.00.

$\text{UBr}_4[(1,2\text{-Me}_2\text{P})_2\text{C}_2\text{H}_4]_2$: $\text{UBr}_4(\text{tmed})_{1-2}$ was prepared from 0.69 g of $\text{UCl}_4(\text{tmed})_2$ and 3 mL of Me_3SiBr as described.¹⁹ All volatile materials were removed under reduced pressure and the solid suspended in toluene (30 mL). The addition of 1,2-bis(dimethylphosphino)ethane (0.41 mL, 2.5 mmol) gave a clear green solution. After stirring for 2 h the solution was filtered, concentrated to saturation and cooled slowly to -20°C. The green solid was separated by filtration and dried under reduced pressure. Yield: 0.97 g, 64%. The complex does not melt to 360°C. ^1H NMR (toluene- d_8 , 26°C): δ 3.35 (s, Me_2P , 12 H), -13.4 (s, CH_2 , 4 H). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8 , 30°C): δ 1773 ($\nu_{1/2}$ = 116 Hz). IR (Nujol, CsI): 1293(m), 1276(m), 1260(m), 1132(m), 1086(br m), 1020(br w), 995(w), 950(s), 929(s), 890(m), 863(m), 830(w), 800(br m), 731(sh s), 700(sh s), and 641(m) cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{32}\text{Br}_4\text{P}_4\text{U}$: C, 16.8; H, 3.73; Br, 37.30. Found: C, 16.9; H, 3.81; Br, 36.98.

$\text{UI}_4[(1,2\text{-Me}_2\text{P})_2\text{C}_2\text{H}_4]_2$: The complex $\text{UCl}_4(\text{tmed})_2$ (0.49 g, 0.80 mmol) was treated in neat Me_3SiI (3 mL) as described in the preparation of $\text{UI}_4(\text{tmed})_{1-2}$.¹⁹ The excess Me_3SiI was removed by vacuum distillation and recycled. The resulting orange solid was suspended in toluene (20 mL) and treated with 1,2-bis(dimethylphosphino)ethane (0.30 mL, 1.8 mmol). The orange solid dissolves rapidly and after stirring for 1 h the solution was concentrated and cooled to -20°C. The orange powder was collected by filtration and dried under reduced pressure. Yield: 0.60 g, 72%. The complex slowly decomposed above 300°C without melting to 350 °C. ^1H NMR (toluene- d_8 , 30°C): δ 5.05 (s, Me_2P , 12 H), -3.35 (s, CH_2 , 4 H). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8 , 30°C): δ 2054 ($\nu_{1/2}$ = 148Hz). IR (Nujol, CsI): 1295(m), 1278(m), 1260(m), 1136(m), 1090(br m), 1020(br m), 1001(w), 946(s), 930(s), 894(m), 867(m), 838(w), 803(br m), 730(s), 702(s), and 644(m) cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{32}\text{I}_4\text{P}_4\text{U}$: C, 13.78; H, 3.08. Found: C, 13.39; H, 2.99.

Exchange Studies. Equimolar quantities of $\text{UCl}_4(\text{diars})_2$ (5.7 mg) and $\text{UCl}_4(\text{diphos})_2$ (4.6 mg) were mixed in toluene- d_8 and filtered into an NMR tube. A ^1H NMR spectrum was acquired at 30 °C within ca. 5 min. The initial ratio of $\text{UCl}_4(\text{diars})_2$ to $\text{UCl}_4(\text{diphos})_2$ was 1.3:1.0 due to

the greater solubility of the diars complex. A spectrum taken after 4 h exhibited six new resonances (δ 2.57(s, Me), 1.45(s, Me), 1.04(m Ar-H), 0.60(m), -3.19(m), and -5.14(m)) which were attributed to the mixed compound $\text{UCl}_4(\text{diars})(\text{diphos})$. After 24 h at 30 °C a spectrum showed an equilibrium mixture involving the three species $\text{UCl}_4(\text{diars})_2$, $\text{UCl}_4(\text{diars})(\text{diphos})$, and $\text{UCl}_4(\text{diphos})_2$ in an approximate statistical ratio of 1 : 2: 1 (corrected for excess $\text{UCl}_4(\text{diars})_2$). The spectrum at 30 °C remained essentially unchanged with additional time or increased temperature. In addition, a variable temperature (30 to 100 °C) ^1H NMR study of the mixture showed that the methyl resonance(s) of each solution species followed Curie-Weiss behavior indicating that **temperature-dependant** processes are slow on the NMR timescale up to 100 °C.

