

Uranium-Mediated Ring Opening of Tetrahydrofuran. Crystal Structure of $U_2(OCH_2CH_2CH_2CH_2I)_2(Ph_3P=O)_2$

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Introduction

Uranium halides constitute a large and important class of actinide compounds.² These compounds are often prepared by high-temperature routes, resulting in polymeric materials unattractive as soluble precursors for nonaqueous inorganic or organometallic chemistry. However, with the recent preparation of soluble halide complexes, prepared by the direct oxidation of uranium metal with a suitable halide source in a coordinating solvent at ambient temperature, there have been advances in the synthesis of novel uranium compounds in the +3 and +4 oxidation states.³

One potential concern of these direct metal oxidation reactions, as evidenced by the synthesis of $U_2I_4(O-i-Pr)_4(HO-i-Pr)_4$, is the role of the solvent as a potential reactant.⁴ Another example is the instability of the uranium(IV) halide toward the solvent itself, as was observed during the course of our efforts to prepare mixed iodo aryl oxide compounds of uranium(IV) starting from the soluble halide precursor $U_4(CH_3CN)_4$.⁵ The present study describes the synthesis and structural characterization of $U_2(OCH_2CH_2CH_2CH_2I)_2(Ph_3P=O)_2$ (**1**).

Experimental Section

General Procedures. All operations were performed using standard Schlenk techniques under oxygen-free UHP grade argon or in a Vacuum Atmospheres drybox under helium. Tetrahydrofuran, hexane, and toluene were dried and distilled from sodium benzophenone or Na–K alloy under nitrogen prior to use. Benzene-*d*₆ and CD₂Cl₂ were dried over CaH₂, vacuum transferred and freeze–pump–thawed three times before use. CDCl₃ was dried by being passed through alumina multiple times. Triphenylphosphine oxide (Ph₃P=O) was purchased from Aldrich. $U_4(CH_3CN)_4$ was prepared by the literature method.^{3b}

¹H NMR spectra (250.13 MHz) were measured on a Bruker AF250 MHz instrument, with the chemical shifts (in ppm) reported relative to the protio impurity of the deuterated solvent. Infrared spectra were obtained on a Bio-Rad FTS-40 infrared spectrometer in Nujol on KBr plates. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer in our laboratories. The samples were prepared and sealed in aluminum capsules in the drybox prior to combustion.

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- (2) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements*; 2nd ed.; Chapman and Hill: London, 1986.
- (3) (a) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. *Inorg. Chem.* **1989**, *28*, 1771. (b) Schake, A. R.; Avens, L. R.; Burns, C. J.; Clark, D. L.; Sattelberger, A. P.; Smith, W. H. *Organometallics* **1993**, *12*, 1497. (c) Deacon, G. B.; Tuong, T. D. *Polyhedron* **1988**, *7*, 249. (d) Deacon, G. B.; Koplick, A. J. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 263. (e) Karraker, D. G. *Inorg. Chim. Acta* **1987**, *139*, 189. (f) Moody, D. C.; Odom, J. D. *J. Inorg. Nucl. Chem.* **1979**, *41*, 533. (g) Du Preez, J. G. H.; Zeelie, B. *Inorg. Chim. Acta* **1986**, *118*, L25.
- (4) (a) Van Der Sluys, W. G.; Huffman, J. C.; Ehler, D. S.; Sauer, N. N. *Inorg. Chem.* **1992**, *31*, 1316. (b) Vilhena, M. T.; Domingos, A. M. T. S.; De Matos, A. P. *Inorg. Chim. Acta* **1984**, *95*, 11.
- (5) Avens, L. R.; Burns, C. J.; McKee, S. D. manuscript in preparation.

Table 1. Crystallographic Data for $U_2(OCH_2CH_2CH_2CH_2I)_2(Ph_3P=O)_2$ (**1**)

empirical formula	$U_4C_{44}H_{46}P_2O_4$	formula weight	1446.4 g/mol
<i>a</i> (Å)	15.219(2)	space group	$P2(1)/n$
<i>b</i> (Å)	9.088(2)	<i>T</i> (°C)	–70
<i>c</i> (Å)	17.306(2)	λ (Å)	Mo K α (0.71073)
β (deg)	95.95(2)	ρ_{calc}	2.018 g/cm ³
<i>V</i> (Å ³)	2380.7(7)	μ	0.067 cm ^{–1}
<i>Z</i>	2	<i>R</i> ^a	4.54
		<i>R</i> _w ^a	7.65

$$^a R = \sum |F_o - F_c| / \sum F_o, R_w = \sum \sqrt{w} |F_o - F_c| / \sum \sqrt{w} F_o.$$

