

A Homoleptic Uranium(III) Tris(aryl) Complex

Michael A. Boreen, Bernard F. Parker, Trevor D. Lohrey, and John Arnold*^{ib}

Department of Chemistry, University of California, Berkeley, and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, United States

S Supporting Information

ABSTRACT: The reaction of 3 equiv of Li–C₆H₃-2,6-(C₆H₄-4-^tBu)₂ (Terph–Li) with U_I₃(1,4-dioxane)_{1.5} led to the formation of the homoleptic uranium(III) tris(aryl) complex (Terph)₃U (1). The U–C bonds are reactive: treatment with excess ⁱPrN=C=NⁱPr yielded the double-insertion product [TerphC(NⁱPr)₂]₂U(Terph) (2). Complexes 1 and 2 were characterized by X-ray crystallography, which showed that the U–C bond length in 2 (2.624(4) Å) is ~0.1 Å longer than the average U–C bond length in 1 (2.522(2) Å). Thermal decomposition of 1 yielded Terph–H as the only identifiable product; the process is unimolecular with activation parameters ΔH[‡] = 21.5 ± 0.3 kcal/mol and ΔS[‡] = –7.5 ± 0.8 cal·mol^{–1} K^{–1}, consistent with intramolecular proton abstraction. The protonolysis chemistry of 1 was also explored, which led to the uranium(IV) alkoxide complex U(OCPh₃)₄(DME) (3·DME).

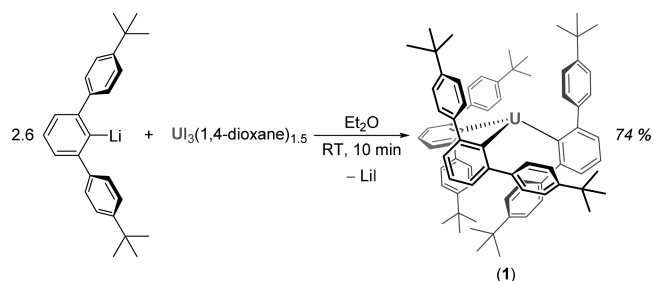
Homoleptic σ-bonded alkyl and aryl complexes of uranium have been synthetic targets since the 1940s, originally as potential volatile species for uranium isotope separation during the Manhattan Project.^{1,2} Despite continuing interest in the nature of U–C σ bonds, homoleptic uranium alkyl complexes are quite rare,^{2–7} as most examples are thermally unstable at or below room temperature. A major breakthrough came in 1989, when Sattelberger and co-workers reported the first homoleptic uranium(III) alkyl complex, U[CH(SiMe₃)₂]₃.⁷ More recently, Hayton and co-workers have stabilized actinide–aryl bonds using an aryl ligand with a pendant amine moiety.^{8,9} Hayton and co-workers also provided the first structural characterization of a thorium(IV) aryl-ate complex, [Th(C₆H₅)₆]^{2–}.¹⁰ There is only a single previous report of related uranium aryl complexes (Li₂UR₆(Et₂O)₈; R = Ph, Me₂NCH₂C₆H₄) that lacks structural details.² Additionally, little is known about the reactivity of the An–C bond in these species. Here we report the synthesis and structural characterization of the first example of a homoleptic uranium(III) aryl complex. We also describe preliminary reactivity studies with this complex.

With the intention of synthesizing stable uranium aryl complexes, we turned to *m*-terphenyl ligands, which have been exploited by Power and co-workers to prepare reactive, low-valent, low-coordinate metal complexes.^{11–13} Specifically, we focused on the C₆H₃-2,6-(C₆H₄-4-^tBu)₂[–] (Terph[–]) group, as we hypothesized that the bulky substituent at the para position of the flanking aryl groups would prevent aggregation and confer adequate steric protection to the uranium center, while the absence of ortho substituents on the flanking aryl groups

would leave the ipso carbon of the central aryl ring accessible for rapid metalation.

