



Full paper/Mémoire

Reactivity of the tethered alkyl uranium bonds of $(\eta^5:\kappa^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2)_2\text{U}$

William J. Evans*, Nathan A. Siladke, Joseph W. Ziller

Department of Chemistry, University of California, Irvine, California 92697-2025, United States

ARTICLE INFO

Article history:

Received 29 December 2009

Accepted after revision 9 February 2010

Available online 26 March 2010

Keywords:

Uranium

Cyclopentadienyl ligands

Insertion

Alkyl ligands

Metallocene

ABSTRACT

Uranium-carbon bond reactivity has been investigated with the bis(tethered silylalkyl) uranium metallocene $(\eta^5:\kappa^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2)_2\text{U}$, **1**. *Tert*-butyl nitrile, $t\text{-BuC}\equiv\text{N}$, inserts into both of the tethered U-C bonds to produce the bis(tethered ketimide) complex $[\eta^5:\kappa^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{C}(t\text{Bu})\text{N}]_2\text{U}$, **2**, which has unusually bent U-N-C bond angles. Carbon dioxide also inserts into both U-C bonds of **1** yielding the bis(tethered carboxylate) $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{CO}_2)_2\text{U}$, **3**. Neither $\text{PhC}\equiv\text{CPh}$ nor $\text{PhC}\equiv\text{CH}$ insert into the U-C bonds, but $\text{PhC}\equiv\text{CH}$ cleaves the silylalkyl tethers in **1** to generate $(\text{C}_5\text{Me}_4\text{SiMe}_3)^{1-}$ ligands in the complex $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{U}(\text{C}\equiv\text{CPh})_2$, **4**.

© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

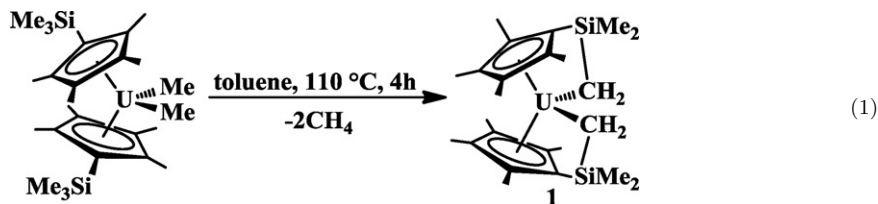
1. Introduction

Insertion reactions constitute one of the classic types of organometallic reactions that define the reactivity of metal carbon bonds [1]. The insertion reactivity of the U-C bond has been extensively studied with $(\text{C}_5\text{Me}_5)_2\text{UME}_2$ [2] and this has resulted in a wealth of actinide complexes with interesting structural features, coordination environments, and reactivity (e.g. Scheme 1) [3–7].

Organoactinide insertion chemistry has also been studied with $(\text{C}_5\text{Me}_5)_2\text{U}(\text{C}\equiv\text{CPh})_2$ [8]. This complex has

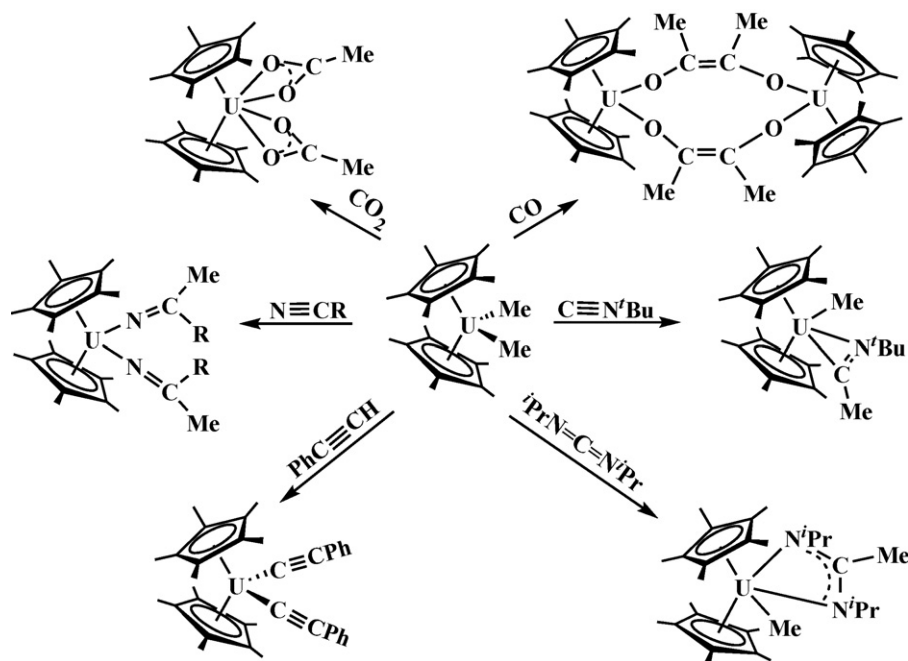
been frequently used as an *in situ* initiator for catalytic processes that involve insertion reactions such as the coupling of nitriles, isocyanides, and terminal alkynes, oligomerization of terminal alkynes, and the hydrosilylation of terminal alkynes [9].

