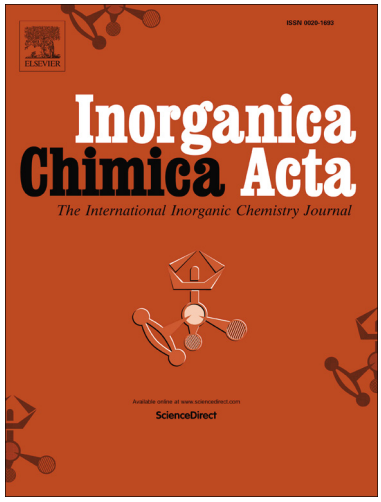

Research paper

Synthesis, characterization, and reactivity of the first uranium metallocene 1,2-bis(diphenylphosphino)acetylene complexes

Justin K. Pagano, Brian L. Scott, David E. Morris, Jaqueline L. Kiplinger

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Synthesis, characterization, and reactivity of the first uranium metallocene 1,2-bis(diphenylphosphino)acetylene complexes.

Justin K. Pagano,[a] Brian L. Scott,[a] David E. Morris,[a,*] and Jaqueline L. Kiplinger[a,*]

[a] *Los Alamos National Laboratory, Los Alamos, NM 87545, USA*

* Corresponding author. Tel: +1-505-665-9553; Fax: +1-505-667-9905; E-mail: kiplinger@lanl.gov (J. L. Kiplinger).

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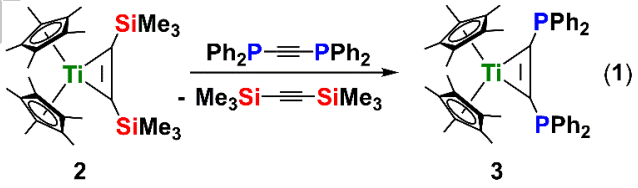
A B S T R A C T

Two new uranium metallacyclopropenes, $(C_5Me_4R)_2U(\eta^2\text{-}Ph_2PC{=}CPPh_2)$ (R = Me, Et) were prepared by reducing the corresponding $(C_5Me_4R)_2UCl_2$ complexes with KC_8 in the presence of 1,2-bis(diphenylphosphino)acetylene ($Ph_2P–C{\equiv}C–PPh_2$). Both compounds were fully characterized by a combination of elemental analysis and multinuclear NMR, UV–visible–NIR, and IR spectroscopies. Differences in the electronic spectra of these novel compounds and the known $(C_5Me_5)_2U(\eta^2\text{-}Me_3SiC{=}CSiMe_3)$ are discussed. Also presented is the solid-state structure of $(C_5Me_4Et)_2U(\eta^2\text{-}Ph_2PC{=}CPPh_2)$, which reveals significant distortions of the coordinated 1,2-bis(diphenylphosphino)acetylene ($Ph_2P–C{\equiv}C–PPh_2$) ligand.

1. Introduction

All-carbon actinide metallacycles have witnessed renewed significance due to their interesting reactivity and spectroscopic properties.[1-5] Since the synthesis of the first actinide metallacyclopentadiene complex, $(C_5Me_5)_2U(\eta^2\text{-}C_4Ph_4)$, by Marks and co-workers in 1981,[6] additional metallacyclopentadiene complexes,[5, 7-10] metallacyclocumulene complexes,[1, 2, 4] and metallacyclopropene complexes[3, 11, 12] of thorium and uranium have been discovered. Recently, our group[1] and Walter's[3, 5] have used the uranium metallacyclopropene complex, $(C_5Me_5)_2U(\eta^2\text{-}Me_3SiC{=}CSiMe_3)$ (**1**), as a reactive low-valent "$(C_5Me_5)_2U$" synthon to prepare a variety of new and electronically diverse uranium complexes. Despite these advances, this area of research is undeveloped for the f-elements when compared to the rich body of work reported group 4 metallacycles.[15, 16] For example, to date, $(C_5Me_5)_2U(\eta^2\text{-}Me_3SiC{=}CSiMe_3)$ (**1**) is the only known $(C_5Me_5)_2U$-based metallacyclopropene complex.

Rosenthal and co-workers reported that reaction of $(C_5Me_5)_2Ti(\eta^2\text{-}Me_3SiC{=}CSiMe_3)$ (**2**) with 1,2-bis(diphenylphosphino)acetylene ($Ph_2P–C{\equiv}C–PPh_2$) afforded $(C_5Me_5)_2Ti(\eta^2\text{-}Ph_2PC{=}CPPh_2)$ (**3**), which is the only structurally characterized metallacyclopropene complex featuring $Ph_2PC{\equiv}CPPh_2$.



2 **3** (**1**)

Given the numerous reported parallels in the chemistry for uranium and titanium,[17-19] we were interested in preparing the uranium metallacyclopropene complex $(C_5Me_5)_2U(\eta^2\text{-}Ph_2PC{=}CPPh_2)$ (**4**) as a potential platform for the preparation of multimetallic uranium complexes to study electronic and magnetic metal-metal interactions.[14] Herein, we disclose the synthesis and full characterization of two new uranium metallacyclopropene complexes $(C_5Me_4R)_2U(\eta^2\text{-}Ph_2PC{=}CPPh_2)$ (R = Me (**4**), Et (**5**)), the electronic and spectroscopic characterization of $(C_5Me_5)_2U(\eta^2\text{-}Me_3SiC{=}CSiMe_3)$ (**1**), as well as our attempts at using compounds **4** and **5** for the preparation of heterobimetallic species and other uranium metallacycles. Finally, the solid-state structure of $(C_5Me_4Et)_2U(\eta^2\text{-}Ph_2PC{=}CPPh_2)$ (**5**) is reported, which shows unique distortions of the coordinated $Ph_2P–C{\equiv}C–PPh_2$ ligand when compared to previously reported titanium and uranium metallacyclopropene complexes.

2. Experimental

2.1 General synthetic procedures