Reaction of $U_4(CH_3CN)_4$ in THF. $U_4(CH_3CN)_4$ (0.100 g, 1.10×10^{-4} mol) was dissolved in ca. 20 mL of THF and permitted to stir for 20 h. The solvent was removed from the mixture under reduced pressure, resulting in the recovery of an oil. The oil was redissolved in ca. 15 mL of toluene, and to this solution was added 0.065 g (2.30×10^{-4} mol) of Ph₃P=O. Addition of Ph₃P=O produced a precipitate, which upon filtration and washing with toluene and hexane yielded 0.130 g of solid **1** (82% yield). Solid **1** was recrystallized from boiling toluene, with the concentrated solution cooled to –40 °C. IR (Nujol, cm^{–1}): 1585 w, 1218 m, 1133 s, 1121 s, 1063 s, 1027 m, 996 m, 932 m, 758 m, 749 m, 728 vs, 693 vs, 539 vs, 440 m. ¹H NMR (CDCl₃, 20 °C): 205 (br s, CH₂), 86 (br s, CH₂), 53 (br s, CH₂), 25 (br s, CH₂), 5.2 (s, para H), 3.7 (s, meta H), –16.7 (s, ortho H). Anal. Calcd for $U_4C_{44}H_{46}P_2O_4$ (**1**): C, 36.54; H, 3.21. Found: C, 36.33; H, 3.11.

$U_4(Ph_3P=O)_2$. $U_4(CH_3CN)_4$ (0.100 g, 1.10×10^{-4} mol) was dissolved in ca. 20 mL of THF. To this solution was added 0.062 g (2.23×10^{-4} mol) of Ph₃P=O. Addition of the Ph₃P=O produced a yellow precipitate, which upon filtration and washing with toluene and hexane yielded 0.130 g of solid **2** (93% yield). IR (Nujol, cm^{–1}): 1586 w, 1160 w, 1124 s, 1116 s, 1033 s, 1011 s, 988 vs, 746 s, 729 vs, 690 s, 537 vs ¹H NMR (CDCl₃, 20 °C): 29.9 (br s, 1H), 11.25 (br s, 2H), 10.55 (br s, 2H). Anal. Calcd for $U_4C_{36}H_{30}P_2O_4$: C, 33.21; H, 2.32. Found: C, 33.60; H, 2.39.

$U_4Br_4(Ph_3P=O)_2$. $U_4(CH_3CN)_4$ (0.100 g, 1.39×10^{-4} mol) was dissolved in ca. 20 mL of THF and permitted to stir for 24 h. To this solution was added 0.077 g (2.77×10^{-4} mol) of Ph₃P=O. Stirring produced a precipitate, which upon filtration and washing with toluene and hexane yielded 0.136 g of solid **3** (88% yield). IR (Nujol, cm^{–1}): 1586 w, 1160 w, 1120 s, 1116 s, 1035 s, 1016 s, 983 vs, 746 s, 727 vs, 689 s, 536 vs. ¹H NMR (CDCl₃, 20 °C): 17.7 (br s, 1H), 9.1 (br s, 2H), 8.9 (br s, 2H).

$U_4Cl_4(Ph_3P=O)_2$. $U_4(CH_3CN)_4$ (0.200 g, 5.27×10^{-4} mol) was dissolved in ca. 20 mL of THF and permitted to stir for 24 h. To this solution was added 0.293 g (1.05×10^{-3} mol) of Ph₃P=O. Stirring produced a blue-green precipitate, which upon filtration and washing with toluene and hexane yielded 0.461 g of solid **4** (94% yield). IR (Nujol, cm^{–1}): 1588 w, 1160 w, 1123 s, 1070 m, 1043 s, 1019 s, 993 s, 751 s, 728 vs, 669 s, 542 vs.

X-ray Diffraction Analysis of **1.** Crystallization of **1** was accomplished by dissolving the solid in CH₂Cl₂ and permitting the slow diffusion of THF at –40 °C. The crystals, because of their air sensitivity, were examined and mounted on a glass fiber with Apiezon “H” grease in mineral oil under an argon stream. All calculations were carried out using the SHELXTL PLUS programs provided by Siemens Analytical. Crystallographic details are summarized in Table 1. Fractional coordinates and equivalent isotropic displacement coefficients are given in Table 2, and selected bond angles and distances are given in Table 3.

