222 *Inorg. Chem.* **2010**, *49*, 222–228
DOI: 10.1021/ic901790t

Inorganic Chemistry
Article

Uranium Metallocene Complexes of the 1,3,4,6,7,8-Hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidinato Ligand, (hpp)$^-$

William J. Evans,*,† Elizabeth Montalvo,† Joseph W. Ziller,† Antonio G. DiPasquale,‡ and Arnold L. Rheingold‡

†*Department of Chemistry, University of California, Irvine, California 92697-2025 and* ‡*Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, MC 0358, La Jolla, California 92093-0358*

Received September 8, 2009

The utility of the 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinato ligand, (hpp)$^-$, in uranium chemistry has been probed by synthesizing metallocene complexes and studying their reactivity. $(C_5Me_5)_2UMe_2$ reacts with 1 equiv of Hhpp to form $(C_5Me_5)_2$(hpp)UMe, **1**, which does not react further with Hhpp. $(C_5Me_5)_2UCl_2$ reacts with Khpp to form $(C_5Me_5)_2$(hpp)UCl, **2**, which similarly does not react with additional Khpp. Complex **2** reacts with NaN_3 to form the azide complex, $(C_5Me_5)_2$(hpp)UN_3, **3**. The trivalent uranium (hpp)$^-$ metallocene complex, $(C_5Me_5)_2$(hpp)U, **4**, can be synthesized by the reaction of $[(C_5Me_5)_2U][BPh_4]$ with Khpp and from **2** with KC_8. Complex **4** can be oxidized with $Ph_3P{=}Se$ to produce the tetravalent product, $[(C_5Me_5)_2(hpp)U]_2(\mu\text{-Se})$, **5**. The reaction of **4** with Me_3SiN_3 provides the pentavalent uranium complex, $(C_5Me_5)_2$(hpp)U(=$NSiMe_3$), **6**

Introduction

The bicyclic guanidinate ligand, (hpp)$^-$, Figure 1, derived from 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, Hhpp, has been extensively investigated with a broad range of transition metals.[1−4] This ligand can have extraordinary effects on redox chemistry. For example, the tungsten complex $W_2(\mu\text{-}\eta^1{:}\eta^1\text{-hpp})_4$ has a lower gas-phase ionization energy than cesium.[2] Although guanidinates[1,3,4] have been extensively studied with yttrium and the lanthanide metals,[5,6] the synthesis of the first uranium guanidinate complexes have only recently been reported.[7] In this case, chelating bridging ligands derived from dicyclohexylcarbodiimide and hydrazine, $\{[(CyHN)(CyN)C{=}N\text{-}]_2\}^{2-}$, were used to make polymetallic uranium products. To our knowledge, there are no examples of actinide complexes containing the (hpp)$^-$ ligand. Since the (hpp)$^-$ ligand has the potential to stabilize higher oxidation states[2,8] and since there is currently great interest in expanding the number of U^{5+} complexes in the literature,[9] we have examined (hpp)$^-$ with uranium.

We chose a metallocene platform to study the uranium-hpp interaction since this has proven to be a reliable route to

---

*To whom correspondence should be addressed. E-mail: wevans@uci.edu.

[1] Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91–141.

[2] Cotton, F. A.; Gruhn, N. E.; Gu, J.; Huang, P.; Lichtenberger, D. L.; Murillo, C. A.; Van Dorn, L. O.; Wilkinson, C. C. *Science* **2002**, *298*, 1971–1975.

[3] Coles, M. P. *Dalton Trans.* **2006**, *8*, 985–1001.

[4] Coles, M. P. *Chem. Commun.* **2009**, *25*, 3659–3676.

[5] (a) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923–927. (b) Trifonov, A. A.; Fedorova, E. A.; Fukin, G. K.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2004**, 4396–4401. (c) Zhang, J.; Cai, R.; Weng, L.; Zhou, X. *Organometallics* **2004**, *23*, 3303–3308. (d) Jing-Lei, C.; Ying-Ming, Y.; Yun-Jie, L.; Li-Ying, Z.; Zhang, Y.; Shen, Q. *J. Organomet. Chem.* **2004**, *689*, 1019–1024. (e) Coles, M. P.; Hitchcock, P. B. *Inorg. Chim. Acta* **2004**, *357*, 4330–4334. (f) Pang, X.; Sun, H.; Zhang, Y.; Shen, Q.; Zhang, H. *Eur. J. Inorg. Chem.* **2005**, 1487–1491. (g) Trifonov, A. A.; Lyubov, D. M.; Fukin, G. K.; Baranov, E. V.; Kurskii, Y. A. *Organometallics* **2006**, *25*, 3935–3942. (h) Trifonov, A. A.; Lyubov, D. M.; Fedorova, E. A.; Fukin, G. K.; Schumann, H.; Muhle, S.; Hummert, M.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2006**, 747–756. (i) Zhang, W. X.; Nishiura, M.; Hou, Z. *Synlett* **2006**, 1213–1216. (j) Yuan, F.; Zhu, Y.; Xiong, L. *J. Organomet. Chem.* **2006**, *691*, 3377–3382. (k) Heitmann, D.; Jones, C.; Junk, P. C.; Lippert, K. A.; Stasch, A. *Dalton Trans.* **2007**, 187–189.