Recently, an analog of $(\text{C}_5\text{Me}_5)_2\text{UME}_2$ was synthesized, namely $(\eta^5:\kappa^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2)_2\text{U}$, **1**, that made it possible to examine U-C bond reactivity of a tethered alkyl [10]. Complex **1** is generated from $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{UME}_2$ by metalation of each of the $(\text{C}_5\text{Me}_4\text{SiMe}_3)^{1-}$ ligands, Eq. (1) [10]. The U-C bonds in **1** are in a coordination environment similar to



* Corresponding author.

E-mail address: wevans@uci.edu (W.J. Evans).

Scheme 1. Insertion reactivity of $(C_5Me_5)_2UME_2$.

with carbon monoxide and *tert*-butyl isocyanide demonstrated that **1** provides both structural data and reactivity modes that are not accessible from $(C_5Me_5)_2UME_2$ [10]. With these promising results, we continued our study of this tethered system and report here on the reactivity of **1** with *tert*-butyl nitrile, carbon dioxide, phenylacetylene, and diphenylacetylene.

2. Experimental

The syntheses and manipulations described below were conducted under nitrogen or argon with rigorous exclusion of air and water using glovebox, Schlenk, and vacuum-line techniques. All reactions were performed at room temperature unless otherwise noted. Solvents were dried over columns containing Q-5 and 4A molecular sieves. Benzene- d_6 was dried over NaK alloy, degassed using three freeze-pump-thaw cycles, and vacuum transferred before use. *Tert*-butyl nitrile and $PhC\equiv CH$ were dried over 4A molecular sieves and degassed using three freeze-pump-thaw cycles before use. $PhC\equiv CPh$ was purchased from Aldrich and used as received. Ultrahigh purity carbon dioxide was purchased from Airgas and used as received. $(\eta^5:\kappa^1-C_5Me_4SiMe_2CH_2)_2U$, **1**, was prepared as previously reported [10]. 1H NMR spectra were recorded with a Bruker GN 500 MHz spectrometer and ^{13}C NMR spectra were recorded with a Bruker CRYO 500 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Varian 1000 FT-IR spectrometer. Elemental analysis was performed on a Perkin Elmer 2400 Series II CHN analyzer.

$[\eta^5:\kappa^1-C_5Me_4SiMe_2CH_2C(^tBu)N]_2U$, **2**. In a glovebox, a red solution of **1** (230 mg, 0.37 mmol) in toluene (10 mL) was added to a stirred solution of $^tBuC\equiv N$ (61 mg, 0.74 mmol) in toluene (5 mL). After 12 h, solvent was removed under vacuum from the red solution to yield **2** as