Results and Discussion

$U_4(CH_3CN)_4$ dissolves in THF to give a deep red solution that changes color after several hours to produce a brown-colored solution. Removal of the solvent yields an intractable oil. Dissolution of the oil in toluene and addition of triphenylphosphine oxide yield the base adduct $U_2(OCH_2CH_2CH_2CH_2I)_2(Ph_3P=O)_2$, **1** (eq 1). Compound **1** is isolated in 82% yield.

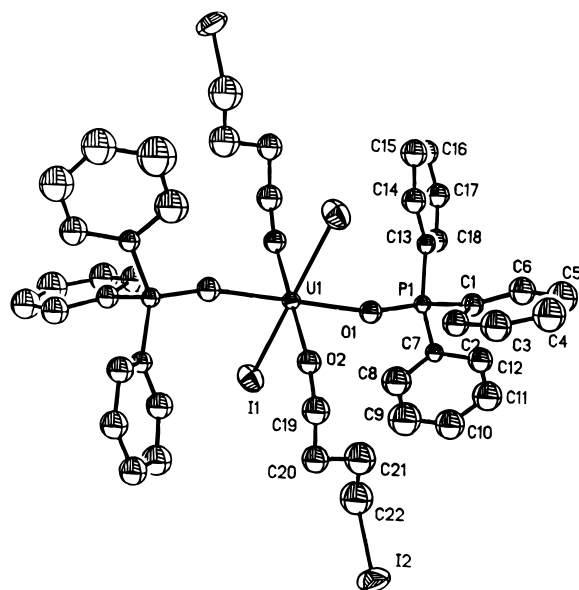
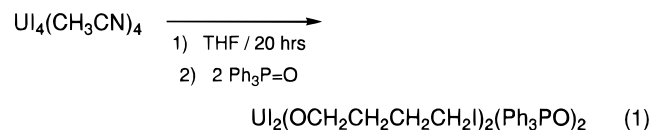


Figure 1. ORTEP drawing of $\text{U}_2(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I})_2(\text{Ph}_3\text{P}=\text{O})_2$ (**1**) with the atomic numbering scheme. The hydrogen atoms are omitted for clarity.



The formulation of **1** as an iodobutoxide compound is supported by elemental analysis and by ^1H NMR and IR spectroscopies. Bulk elemental analysis is consistent with the empirical formula for **1**. Furthermore, hydrolysis of **1** and subsequent isolation of the organic component establish the product of the hydrolysis reaction to be $\text{HO}(\text{CH}_2)_4\text{I}$.⁶

Resonances in the ^1H NMR spectrum of **1** are broad ($\nu_{1/2} > 16$ Hz) and paramagnetically shifted, a phenomenon commonly observed in the spectra of uranium(IV) compounds.⁷ The IR spectrum of **1** is similar to compounds of the general formula $\text{UX}_4(\text{Ph}_3\text{P}=\text{O})_2$ ($X = \text{I}$, **2**; Br , **3**; Cl , **4**), except for the added appearance of a very strong band at 1063 cm^{-1} , which is assigned to the $\nu_{\text{C}-\text{O}}$ stretch.⁸ Strong IR active bands in the 1100 cm^{-1} region have been assigned to the C–O stretching mode observed in uranium–alkoxide complexes.⁹ A band of medium intensity at 1221 cm^{-1} is assigned to the wagging band of the CH_2-I group.¹⁰ Finally, the complexity of the infrared spectrum of **1** in the $1200-900 \text{ cm}^{-1}$ region makes an accurate assignment of the $\nu_{\text{P}=\text{O}}$ stretch difficult.^{8,11}

- (6) Buijs, W.; van Elburg, P.; van der Gen, A. *Synth. Commun.* **1983**, *13*, 387.
- (7) (a) Ammon, R.; Fischer, R. D.; Kanellakopoulos, B. *Chem. Ber.* **1972**, *105*, 45. (b) Ammon, R.; Kanellakopoulos, B.; Fischer, R. D. *Radiochim. Acta* **1969**, *11*, 162. (c) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529. (d) Fischer, R. D. In *Fundamental and Technical Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; NATO ASI Series C; D. Reidel: Dordrecht, 1985; Vol. 155.
- (8) (a) Bombieri, G.; Benetollo, F.; Bagnall, K. W.; Plews, M. J.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1983**, 343. (b) Bombieri, G.; Brown, D.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1975**, 1873.
- (9) (a) Cuellar, E. A.; Miller, S. S.; Marks, T. J.; Weitz, E. *J. Am. Chem. Soc.* **1983**, *105*, 4580. (b) Cuellar, E. A.; Marks, T. J. *Inorg. Chem.* **1981**, *20*, 2129. (c) Duttera, M. R.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2907. (d) Brunelli, M.; Perego, G.; Lugli, G.; Mazzer, A. *J. Chem. Soc., Dalton Trans.* **1979**, 861.
- (10) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981.
- (11) Deacon, G. B.; Green, J. H. S. *Spectrochim. Acta* **1968**, *24A*, 845.