Terph–Li reacted quickly with U_I₃(1,4-dioxane)_{1.5}¹⁴ in diethyl ether at room temperature to form the homoleptic uranium(III) aryl complex (Terph)₃U (1), as shown in Scheme 1. While initially appearing to form black crystals, thin plates of

Scheme 1. Synthesis of (Terph)₃U (1)



1 appear yellow when viewed under a microscope. Similarly, solutions of 1 are dark yellow, and the UV–vis spectrum of 1 reveals broad absorption features throughout the visible range (Figure S1). Complex 1 can be synthesized in gram quantities and 74% yield with a reaction time of 10 min.

As expected, 1 is extremely air- and moisture-sensitive: solid samples decomposed exothermically when exposed to air. It is soluble in diethyl ether, hydrocarbon solvents, and hexamethyldisiloxane (HMDSO), although slow decomposition was observed in all solutions of 1 at room temperature. As monitored by ¹H NMR spectroscopy in C₆D₆, *t*_{1/2} = 10.3 ± 0.2 h at 23 °C. Solid samples of complex 1 decomposed nearly to completion within 3 weeks at room temperature. Solid samples of 1 can be stored at –40 °C for over a month with no sign of decomposition.

In both solution and the solid state, the major product of decomposition was identified as Terph–H,¹⁵ with other paramagnetic and diamagnetic products present in small quantities. Samples of 1 that were allowed to decompose to completion in C₆D₆ showed no sign of deuterium incorporation into soluble products on the basis of ²H NMR spectroscopy.

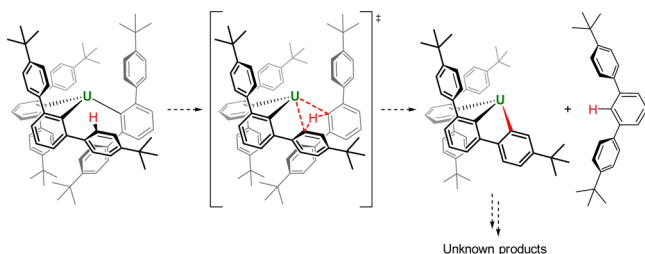
To elucidate the mechanism by which 1 decomposed, the decomposition reaction was monitored by ¹H NMR spectroscopy at several different temperatures between 23 and 80 °C. Within this range, decomposition was first order in 1, and a graph of ln(*k*/*T*) versus 1/*T* was found to be linear. Eyring

Received: October 26, 2016

Published: December 1, 2016

analysis afforded $\Delta H^\ddagger = 21.5 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -7.5 \pm 0.8$ cal·mol⁻¹ K⁻¹ (Figure S2). The negative value of ΔS^\ddagger , as well as the lack of deuterium incorporation in Terph-H formed by decomposition, provides evidence against a mechanism involving homolytic cleavage of a U-C bond. Therefore, we propose that decomposition occurs by proton abstraction from an ortho carbon on a flanking C₆H₄-4^tBu group by a neighboring terphenyl ligand. The proposed transition state for this process is shown in Scheme 2. This

Scheme 2. Proposed Mechanism for Decomposition of (Terph)₃U



mechanism is similar to the mechanism proposed for the decomposition of Cp₃UR (R = alkyl, vinyl, aryl), in which a proton is abstracted from a cyclopentadienyl ligand by the R group.¹⁶ Additionally, two ortho C-H bonds of the related terphenyl ligand C₆H₃-2,6-(C₆H₄-4-Me)₂ were found to undergo σ -bond metathesis with methyl substituents in a tantalum complex to form a κ^3 -CCC doubly cyclometalated complex.¹⁷

Despite the thermal instability of complex **1**, pure samples were obtained by recrystallization from diethyl ether (Figure S4). Additionally, X-ray-quality crystals of **1** were formed by cooling a hexane/HMDSO solution of **1** to -40 °C. The solid-state structure of **1** is shown in Figure 1. The uranium center exhibits a three-coordinate trigonal-pyramidal geometry. The U-C(aryl) bond lengths in **1** range from 2.497(3) to 2.544(3)