a dark red microcrystalline solid (280 mg, 97%). X-ray quality crystals of **2** were grown from a concentrated hexane solution at $-35^\circ C$. 1H NMR (C_6D_6): δ -36.3 (s, $C_5Me_4SiMe_2CH_2C(^tBu)N$, 6H), -24.7 (s, $C_5Me_4SiMe_2CH_2C(^tBu)N$, 6H), -6.56 (s, $C_5Me_4SiMe_2CH_2C(^tBu)N$, 6H), -4.95 (s, $C_5Me_4SiMe_2CH_2C(^tBu)N$, 6H), -2.45 (s, $C_5Me_4SiMe_2CH_2C(^tBu)N$, 18H), 7.61 (s, $C_5Me_4SiMe_2CH_2C(^tBu)N$, 6H), 20.3 (s, $C_5Me_4SiMe_2CH_2C(^tBu)N$, 6H), 32.0 (d, $C_5Me_4SiMe_2CH_2C(^tBu)N$, 2H, $^2J_{HH} = 11.4$ Hz), 32.4 (d, $C_5Me_4SiMe_2CH_2C(^tBu)N$, 2H, $^2J_{HH} = 11.4$ Hz). ^{13}C NMR (125.5 MHz, C_6D_6): δ -114 ($C_5Me_4SiMe_2CH_2C(^tBu)N$), -89.1 ($C_5Me_4SiMe_2CH_2C(^tBu)N$), -83.8 ($C_5Me_4SiMe_2CH_2C(^tBu)N$), -79.9 ($C_5Me_4SiMe_2CH_2C(^tBu)N$), -51.3 ($C_5Me_4SiMe_2CH_2C(^tBu)N$), -18.9 ($C_5Me_4SiMe_2CH_2C(^tBu)N$), 18.4 ($C_5Me_4SiMe_2CH_2C(^tBu)N$), 33.5 ($C_5Me_4SiMe_2CH_2C(^tBu)N$). IR: 2958 s, 2901 s, 1605 s, 1457 m, 1383 m, 1326 m, 1247 s, 1160 m, 1046 m, 1020 m, 991 m, 833 s, 666 m cm^{-1} . Anal. Calcd for $C_{34}H_{58}Si_2N_2U$: C, 51.75; H, 7.41; N, 3.55. Found: C, 51.22; H, 7.87; N, 3.08.

$(C_5Me_4SiMe_2CH_2CO_2)_2U$, **3**. A red solution of **1** (320 mg, 0.51 mmol) in benzene (25 mL) in a 100 mL Schlenk flask was attached to a high vacuum line and degassed by three freeze-pump-thaw cycles. One atmosphere of CO_2 was introduced to the reaction flask, the solution was stirred for 15 min, and the solution became yellow-brown. The reaction was degassed by one freeze-pump-thaw cycle, brought into a glovebox, and the solvent was removed under vacuum to yield **3** as a gold powder (350 mg, 96%). 1H NMR (C_6D_6): δ -10.0 (s, $C_5Me_4SiMe_2CH_2CO_2$, 6H), -5.72 (s, $C_5Me_4SiMe_2CH_2CO_2$, 6H), -5.58 (s, $C_5Me_4SiMe_2CH_2CO_2$, 2H), -3.46 (s, $C_5Me_4SiMe_2CH_2CO_2$, 6H), -3.10 (s, $C_5Me_4SiMe_2CH_2CO_2$, 6H), 0.63 (s, $C_5Me_4SiMe_2CH_2CO_2$, 6H), 14.7 (s, $C_5Me_4SiMe_2CH_2CO_2$, 2H), 15.6 (s, $C_5Me_4SiMe_2CH_2CO_2$, 6H). ^{13}C NMR (125.5 MHz, C_6D_6): δ -40.5 ($C_5Me_4SiMe_2CH_2CO_2$), -13.8 ($C_5Me_4SiMe_2CH_2CO_2$), -1.69 ($C_5Me_4SiMe_2CH_2CO_2$), -0.616 ($C_5Me_4SiMe_2CH_2CO_2$), 3.30 ($C_5Me_4SiMe_2CH_2CO_2$),

16.5 ($C_5Me_4SiMe_2CH_2CO_2$), 60.9 ($C_5Me_4SiMe_2CH_2CO_2$). IR: 2955m, 2914m, 1562s, 1492s, 1443m, 1329m, 1284m, 1046m, 966m, 729w, 834m cm^{-1} . Anal. Calcd for $C_{26}H_{40}Si_2O_4U$: C, 43.93; H, 5.67. Found: C, 44.20; H, 5.61.