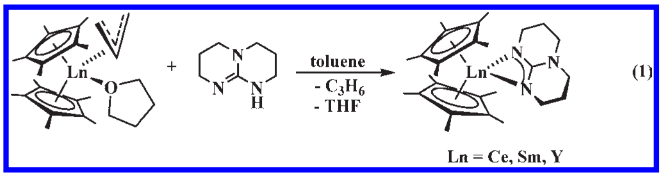
[6] Evans, W. J.; Montalvo, E.; Dixon, D. J.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *Inorg. Chem.* **2008**, *47*, 11376–11381.

[7] Villiers, C.; Thuery, P.; Ephritikhine, M. *Chem. Commun.* **2007**, 2832–2834.

[8] (a) Soria, D. B.; Grundy, J.; Coles, M. P.; Hitchcock, P. B. *J. Organomet. Chem.* **2005**, *690*, 2278–2284. (b) Berry, J. F.; Cotton, F. A.; Huang, P.; Murillo, C. A.; Wang, X. *Dalton Trans.* **2005**, 3713–3715. (c) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Polyhedron* **2002**, *21*, 619–627.

[9] (a) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2007**, *129*, 11914–11915. (b) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. *Organometallics* **2008**, *27*, 3335–3337. (c) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272–5285. (d) Graves, C. R.; Vaughn, A. E.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.* **2008**, *47*, 11879–11891. (e) Graves, C. R.; Kiplinger, J. L. *Chem. Commun.* **2009**, 3831–3853. (f) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. *Chem. Commun.* **2009**, 776–778. (g) Horeglad, P.; Nocton, G.; Filinchuk, Y.; Pecaut, J.; Mazzanti, M. *Chem. Commun.* **2009**, 1843–1845. (h) Nocton, G.; Horeglad, P.; Pecaut, J.; Mazzanti, M. *J. Am. Chem. Soc.* **2008**, *130*, 16633–16645. (i) Berthet, J. C.; Siffredi, G.; Thuery, P.; Ephritikhine, M. *Dalton Trans.* **2009**, 3478–3494. (j) Spencer, L. P.; Schelter, E. J.; Yang, P.; Gdula, R. L.; Scott, B. L.; Thompson, J. D.; Kiplinger, J. L.; Batista, E. R.; Boncella, J. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3795–3798.

investigate new ligands in f element chemistry in the past.[6,10] We recently reported the synthesis of a series of lanthanide metallocene guanidinate complexes of the (hpp)$^-$ ligand, $(C_5Me_5)_2(hpp)Ln$.[6] These complexes were synthesized by the protonolysis reaction of $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)(THF)$ (Ln = Ce, Sm, Y) with Hhpp, eq 1. A similar protonolysis approach was examined with actinide metallocenes in this study as well as ionic metathesis reactions with Khpp. We report here the synthesis and reactivity of these (hpp)$^-$ metallocenes which includes trivalent, tetravalent, and pentavalent uranium complexes.



Experimental Section

The manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were sparged with UHP argon and dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium—potassium alloy, degassed by three freeze—pump—thaw cycles, and vacuum-transferred before use. $(C_5Me_5)_2UMe_2$,[11] $(C_5Me_5)_2UCl_2$,[11] $[(C_5Me_5)_2U][BPh_4]$,[12] and KC_8[13] were prepared according to literature methods. Hhpp (Sigma-Aldrich) was purified by vacuum sublimation prior to use. Potassium bis(trimethylsilyl)amide was obtained from Sigma-Aldrich and used without further purification. Khpp was prepared by deprotonation of Hhpp with 1 equiv of potassium bis(trimethylsilyl)amide in hexane.[6] Me_3SiN_3 (Sigma-Aldrich) was distilled under argon before use. $Ph_3P{=}Se$ and NaN_3 (Sigma-Aldrich) were placed under vacuum for 12 h before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer at 25 °C. NMR spectra of all of the products are included in the Supporting Information. Infrared spectra were recorded as KBr pellets on a Varian 1000 FTIR spectrophotometer at 25 °C. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS analyzer.