Table 2. Fractional Coordinates and Equivalent Isotropic Displacement Coefficients^a for $\text{U}_2(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I})_2(\text{Ph}_3\text{P}=\text{O})_2$ (**1**)

	10^4x	10^4y	10^4z	$10^3U(\text{eq})$ (\AA^2)
U(1)	0	0	0	23(1)
I(1)	1537(1)	-2085(1)	-5(1)	51(1)
I(2)	4557(1)	2514(1)	-149(1)	71(1)
P(1)	103(1)	1242(2)	-2081(1)	22(1)
O(1)	224(4)	691(7)	-1260(3)	36(2)
O(2)	895(4)	1582(7)	446(3)	36(2)
C(1)	-17(6)	3221(10)	-2104(6)	33(3)
C(2)	167(7)	3976(12)	-1388(7)	48(4)
C(3)	107(8)	5416(15)	-1374(10)	63(5)
C(4)	-55(9)	6148(13)	-2045(12)	83(7)
C(5)	-249(9)	5437(13)	-2778(10)	70(5)
C(6)	-249(7)	3968(12)	-2780(7)	50(4)
C(7)	1054(5)	740(9)	-2563(5)	28(2)
C(8)	1648(9)	-220(13)	-2201(9)	63(5)
C(9)	2411(11)	-564(20)	-2545(12)	87(6)
C(10)	2533(9)	33(16)	-3253(12)	83(7)
C(11)	1929(9)	907(16)	-3633(8)	72(5)
C(12)	1205(7)	1305(11)	-3286(6)	49(4)
C(13)	-868(5)	525(9)	-2591(5)	26(2)
C(14)	-1647(6)	656(13)	-2277(6)	44(3)
C(15)	-2431(8)	96(13)	-2631(9)	57(4)
C(16)	-2421(7)	-676(11)	-3303(6)	46(4)
C(17)	-1659(7)	-854(10)	-3625(6)	47(3)
C(18)	-880(7)	-317(11)	-3277(7)	40(3)
C(19)	1577(7)	2440(12)	747(7)	50(4)
C(20)	2472(6)	1888(13)	547(6)	49(3)
C(21)	2565(7)	1922(17)	-293(7)	72(5)
C(22)	3388(10)	1191(17)	-538(9)	81(4)

$$^a U(\text{eq}) = \frac{1}{3} [U_{11} + U_{22} + U_{33}].$$

Table 3. Selected Bond Distances (\AA) and Bond Angles (deg) for $\text{U}_2(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I})_2(\text{Ph}_3\text{P}=\text{O})_2$ (**1**)

Distances			
U(1)–I(1)	3.011(1)		
U(1)–O(1)	2.329(6)	U(1)–O(2)	2.074(6)
O(1)–P(1)	1.449(6)	P(1)–C(1)	1.808(9)
P(1)–C(7)	1.802(9)	P(1)–C(13)	1.765(10)
O(2)–C(19)	1.358(12)		
C(19)–C(20)	1.525(15)		
C(20)–C(21)	1.476(17)		
C(21)–C(22)	1.515(20)	C(22)–I(2)	2.194(15)
Angles			
I(1)–U(1)–O(1)	88.7(2)	I(1)–U(1)–O(2)	87.5(2)
O(1)–U(1)–O(2)	90.4(2)	U(1)–O(1)–P(1)	164.1(4)
U(1)–O(2)–C(19)	170.9(6)		

Single crystals of **1** were obtained by dissolving the solid in methylene chloride and permitting the slow diffusion of THF at -40°C . In the solid state, **1** is mononuclear with an octahedral geometry about the uranium atom as shown in Figure 1. The triphenylphosphine oxide groups are oriented in a *trans* fashion, with a U–O–P angle of $164.1(4)^\circ$. The U–O and O–P distances for the coordinated triphenylphosphine oxide groups are 2.329(6) and 1.499(6) \AA , respectively. Observation of a nearly linear U–OPPh₃ moiety is common in these compounds.¹² Bis(triphenylphosphine oxide) compounds of the uranium(IV) halides have, in general, been shown to adopt a *trans* disposition, but a *cis* geometry has also been observed.⁸ The U–I distance of 3.011(1) \AA is comparable to reported U–I