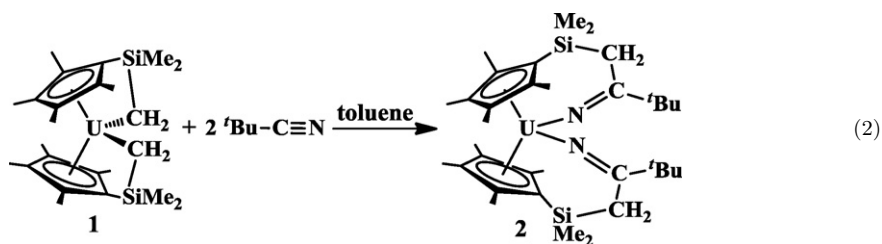
($C_5Me_4SiMe_3$)₂U($C\equiv CPh$)₂, 4. A solution of **1** (240 mg, 0.39 mmol) in toluene (10 mL) was added to a stirred solution of $PhC\equiv CH$ (79 mg, 0.77 mmol) in toluene (5 mL). After 12 h, the solvent was removed from the red solution under vacuum to yield **4** as a red powder (303 mg, 95%). X-ray quality crystals of **4** were grown from a concentrated hexane solution at $-35^\circ C$. 1H NMR (C_6D_6): δ -11.1 (d, $C\equiv CPh$, 4H, $^3J_{HH} = 11.4$ Hz), -4.96 (s, $C_5Me_4SiMe_3$, 12H), -2.52 (s, $C_5Me_4SiMe_3$, 18H), -1.72 (t, $C\equiv CPh$, 4H, $^3J_{HH} = 11.4$ Hz), 3.79 (t, $C\equiv CPh$, 2H, $^3J_{HH} = 11.4$ Hz), 17.2 (s, $C_5Me_4SiMe_3$, 12H). ^{13}C NMR (125.5 MHz, C_6D_6): δ -41.2 ($C_5Me_4SiMe_3$), 4.09 ($C_5Me_4SiMe_3$), 4.53 ($C_5Me_4SiMe_3$), 51.2 ($C\equiv CPh$), 99.1 ($C\equiv CPh$), 127 ($C\equiv CPh$). IR: 3077w, 2962s, 2950s, 2902s, 2730w, 2055s, 1977w, 1875w, 1800w, 1594m, 1570w, 1485m, 1441m, 1381w, 1347w, 1327m, 1242s, 1198m, 1125m, 1070w, 1024m, 988w, 912w, 846s,

determined by the 1H NMR spectrum of the isolated solid as only resonances for **1** and $PhC\equiv CPh$ were observed.

3. Results and discussion

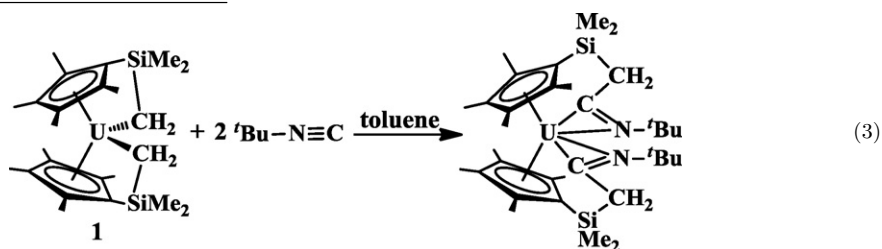
Reactivity of 1 with $tBuC\equiv N$. The insertion of nitriles into U-C bonds to form uranium ketimides is well-known from studies with the amide metallacycle $[(Me_3Si)_2N]_2U(CH_2SiMe_2NSiMe_3)$ [13] and with $(C_5Me_5)_2UR_2$ metallocenes [6,14]. Actinide ketimides have also been postulated as intermediates in hydroamination reactions with alkynes [9a]. With such a well-established body of work on nitrile insertion into terminal U-C bonds for comparison, it was of interest to investigate the reactivity of **1** with nitriles.

Insertion into both of the tethered U-C bonds of **1** occurs with $tBuC\equiv N$ to produce $[\eta^5:\kappa^1-C_5Me_4SiMe_2CH_2C(t-Bu)N]_2U$, **2**, as a dark red microcrystalline solid in 97% yield, Eq. (2). Complex **2** has been characterized by NMR and IR spectroscopy, elemental analysis, and



781m, 755s, 690m, 633m, 571w, 533m cm^{-1} . Anal. Calcd for $C_{40}H_{52}Si_2U$: C, 58.09; H, 6.34. Found for three separate samples of crystalline material: C, 55.36–56.63; H, 5.83–6.09. The C:H ratio of each sample; 9.2:1, 9.5:1, and 9.3:1 are consistent with that calculated of 9.2:1. Evidently, incomplete combustion occurs with this sample. Similar problems have been observed in the past [12].