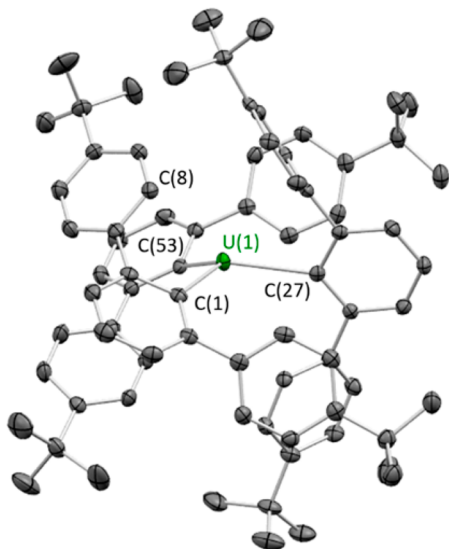


Figure 1. X-ray crystal structure of **1** with 50% probability ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)-C(1) 2.544(3), U(1)-C(27) 2.497(3), U(1)-C(53) 2.524(3), C(1)-U(1)-C(27) 110.96(9), C(1)-U(1)-C(53) 120.07(9), C(27)-U(1)-C(53) 120.19(9).

Å and are similar to the U-C(alkyl) bond length of 2.48(2) Å in U[CH(SiMe₃)₂]₃⁷ and the U-C(phenyl) bond length of 2.513(2) Å in (C₅Me₅)₂(hpp)UPh (hpp⁻ = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinato).¹⁸ There is a single close contact in **1** between the uranium center and an ortho carbon on a flanking aryl ring [U(1)-C(8) = 2.901(3) Å]. The uranium center is 0.442(2) Å out of the plane of the coordinating aryl carbon atoms. Deviation from planarity in three-coordinate uranium(III) complexes has been well-reported;^{7,19-22} it can be explained by the polarized ion model,¹⁹ which states that a more pyramidal geometry results in a more favorable charge-dipole interaction between the metal and the ligands.

The ¹H NMR spectrum of **1** displays only five resonances, indicating that all three ligands are equivalent on the NMR time scale (Figure S4). While the ^tBu and central aryl ring protons were assigned solely on the basis of integrations, the two resonances from the flanking aryl rings at -6.51 and -14.56 ppm correspond to equivalent numbers of protons. On the basis of the solid-state structure, the protons bonded to the carbon atoms ortho to the central aryl ring are closer in space on average to the uranium center. Therefore, we tentatively assigned these protons to the broadest, most upfield resonance.¹⁶ Additional support for this assignment was provided by a 1D selective ¹H NOESY experiment (Figure S9).

Variable-temperature ¹H NMR experiments on **1** showed no splitting of the five resonances down to -70 °C (Figure S7), implying that any U(1)-C(8) interaction is weak. Plots of the ¹H chemical shifts versus 1/T are linear down to -70 °C for all five resonances (Figure S8), as expected for a paramagnetic complex following Curie-Weiss behavior.²³ The room-temperature μ_{eff} value of **1** was determined by the Evans NMR method to be 3.6(1) μ_{B} , which is toward the higher end of the reported range for uranium(III) complexes.²⁴

With complex **1** successfully isolated and characterized, we sought to explore its reactivity. On the basis of previous reports by Evans and co-workers of carbodiimide insertion into U(IV)-C(phenyl) bonds,^{25,26} we treated **1** with an excess of ^tPrN=C=N^tPr. A rapid reaction ensued, resulting in a green solution containing [TerphC(N^tPr)₂]₂U(Terph) (**2**) as the only product by ¹H NMR spectroscopy. Complex **2** is sparingly soluble in benzene at room temperature but insoluble in other hydrocarbon solvents, diethyl ether, THF, and pyridine. Despite the low solubility of **2** in benzene, it was slow to crystallize out of solution when formed by the reaction of **1** with ^tPrN=C=N^tPr in benzene. Thus, ¹H NMR spectra of **2** with sufficient concentration were obtained using crude reaction mixtures (Figure S5).