Crystallographic Analyses for $\text{UCl}_4(\text{diars})_2$. A fragment of a gray block-like crystal of $\text{C}_{20}\text{H}_{32}\text{As}_4\text{Cl}_4\text{U}$ having approximate dimensions of 0.11 x 0.09 x 0.08 mm was mounted on a Kapton loop using Paratone N hydrocarbon oil. It was transferred to a APEX II QUAZAR diffractometer with CCD area detector,²⁰ centered in the beam, and the crystal was cooled during data collection by a nitrogen flow low-temperature apparatus previously calibrated by a thermocouple placed at the same position as the crystal ($T = 100$ K). Preliminary orientation matrixes and cell constants were determined by collection of 36 10-s frames, followed by spot integration and least-squares refinement. A data collection strategy was computed with COSMO to ensure a redundant and complete data set, and the raw data were integrated using SAINT.²¹ The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.²² XPREP²³ was used to determinate the space group. The structures were solved using SIR-97²⁴ and refined on all data by full-matrix least-squares with SHELXL-2013.²⁵ Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms found in the Fourier map and refined isoropically. ORTEP diagrams were created using ORTEP-32.²⁶

Crystallographic Analyses for $\text{UCl}_4(\text{diphos})_2$. Crystallographic Analyses. A fragment of a blue-violet orthogonal-like crystal of $\text{C}_{20}\text{H}_{32}\text{P}_4\text{Cl}_4\text{U}$, obtained by crystallization from warm toluene solution cooled slowly to -20°C, having approximate dimensions of 0.15 x 0.31 x 0.40 mm was mounted ($T = 198$ K) in a Enraf-Nonius CAD-4 diffractometer. The data obtained (959 reflections) were solved using SIR-97²⁴ and refined on all data by full-matrix least-squares with

SHELXL-2013.²⁵ (Originally, the data were solved using TEXAN, in which 521 unique reflections were considered giving rise to the following values for 60 variables refined against the 519 data for which $F^2 > 3\sigma(F^2)$: R = 1.38 %, wR = 1.53 %, GOF = 0.918), the SHELXL-2013 found 311 unique reflections, which gave R = 12.70 %, wR = 2.87 %, GOF = 1.070. Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed based on the expected geometry at the carbon atom to which they were attached. ORTEP diagrams were created using ORTEP-32.²⁶

Conclusions.

The chemical and physical properties of the diars and diphos complexes of UCl_4 complete the destruction of the myth that the *5f-block* metals thorium and uranium, and by implication some of the transuranic metals, do not form isolable coordination complexes with arsine and phosphine Lewis bases. Indeed, a convenient synthesis of the phosphine complexes is by ligand displacement of the chelating diamine ligand from $UCl_4(tmed)_2$, showing that the phosphorus chelate is better sigma donor ligand. The coordination complexes do not undergo intermolecular ligand exchange with free ligand on the NMR time scale at 110°C but they do undergo intermolecular bidentate ligand exchange between each other on a chemical time scale. In contrast to $UCl_4(tmed)_2$ in which intramolecular axial-equatorial exchange between the CH_2CH_2 groups in the five-member chelate ring is rapid at 20°C but slow at -50°C, the exchange is still rapid at -80°C in the $UX_4(dmpe)_2$ complexes.²⁷

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Supporting Information Available: Plots of chemical shift (δH) vs. $1/T$ for uranium complexes, Crystal data for $UCl_4(diars)_2$ and the ORTEP and crystal data for $UCl_4(diphos)_2$.

Appendix A. Supplementary data: CCDC 1452257-1452258 contains the supplementary crystallographic data for $\text{UCl}_4[(1,2\text{-Me}_2\text{As})\text{C}_6\text{H}_4]_2$ and $\text{UCl}_4[(1,2\text{-Me}_2\text{P})\text{C}_6\text{H}_4]_2$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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