X-ray crystallography (Fig. 1). Complex **2** has two tethered ketimide ligands as a result of a 1,2-insertion of $tBuC\equiv N$ into both the tethered alkyl bonds of **1**. In contrast, the isocyanide $tBuN\equiv C$ inserts by a 1,1-insertion into both U-C bonds of **1**, as shown in Eq. (3) [10]. Complex **2** is



Reaction of 1 and $PhC\equiv CPh$. A solution of **1** (52 mg, 0.08 mmol) in toluene (5 mL) was added to a stirred solution of $PhC\equiv CPh$ (29 mg, 0.17 mmol) in toluene (3 mL). After 12 h, the solvent was removed from the red solution under vacuum. No reaction was observed as

the first example of an actinide metallocene complex containing tethered ketimide ligands.

The 1H NMR spectrum of **2** contains nine resonances consistent with insertion of one equiv of $tBuC\equiv N$ into each of the U-C bonds of **1**. The resonances can be assigned to

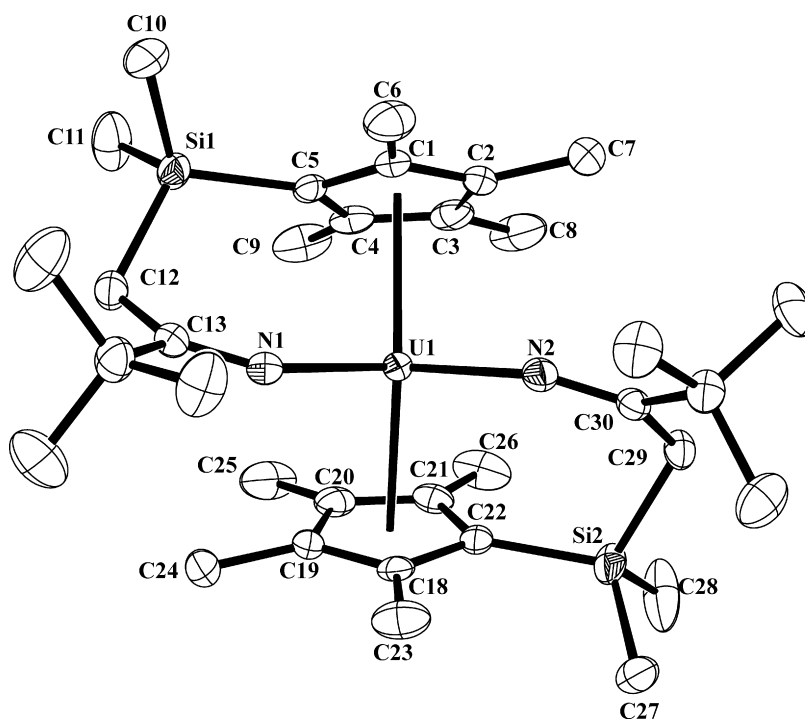


Fig. 1. Thermal ellipsoid plot of $[\eta^5\text{-}\kappa^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{C}(\text{t-Bu})\text{N}]_2\text{U}$, **2**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

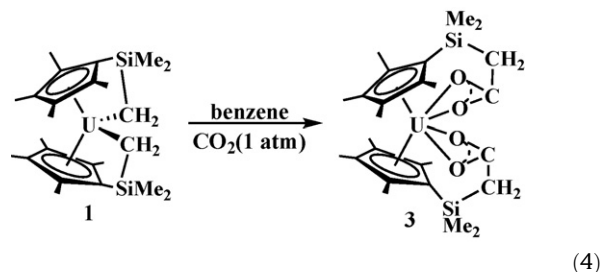
the four unique methyl groups on each cyclopentadienyl ring, two unique methyl groups on each silicon atom, two non-equivalent protons on the methylene groups, and one resonance for the two equivalent *tert*-butyl groups. Unlike the ^1H NMR spectrum of **1**, which lacks any resonance assignable to the $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2)^{2-}$ methylene groups bound to the paramagnetic uranium [10], the appearance of resonances for the methylene groups in **2** is consistent with an insertion that moves the methylene groups further from the paramagnetic metal.