Complex **2** was also isolated through a one-pot synthesis by the in situ reaction of **1** with ^tPrN=C=N^tPr in benzene (Scheme 3). Dark-green X-ray-quality crystals of **2** were formed in 42% yield after 2 weeks. The structure of **2** was determined by X-ray crystallography, which confirmed that diisopropylcarbodiimide inserted into only two of the three U-C bonds in **1** to give the uranium(III) bis(amidinate) aryl complex **2** (Figure 2). Complex **2** has a τ_5 value of 0.51, indicating a geometry halfway between ideal square-pyramidal ($\tau_5 = 0$) and trigonal-bipyramidal ($\tau_5 = 1$).²⁷ The U-C(aryl) bond length, 2.624(4) Å, is considerably longer than those found in complex **1**, likely because of the higher coordination number and increased steric pressure imposed by the amidinate ligands.

In contrast to **1**, **2** displayed high thermal stability: solid samples of **2** under N₂ began to decompose only when heated

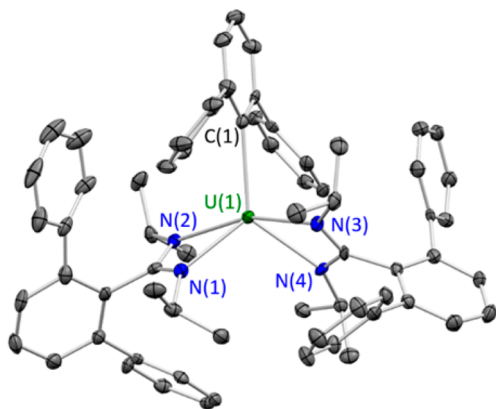
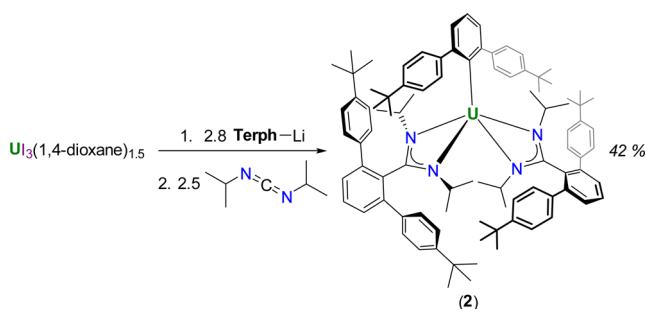
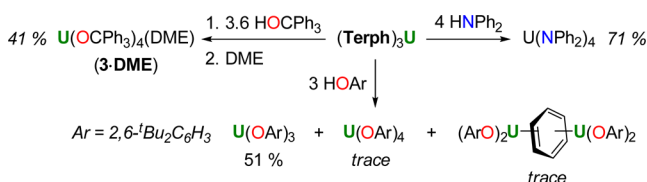
Scheme 3. One-Pot Synthesis of [TerphC(N^tPr)₂]₂U(Terph) (2)


Figure 2. X-ray crystal structure of **2** with 50% probability ellipsoids. H atoms and ^tBu groups have been omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)–C(1) 2.624(4), U(1)–N(1) 2.457(3), U(1)–N(2) 2.534(3), U(1)–N(3) 2.533(3), U(1)–N(4) 2.467(3), N(1)–U(1)–N(2) 53.5(1), N(3)–U(1)–N(4) 52.7(1).

above 211 °C. Traces of amidine²⁸ and arene were detected when a solution of **2** in C₆D₆ was heated at 100 °C in a sealed NMR tube for 16 h. The thermal stability of **2** supports previous experimental work showing that U–C(aryl) bonds are not in general expected to be thermodynamically unstable.²⁹ Blocking kinetic pathways to decomposition with bulky ligands can thus lead to stable U–C(aryl) bonds.