$(C_5Me_5)_2$(hpp)UMe, 1. Hhpp (96 mg, 0.69 mmol) was added to a solution of $(C_5Me_5)_2UMe_2$[11] (310 mg, 0.58 mmol) in toluene (10 mL) while stirring. Excess of Hhpp was used to ensure all of the uranium reagent reacted. After the reaction mixture was stirred for 12 h, the volatiles were removed under reduced pressure to yield **1** as a dark yellow solid (369 mg, 97%). A resonance consistent with the formation of methane was observed in the ^{1}H NMR spectrum of a reaction done in a sealed J-Young tube. X-ray quality crystals of **1** were grown from slow evaporation of a concentrated benzene solution at 25 °C. ^{1}H NMR (C_6D_6) δ 26.20 (s, $\Delta\nu_{1/2}$ = 19 Hz, 2H, $C_7H_{12}N_3$), 8.31 (s, $\Delta\nu_{1/2}$ = 16 Hz, 2H, $C_7H_{12}N_3$), 2.65 (s, $\Delta\nu_{1/2}$ = 8 Hz, 2H, $C_7H_{12}N_3$), −1.72 (s, $\Delta\nu_{1/2}$ = 5 Hz, 30H, C_5Me_5), −8.40 (s, $\Delta\nu_{1/2}$ = 12 Hz, 2H, $C_7H_{12}N_3$), −18.39 (s, $\Delta\nu_{1/2}$ = 16 Hz, 2H, $C_7H_{12}N_3$), −30.0 (s, $\Delta\nu_{1/2}$ = 16 Hz, 2H, $C_7H_{12}N_3$), −219.70 (s, $\Delta\nu_{1/2}$ = 50 Hz, 3H, Me). ^{13}C NMR (C_6D_6) δ 79.1 ($C_7H_{12}N_3$), 61.3 ($C_7H_{12}N_3$), 32.9, 31.6 ($C_7H_{12}N_3$), 14.9 ($C_7H_{12}N_3$), −18.9 ($C_7H_{12}N_3$), −37.9, −57.7 (C_5Me_5), −61.8 ($C_7H_{12}N_3$). IR: 2928s, 2893s, 2851s, 2720w, 1603w, 1541s, 1501s, 1470 m, 1451s, 1437s, 1377 m, 1359 m, 1340w, 1319s, 1292 m, 1261 m, 1201 m, 1145 m, 1109w, 1095 m, 1061 m, 1025 m, 934w, 914w, 898w, 876w, 802w, 727 m, 693w, 604w cm^{-1}. Anal. Calcd for $UC_{28}H_{45}N_3$: C, 50.82; H, 6.85; N, 6.35. Found: C, 50.66; H, 6.70; N, 7.19. Crystal system: Monoclinic; Space group: $P2_1/n$; Unit cell dimensions a = 8.7354(10) Å, b = 16.9098(19) Å, c = 18.533(2) Å, α = 90°, β = 101.024(2)°, γ = 90°; V = 2687.1(5) Å^3.