The IR spectrum of **2** contained an absorption at 1605 cm^{-1} attributable to a C=N bond stretch that is lower than that of free $^t\text{BuC}\equiv\text{N}$ at 2231 cm^{-1} [15]. This C=N absorbance is similar to the 1620 cm^{-1} absorption observed for the uranium metallacycle $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{U}[\text{N}=\text{C}(\text{Me})\text{CH}_2\text{SiMe}_2\text{NSiMe}_3]$ [13,16], formed from an insertion reaction similar to that shown in Eq. (2).

The metallocene structure of **2** is not unusual, but the uranium ketimide linkages were affected by the tethering. Selected bond distances and angles for **2** are given in Table 2. The 2.473 and 2.482 \AA U-(ring centroid) bond distances and the 139.7° (ring centroid)-U-(ring centroid) bond angle are typical of U^{4+} metallocene complexes with the $(\text{C}_5\text{Me}_4\text{SiMe}_3)^{1-}$ ligand [10]. The $1.264(3)$ and $1.268(3)\text{ \AA}$ N1-C13 and N2-C30 bond distances of the tethered ketimide ligand are similar to those of untethered ketimide ligands [6,14] and are consistent with the IR data that suggested a C=N bond. The short U1-N1 and U1-N2 bond distances, both of which are $2.173(2)\text{ \AA}$, are also similar to these in other uranium-ketimide complexes [6,14]. In general, U-N ketimide bond distances are typically shorter than those of U-N amide bonds and this has been

attributed to π -bonding between uranium and the nitrogen of the ketimide ligand [6,14]. This π -bonding interaction has also been used to explain the near linear U-N-C bond angles present in untethered ketimide ligands [6]. In contrast, the $152.64(2)$ and $152.47(2)^\circ$ U-N-C bond angles in **2** deviate significantly from linearity due to the restraints imposed by the tethering. It has previously been shown that short metal-ligand bond distances and linear M-A-B angles are not necessarily correlated [17].

Reactivity of 1 with CO₂. Since spectroscopic data on the reaction of $(\text{C}_5\text{Me}_5)_2\text{U}(\text{O}_2\text{CMe}_2)$ with CO_2 to form $(\text{C}_5\text{Me}_5)_2\text{U}(\text{O}_2\text{CMe}_2)_2$ has been reported [7], it was expected that **1** would also react with this substrate. The reaction of **1** with CO_2 (1 atm) formed a complex consistent with the tethered bis(tethered carboxylate), $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{CO}_2)_2\text{U}$, **3**, Eq. (4).



Complex **3** was characterized by NMR and IR spectroscopy and by elemental analysis, but like $(\text{C}_5\text{Me}_5)_2\text{U}(\text{O}_2\text{CMe}_2)_2$ [7], single crystals were not obtained. The spectroscopic data are consistent with CO_2 insertion into both U-C bonds of **1** as observed with $^t\text{BuC}\equiv\text{N}$ and $^t\text{BuN}\equiv\text{C}$. The ^1H NMR spectrum

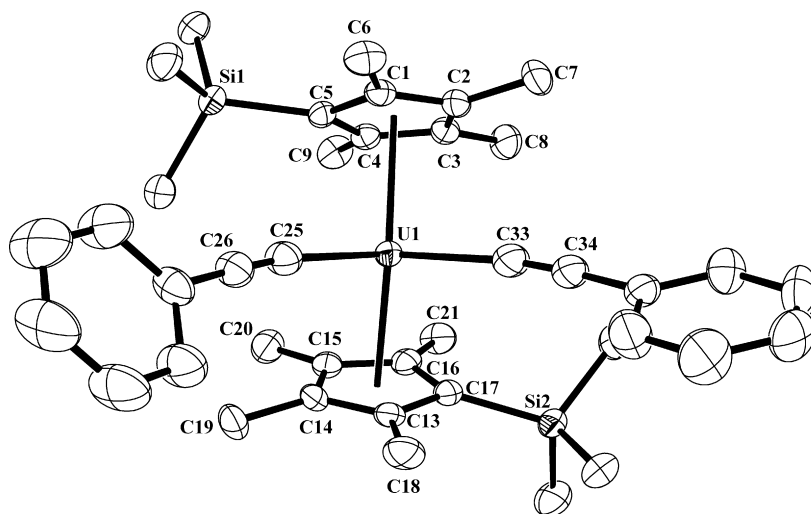


Fig. 2. Thermal ellipsoid plot of $(C_5Me_4SiMe_3)_2U(C\equiv CPh)_2$, **4**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