The protonolysis chemistry of **1** was also explored (Scheme 4). When 3 equiv of HO-2,6-^tBu₂C₆H₃ (HODtbp) was allowed

Scheme 4. Protonolysis Reactivity of (Terph)₃U (1)^a


^aThe isolated yield is shown for **3·DME**. The percent conversion by ¹H NMR spectroscopy is shown for the other substrates.

to react with **1**, the uranium(III) tris(aryloxy) complex U(ODtbp)₃ was observed as the major product (51% conversion) by ¹H NMR spectroscopy.³⁰ However, traces of the uranium(IV) tetrakis(aryloxy) complex U(ODtbp)₄ and the inverse sandwich complex [(DtbpO)₂U]₂(μ-η⁶,η⁶-C₆D₆) were also observed in the ¹H NMR spectrum (Figure S10).³¹ Alcohols have previously been observed to oxidize U(III) to

U(IV) through mechanisms proposed to involve disproportionation of U(III) intermediates.³²

We reasoned that use of a less bulky alcohol or amine would lead to the corresponding U(IV) tetrakis(alkoxide) or tetrakis(amide) complexes as the major products. When 3 equiv of Ph₃COH were added to a toluene solution of **1** at room temperature, a green-brown solid rapidly precipitated. After recrystallization from DME, ¹H NMR and elemental analysis data indicated that the light-blue product was the new uranium(IV) tetrakis(alkoxide) complex U(OCPh₃)₄(DME) (**3·DME**) (Figure S6). The identity of this product was confirmed by X-ray crystallography (Figure S12). When **1** was treated with excess HNPh₂ in C₆D₆, 71% conversion to the uranium(IV) tetrakis(amide) complex U(NPh₂)₄³³ was observed by ¹H NMR spectroscopy (Figure S11).

In conclusion, we have isolated the homoleptic uranium(III) tris(aryl) complex (Terph)₃U (**1**) in high yield. Its X-ray crystal structure represents the first full structural characterization of such a species. Decomposition studies indicated that intramolecular proton abstraction is responsible for its thermal instability. In the presence of excess ^tPrN=C=N^tPr, it is rapidly and cleanly converted to the double-insertion product [TerphC(N^tPr)₂]₂U(Terph) (**2**), which, in contrast to **1**, is thermally stable. The U–C bonds are also prone to protonolysis, yielding uranium(IV) tetrakis(alkoxide) or tetrakis(amide) products. Use of a bulkier alcohol, HODtbp, suppressed oxidation of uranium, leading to the uranium(III) tris(aryloxy) as the major product. These results indicate that the use of bulky terphenyl ligands in actinide chemistry is a fruitful endeavor that we aim to develop further in ongoing studies.

■ ASSOCIATED CONTENT
📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11182.

Crystallographic data for 1·1.5C₆H₁₄ (CIF)

Crystallographic data for 2·0.5C₆H₆ (CIF)

Crystallographic data for 3·DME (CIF)

Experimental procedures, UV–vis spectrum of **1**, Eyring plot for decomposition of **1**, NMR data, and crystallographic data (PDF)

■ AUTHOR INFORMATION
Corresponding Author

*arnold@berkeley.edu

ORCID

John Arnold: 0000-0001-9671-227X

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences Heavy Element Chemistry Program of the U.S. Department of Energy (DOE) at LBNL under Contract DE-AC02-05CH11231. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract DE-AC02-05CH11231. The authors acknowledge Dr. Simon Teat of ALS station 11.3.1 for his assistance with

crystallographic data collection for 3•DME. M.A.B. thanks UC Berkeley for a graduate research fellowship.

Barnes, C. L., Walensky, J. R. (2016). Chemical Communications. <http://doi.org/10.1039/C6CC08105C>.