- (12) (a) Bombieri, G.; Forsellini, E.; Day, J. P.; Azeez, W. I. *J. Chem. Soc., Dalton Trans.* **1978**, 677. (b) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1986**, *25*, 1761. (c) Bombieri, G.; Brown, D.; Mealli, C. *J. Chem. Soc., Dalton Trans.* **1976**, 2025. (d) Alcock, N. W.; Roberts, M. M.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1982**, 25. (e) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Acta Crystallogr.* **1984**, *C40*, 1186.

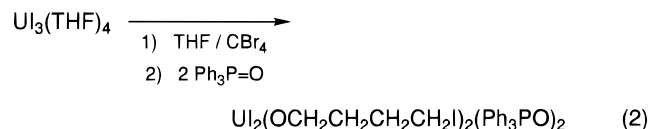
distances of 3.034(3) and 3.050(3) Å found in the uranium(IV) dimer $U_2I_4(O-i-Pr)_4(HO-i-Pr)_2$ and distances of 2.996(3) and 3.027(3) Å in the octahedral complex *trans*- $UI_4(tmu)_2$ (*tmu* = tetramethylurea).^{4a,13} The U–O distance of 2.074(6) Å in the alkoxide moiety is longer than the 2.02(1) Å observed for the terminal alkoxides in $UI_2(O-i-Pr)_4(HO-i-Pr)_2$.^{4a}

Ring-opening reactions involving Lewis acidic metals to mediate the nucleophilic attack of THF are well established.¹⁴ The activation of THF in this manner has been speculated to be an undesirable side reaction in the synthesis of $UI_3(THF)_4$.¹⁵ For uranium, there are several examples in the ring opening of THF, including the recently characterized hydrotris(pyrazolyl)borate complex $[UI(OCH_2CH_2CH_2CH_2I)(HBpz_3)_2]$, which is also terminated by iodide.¹⁶ Several unique ring-opened THF compounds have been structurally characterized in transition metal and lanthanide compounds, with a variety of terminal groups involved as the nucleophile in such transformations.¹⁷

The instability of $UI_4(CH_3CN)_4$ in THF is not too surprising given that uranium tetraiodide is the least thermodynamically stable of the binary uranium(IV) halides.^{2,3a} Similar reactions with either $UBr_4(CH_3CN)_4$ or UCl_4 in THF fail to produce a ring-opening product, but rather result in the formation and isolation of the bis(phosphine oxide) derivatives **3** and **4**. Further, the instability of the uranium tetraiodide is in sharp contrast to the stability of the thorium analog, which can be isolated as $ThI_4(THF)_4$.¹⁸ A room-temperature-solution NMR spectrum of $UI_4(CH_3CN)_4$ in THF-*d*₈ suggests that dissociation of the coordinated CH_3CN for THF is facile and occurs before ring opening. However, the ring-opening process is slow because the immediate addition of $Ph_3P=O$ to a THF solution of $UI_4(CH_3CN)_4$ yields $UI_4(Ph_3P=O)_2$, **2**, in high yield. The apparent lack of stability of $UI_4(THF)_x$ readily explains our unsuccessful attempts to prepare “ UI_4 ” by other routes in this solvent.

Attempts to isolate the proposed intermediate product of eq 1, $UI_2(OCH_2CH_2CH_2CH_2I)_2(THF)_x$, have not been successful.¹⁹ Removal of the THF solvent from the reaction mixture yields an oil that is soluble in toluene but remains an oil when triturated with hexane. Only upon the addition of $Ph_3P=O$ was it possible to isolate a solid compound.