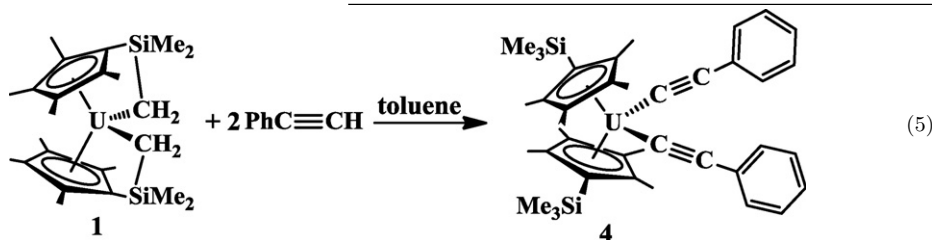
of **3** is similar to that of **2** in that resonances assignable to the $(C_5Me_4SiMe_2CH_2)^{2-}$ methylene protons are present. This again indicates that the methylene groups have been moved away from the metal by an insertion reaction. The IR spectrum is also consistent with the insertion of CO_2 into the U-C bonds of **1** since an absorption assignable to a carboxylate C-O stretch is present at 1562 cm^{-1} , which is similar to the 1540 cm^{-1} C-O stretch reported for $(C_5Me_5)_2U(O_2CMe)_2$ [7].

Reactivity of 1 with $PhC\equiv CH$. The reaction of **1** with $PhC\equiv CH$ was examined to determine whether insertion is possible or if cleavage of the tethered U-C bond would occur to form an alkynide. Straub and co-workers have found that terminal alkynes can display both types of reactivity with uranium metallocenes [9]. The reaction of **1** with two equiv of $PhC\equiv CH$ produced $(C_5Me_4SiMe_3)_2U(C\equiv CPh)_2$, **4**, as a red powder in 94% yield, Eq. (5). Complex **4** was characterized

alkynides such as 2056 cm^{-1} in $(C_5Me_5)_2U(C\equiv CPh)_2$ [8b] and 2062 cm^{-1} in $(C_5Me_5)_2U(NPh_2)(C\equiv CPh)$ [18].

X-ray crystallography revealed that the structure of **4** is similar to those of $(C_5Me_4SiMe_3)_2UCl_2$ and $(C_5Me_4SiMe_3)_2UMe_2$ in terms of the 2.448 and 2.451 Å U1-(ring centroid) bond distances as well as the 143.8° (ring centroid)-U1-(ring centroid) bond angle [10]. As observed in these other complexes, the trimethylsilyl group of **4** is bent away from the metal and therefore does not distort the metallocene structure [10]. The 2.390(2) Å U1-C25 and 2.369(3) Å U1-C33 bond lengths are shorter than the 2.425(2) Å U-C(Me) bond distance of $(C_5Me_4SiMe_3)_2UMe_2$ [10], but similar to the U-C bond lengths of 2.398(5) Å in $(C_5Me_5)_2U(C\equiv CPh)_2$ [8].

The reaction of **1** with $PhC\equiv CPh$ was also investigated to assess the possibility of alkyne insertion into the tethered U-C bonds without the option for sigma bond metathesis of the U-C bonds as occurs with $PhC\equiv CH$. However, no reaction was observed with $PhC\equiv CPh$.



by NMR and IR spectroscopy, elemental analysis and X-ray crystallography (Fig. 2).

The cleavage of the tethered U-C bond by $PhC\equiv CH$ was evident from the 1H NMR spectrum, which resembled that of $(C_5Me_4SiMe_3)_2UCl_2$ [10] rather than the more complicated spectra of **1–3**. The IR spectrum of **4** contained a strong absorbance at 2055 cm^{-1} , attributable to the $C\equiv C$ bond, which is similar to those previously reported for uranium

4. Conclusion

Complex **1** provides a platform to study the insertion reactivity of uranium-alkyl bonds in a tethered system. *Tert*-butyl nitrile undergoes a 1,2-insertion into both tethered U-C bonds of **1** to produce a bis(tethered ketimide), **2**, that differs from untethered uranium ketimides in that the U-N-C bond angles are not linear.