■ REFERENCES

- (1) Cotton, S. *Lanthanide and Actinide Chemistry*; John Wiley & Sons: Chichester, U.K., 2006.
- (2) Sigurdson, E. R.; Wilkinson, G. J. *Chem. Soc., Dalton Trans.* **1977**, 812.
- (3) Seaman, L. A.; Walensky, J. R.; Wu, G.; Hayton, T. W. *Inorg. Chem.* **2013**, *52*, 3556.
- (4) Fortier, S.; Melot, B. C.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2009**, *131*, 15512.
- (5) Fortier, S.; Walensky, J. R.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2011**, *133*, 11732.
- (6) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. *J. Am. Chem. Soc.* **2012**, *134*, 6160.
- (7) Van Der Sluys, W. G.; Burns, C. J.; Sattelberger, A. P. *Organometallics* **1989**, *8*, 855.
- (8) Seaman, L. A.; Pedrick, E. A.; Tsuchiya, T.; Wu, G.; Jakubikova, E.; Hayton, T. W. *Angew. Chem., Int. Ed.* **2013**, *52*, 10589.
- (9) Pedrick, E. A.; Seaman, L. A.; Scott, J. C.; Griego, L.; Wu, G.; Hayton, T. W. *Organometallics* **2016**, *35*, 494.
- (10) Pedrick, E. A.; Hrobárik, P.; Seaman, L. A.; Wu, G.; Hayton, T. W. *Chem. Commun.* **2016**, *52*, 689.
- (11) Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem.* **1999**, *44*, 1.
- (12) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047.
- (13) Ni, C.; Power, P. P. *Struct. Bonding (Berlin, Ger.)* **2010**, *136*, 59.
- (14) Monreal, M. J.; Thomson, R. K.; Cantat, T.; Travia, N. E.; Scott, B. L.; Kiplinger, J. L. *Organometallics* **2011**, *30*, 2031.
- (15) Finke, A. D.; Moore, J. S. *Org. Lett.* **2008**, *10*, 4851.
- (16) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529.
- (17) Sattler, A.; Parkin, G. *J. Am. Chem. Soc.* **2012**, *134*, 2355.
- (18) Montalvo, E.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L.; Evans, W. J. *Organometallics* **2010**, *29*, 2104.
- (19) Stewart, J. L.; Andersen, R. A. *Polyhedron* **1998**, *17*, 953.
- (20) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 9036.
- (21) Roger, M.; Barros, N.; Arliguie, T.; Thuéry, P.; Maron, L.; Ephritikhine, M. *J. Am. Chem. Soc.* **2006**, *128*, 8790.
- (22) Mansell, S. M.; Perandones, B. F.; Arnold, P. L. *J. Organomet. Chem.* **2010**, *695*, 2814.
- (23) Lukens, W. W.; Beshouri, S. M.; Bloch, L. L.; Stuart, A. L.; Andersen, R. A. *Organometallics* **1999**, *18*, 1235.
- (24) Kindra, D. R.; Evans, W. J. *Chem. Rev.* **2014**, *114*, 8865.
- (25) Evans, W. J.; Walensky, J. R.; Ziller, J. W.; Rheingold, A. L. *Organometallics* **2009**, *28*, 3350.
- (26) Evans, W. J.; Takase, M. K.; Ziller, J. W.; Rheingold, A. L. *Organometallics* **2009**, *28*, 5802.
- (27) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
- (28) Schmidt, J. A. R.; Arnold, J. J. *Chem. Soc., Dalton Trans.* **2002**, 2890.
- (29) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275.
- (30) Van Der Sluys, W. G.; Burns, C. J.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 5924.
- (31) Arnold, P. L.; Mansell, S. M.; Maron, L.; McKay, D. *Nat. Chem.* **2012**, *4*, 668.
- (32) Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics* **1990**, *9*, 1623.
- (33) Turman, S. E.; Van Der Sluys, W. G. *Polyhedron* **1992**, *11*, 3139.

■ NOTE ADDED IN PROOF

A new U(III) tris(alkyl) complex was just reported: Behrle, A. C., Myers, A. J., Rungthanaphatsophon, P., Lukens, W. W.,