$(C_5Me_5)_2$(hpp)UCl, 2. Khpp (111 mg, 0.63 mmol) was added to a solution of $(C_5Me_5)_2UCl_2$[11] (304 mg, 0.52 mmol) in toluene (10 mL) while stirring. Excess of Khpp was used to ensure all of the uranium reagent reacted. After the reaction mixture was stirred for 12 h, an insoluble material was removed from the mixture via centrifugation and filtration. Solvent was removed under vacuum leaving **2** as a dark yellow solid (325 mg, 91%). Yellow crystals of **2** suitable for X-ray diffraction were grown from a concentrated toluene/benzene solution at 25 °C. ^{1}H NMR (C_6D_6) δ 22.11 (s, $\Delta\nu_{1/2}$ = 15 Hz, 2H, $C_7H_{12}N_3$), 8.24 (s, $\Delta\nu_{1/2}$ = 17 Hz, 2H, $C_7H_{12}N_3$), 3.71 (s, $\Delta\nu_{1/2}$ = 2 Hz, 30H, C_5Me_5), 3.10 (s, $\Delta\nu_{1/2}$ = 16 Hz, 2H, $C_7H_{12}N_3$), −3.33 (s, $\Delta\nu_{1/2}$ = 13 Hz, 2H, $C_7H_{12}N_3$), −8.41 (s, $\Delta\nu_{1/2}$ = 16 Hz, 2H, $C_7H_{12}N_3$), −13.31 (s, $\Delta\nu_{1/2}$ = 14 Hz, 2H, $C_7H_{12}N_3$). ^{13}C NMR (C_6D_6) δ 51.9 ($C_7H_{12}N_3$), 48.3 ($C_7H_{12}N_3$), 48.0 ($C_7H_{12}N_3$), 37.5 ($C_7H_{12}N_3$), 30.8 ($C_7H_{12}N_3$), −27.9 ($C_7H_{12}N_3$), −41.8 (C_5Me_5). IR: 2944s, 2895s, 2850s, 2721w, 1607m, 1549s, 1500s, 1470m, 1452s, 1437s, 1382s, 1379s, 1317s, 1291m, 1260m, 1203m, 1147m, 1111m, 1062m, 1025m, 938w, 899w, 876w, 805w, 728m, 693w, 607w cm^{-1}. Anal. Calcd for $UC_{27}H_{42}N_3Cl$: C, 47.54; H, 6.21; N, 6.16. Found: C, 47.45; H, 6.63; N, 6.21.

$(C_5Me_5)_2$(hpp)UN$_3$, 3. NaN_3 (100 mg, 1.54 mmol) was added to a solution of $(C_5Me_5)_2$(hpp)UCl, **2**, (253 mg, 0.37 mmol) in THF (20 mL) while stirring. After the reaction mixture was stirred for 12 h, an insoluble material was removed from the mixture via centrifugation and filtration. Solvent was removed under vacuum leaving **3** as a deep yellow solid (240 mg, 94%). Orange crystals of **3** suitable for X-ray diffraction were grown from a concentrated toluene solution at −35 °C. ^{1}H NMR (C_6D_6) δ 42.35 (s, $\Delta\nu_{1/2}$ = 15 Hz, 2H, $C_7H_{12}N_3$), 15.00 (s, $\Delta\nu_{1/2}$ = 18 Hz, 2H, $C_7H_{12}N_3$), 4.98 (s, $\Delta\nu_{1/2}$ = 17 Hz, 2H, $C_7H_{12}N_3$), 1.66 (s, $\Delta\nu_{1/2}$ = 3 Hz, 30H, C_5Me_5), −5.80 (s, $\Delta\nu_{1/2}$ = 11 Hz, 2H, $C_7H_{12}N_3$), −13.24 (s, $\Delta\nu_{1/2}$ = 17 Hz, 2H, $C_7H_{12}N_3$), −23.58 (s, $\Delta\nu_{1/2}$ = 14 Hz, 2H, $C_7H_{12}N_3$). ^{13}C NMR (C_6D_6) δ 90.3 ($C_7H_{12}N_3$), 57.9 ($C_7H_{12}N_3$), 53.0 ($C_7H_{12}N_3$), 34.9 ($C_7H_{12}N_3$), 21.5 ($C_7H_{12}N_3$), −48.3 (C_5Me_5), −62.5 ($C_7H_{12}N_3$). IR: 2940s, 2899s, 2847s, 2721w, 2076s, 1618w, 1554s, 1494s, 1474m, 1450s, 1378s, 1363s, 1318s, 1286m, 1258m, 1207s, 1146s, 1111w, 1057 m, 1025m, 875w, 804w, 726m, 692w cm^{-1}. Anal. Calcd for $UC_{27}H_{42}N_6$: C, 47.09; H, 6.15; N, 12.20. Found: C, 47.19; H, 6.41; N, 12.53.

$(C_5Me_5)_2$(hpp)U, 4. Khpp (78 mg, 0.44 mmol) was added to a solution of $[(C_5Me_5)_2U][BPh_4]$[12] (302 mg, 0.36 mmol) in benzene (10 mL) while stirring. After the reaction mixture was stirred for 12 h, an insoluble material was removed from the mixture via centrifugation and filtration. Solvent was removed under vacuum leaving **4** as a dark olive green solid (215 mg, 91%). ^{1}H NMR (C_6D_6) δ 0.28 (s, $\Delta\nu_{1/2}$ = 26 Hz, 4H, $C_7H_{12}N_3$), −3.10 (s, $\Delta\nu_{1/2}$ = 27 Hz, 4H, $C_7H_{12}N_3$), −12.87 (s, $\Delta\nu_{1/2}$ = 31 Hz, 30H, C_5Me_5), −20.17 (s, $\Delta\nu_{1/2}$ = 29 Hz, 4H, $C_7H_{12}N_3$). ^{13}C NMR (C_6D_6) δ 71.5 (C_5Me_5), 44.5 ($C_7H_{12}N_3$), 27.5 ($C_7H_{12}N_3$), −54.9 ($C_7H_{12}N_3$). IR: 2922s, 2852s, 2723w, 1645w, 1532s, 1491s, 1470m, 1449s, 1379s, 1359w, 1319s, 1290m, 1259m, 1197s, 1145m, 1111w, 1065m, 1024m, 801w, 718m, 677w cm^{-1}. Anal. Calcd for $UC_{27}H_{42}N_3$: C, 50.15; H, 6.55; N, 6.50. Found: C, 50.44; H, 6.76; N, 6.20.