CO₂ also inserts into both U–C bonds to produce a bis(tethered carboxylate). PhC≡CH does not undergo insertion, but provides a convenient route to cleave the tethered U–C bonds of **1** to form an untethered product with an easily identifiable infrared label.

5. Crystallographic data

CCDC 759467 (**2**) and CCDC 759466 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy for support and Michael K. Takase for assistance with the X-ray crystallography.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at: <http://www.sciencedirect.com> and doi:10.1016/j.crci.2010.02.003.

References

- [1] R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Ed. 4, John Wiley & Sons, Inc, Hoboken, New Jersey, 2005.
- [2] P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam, T.J. Marks, *J. Am. Chem. Soc.* 103 (1981) 6650.
- [3] J.M. Manriquez, P.J. Fagan, T.J. Marks, *J. Am. Chem. Soc.* 100 (1978) 3939.
- [4] A. Dormond, A.A. Elbouadili, C. Moise, *J. Chem. Soc., Chem. Commun.* (1984) 749.
- [5] W.J. Evans, J.R. Walensky, J.W. Ziller, A.L. Rheingold, *Organometallics* 28 (2009) 3350.
- [6] K.C. Jantunen, C.J. Burns, I. Castro-Rodriguez, R.E. Da Re, J.T. Golden, D.E. Morris, B.L. Scott, F.L. Taw, J.L. Kiplinger, *Organometallics* 23 (2004) 4682.
- [7] K.G. Moloy, T.J. Marks, *Inorg. Chim. Acta* 110 (1985) 127.
- [8] (a) T. Straub, W. Frank, G.J. Reiss, M.S. Eisen, *J. Chem. Soc., Dalton Trans.* (1996) 2541;
(b) W. J. Evans, J. R. Walensky, J. W. Ziller, *Organometallics*, submitted.
- [9] (a) E. Barnea, M.S. Eisen, *Coord. Chem. Rev.* 250 (2006) 855;
(b) E. Barnea, T. Andrea, J.C. Berthet, M. Ephritikhine, M.S. Eisen, *Organometallics* 27 (2008) 3103.
- [10] W.J. Evans, N.A. Siladke, J.W. Ziller, *Chem. Eur. J.* (2010) 796.
- [11] (a) J.X. McDermott, M.E. Wilson, G.M. Whitesides, *J. Am. Chem. Soc.* 98 (1976) 6529;
(b) M.E. Van der Boom, D. Milstein, *Chem. Rev.* 103 (2003) 1759;
(c) S.T. Liddle, I.S. Edworthy, P.L. Arnold, *Chem. Soc. Rev.* 36 (2007) 1732.
- [12] (a) A.J. Gaunt, B.L. Scott, M.P. Neu, *Inorg. Chem.* 45 (2006) 7401;
(b) J.H. Melman, C. Rohde, T.J. Emge, J.G. Brennan, *Inorg. Chem.* 41 (2002) 28;
(c) D. Freedman, T.J. Emge, J.G. Brennan, *Inorg. Chem.* 38 (1999) 4400.
- [13] S.J. Simpson, R.A. Andersen, *J. Am. Chem. Soc.* 103 (1981) 4063.
- [14] (a) J.L. Kiplinger, D.E. Morris, B.L. Scott, C.J. Burns, *Organometallics* 21 (2002) 3073;
(b) P.L. Diaconescu, C.C. Cummins, *J. Am. Chem. Soc.* 124 (2002) 7660;
(c) R.E. Cramer, K. Panchanatheswaran, J.W. Gilje, *J. Am. Chem. Soc.* 106 (1984) 1853.
- [15] V. Chebolu, R.R. Whittle, A. Sen, *Inorg. Chem.* 24 (1985) 3082.
- [16] A. Dormond, A. Elbouadili, C. Moise, *J. Org. Chem.* 54 (1989) 3747.
- [17] (a) W.A. Howard, T.M. Trnka, G. Parkin, *Inorg. Chem.* 34 (1995) 5900;
(b) B.D. Steffey, P.E. Fanwick, I.P. Rothwell, *Polyhedron* 9 (1990) 963.
- [18] (a) C.R. Graves, B.L. Scott, D.E. Morris, J.L. Kiplinger, *Organometallics* 27 (2008) 3335;
(b) R.K. Thomson, C.R. Graves, B.L. Scott, J.L. Kiplinger, *Eur. J. Inorg. Chem.* (2009) 1451.