While the ring opening of THF by $UI_4(CH_3CN)_4$ represents an interesting transformation, a similar transformation is observed when $UI_3(THF)_4$ is oxidized by CBr_4 in THF solvent (eq 2). However, the yield is very low (<30%), and it is uncertain what other products are formed. When the same oxidation was carried out in toluene solvent under identical conditions, workup of the reaction afforded a brilliant orange solid that by elemental analysis was consistent with $UI_3Br(THF)_2$. The presence of coordinated THF was supported by IR and ¹H NMR spectroscopies. Replacement of the coordinated THF with tetramethylurea (*tmu*) established that the product was not the desired mixed halide $UI_3Br(tmu)_2$, but rather a mixture of every possible halide combination $UI_xBr_{4-x}(tmu)_2$ (*x* = 0–4). This was verified by NMR experiments where equal molar quantities of $UI_4(tmu)_2$ and $UBr_4(tmu)_2$ (independently prepared from the uranium halide and tetramethylurea) were mixed together. The halide exchange is very facile and suggests that the original orange solid isolated was not $UI_3Br(THF)_2$, but rather the mixture $UI_xBr_{4-x}(THF)_2$. Similarly, oxidation of $UI_3(THF)_4$ with CCl_4 leads to a similar mixture with the formula $UI_xCl_{4-x}(L)_2$ (*L* = THF, CH_3CN , $Ph_3P=O$, and *tmu*). Attempts to oxidize $UI_3(THF)_4$ with Cl_4 in toluene yields an intractable oil. The aspect of halide exchange is not new for uranium(IV) compounds. Finke and co-workers have observed a similar situation where the oxidative addition of $Cp^*_2UCl(THF)$ with alkyl iodides and bromides produced all possible halide combinations.²⁰



The current study examines the instability of $UI_4(CH_3CN)_4$ in THF solvent. Whereas $UBr_4(CH_3CN)_4$ and UCl_4 are stable in THF under the experimental conditions employed here, $UI_4(CH_3CN)_4$ slowly reacts to form $UI_2(OCH_2CH_2CH_2CH_2I)_2(Ph_3P=O)_2$, **1**.²¹ Uranium(IV) halides have an interesting but not well-understood chemistry that continues to generate a lot of inquiry.²² Studies on the role of halide and ancillary ligands will continue.

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Supporting Information Available: Tables providing hydrogen coordinates and isotropic displacement information, anisotropic displacement parameters, bond lengths, and bond angles for **1** (8 pages). Ordering information is given on any current masthead page.

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- (13) (a) du Preez, J. G. H.; Zeelie, B.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1987**, *103*, 677. (b) du Preez, J. G. H.; Rohwer, H. E.; van Brecht, B. J. A. M.; Zeelie, B.; Casellato, U.; Graziana, R. *Inorg. Chim. Acta* **1991**, *189*, 67.
- (14) (a) Van Der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255. (b) Olah, G. A.; Narang, S. C. *Tetrahedron* **1982**, *38*, 2225. (c) Woodhouse, M. E.; Lewis, F. D.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5586. (d) Harwood, L. M.; Jackson, B.; Prout, K.; Witt, F. J. *Tetrahedron. Lett.* **1990**, *31*, 1885. (e) Delaney, P. A.; Johnstone, R. A. W.; Entwistle, I. D. *J. Chem. Soc., Perkin Trans 1* **1986**, 1855. (f) Kern, R. J. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1105.
- (15) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 2248.
- (16) (a) Ter Harr, G. L.; Dubeck, M. *Inorg. Chem.* **1964**, *3*, 1648. (b) McLaren, A. B.; Kanellakopoulos, B.; Dornberger, E. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 223. (c) Campello, M. P. C.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **1994**, *484*, 37.
- (17) (a) Schumann, H.; Palamidis, E.; Loebel, J. *J. Organomet. Chem.* **1990**, *384*, C49. (b) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D. *Organometallics* **1990**, *9*, 2124. (c) Breen, T. L.; Stephan, D. W. *Inorg. Chem.* **1992**, *31*, 4019.
- (18) Clark, D. L.; Frankcom, T. M.; Müller, M. M.; Watkin, J. G. *Inorg. Chem.* **1992**, *31*, 1628.
- (19) The green-brown oil obtained before the addition of $Ph_3P=O$ is proposed to be $UI_2(OCH_2CH_2CH_2CH_2I)_2(THF)_x$ (*x* > 2) on the basis of the ¹H NMR spectrum.

- (20) Finke, R. G.; Hirose, Y.; Gaughan, G. *J. Chem. Soc., Chem. Commun.* **1981**, 232.
- (21) Van Der Sluys, W. G.; Berg, J. M.; Barnhart, D.; Sauer, N. N. *Inorg. Chim. Acta* **1993**, *204*, 251.
- (22) Edwards, P. G.; Weydert, M.; Petrie, M. A.; Andersen, R. A. *J. Alloys Compd.* **1994**, *213–214*, 11.