---

[10] (a) Evans, W. J.; Fujimoto, C. H.; Ziller, J. W. *Organometallics* **2001**, *20*, 4529–4536. (b) Evans, W. J.; Perotti, J. M.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 5204–5212. (c) Evans, W. J.; Perotti, J. M.; Ziller, J. W.; Moser, D. F.; West, R. *Organometallics* **2003**, *22*, 1160–1163.

[11] Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

[12] Evans, W. J.; Nyce, G. W.; Forrestal, K. J.; Ziller, J. W. *Organometallics* **2002**, *21*, 1050–1055.

[13] Bergbreiter, D. E.; Killough, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2126–2134.

$(C_5Me_5)_2$(hpp)U, 4, from $(C_5Me_5)_2$(hpp)UCl, 2. KC_8 (45 mg, 0.33 mmol) was added to a solution of **2** (150 mg, 0.22 mmol) in toluene (10 mL) while stirring. After the reaction mixture was stirred for 12 h, insolubles were removed from the mixture via centrifugation and filtration. Solvent was removed under vacuum leaving **4** as a dark olive green solid (128 mg, 90%).

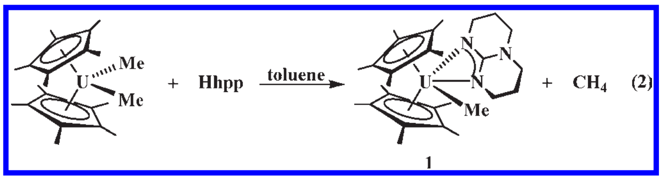
$[(C_5Me_5)_2$(hpp)U$]_2$(μ-Se), 5. $Ph_3P{=}Se$ (54 mg, 0.16 mmol) was added to a stirred solution of $(C_5Me_5)_2$(hpp)U, **4**, (199 mg, 0.31 mmol) in benzene (8 mL). After 12 h, solvent was removed under reduced pressure, and the resulting dark red solid (210 mg) was washed with hexanes and dried under vacuum (179 mg). Complex **5** is extremely soluble in arenes, and separation of residual PPh_3 is problematic. A few red X-ray quality crystals of **5** were obtainable from a concentrated benzene solution at 25 °C in one case. ^{1}H NMR (C_6D_6) δ 30.87 (s, $\Delta\nu_{1/2} = 24$ Hz, 4H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), 5.41 (s, $\Delta\nu_{1/2} = 8$ Hz, 4H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), 2.61 (s, $\Delta\nu_{1/2} = 10$ Hz, 60H, $\mathrm{C_5}\mathit{Me}_5$), 2.32 (s, $\Delta\nu_{1/2} = 18$ Hz, 4H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), 0.60 (s, $\Delta\nu_{1/2} = 15$ Hz, 4H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), −4.73 (s, $\Delta\nu_{1/2} = 18$ Hz, 4H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), −30.3 (s, $\Delta\nu_{1/2} = 21$ Hz, 4H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$). ^{13}C NMR ($C_6D_6$) δ 83.0 ($\mathit{C}_7\mathrm{H_{12}N_3}$), 52.2 ($\mathit{C}_7\mathrm{H_{12}N_3}$), 43.9 ($\mathit{C}_7\mathrm{H_{12}N_3}$), 32.3 ($\mathit{C}_7\mathrm{H_{12}N_3}$), 12.1 ($\mathit{C}_7\mathrm{H_{12}N_3}$), 11.5 ($\mathit{C}_7\mathrm{H_{12}N_3}$), −18.6 ($\mathrm{C_5}\mathit{Me}_5$). IR: 2921s, 2889s, 2849s, 2719w, 1604w, 1542s, 1501s, 1471m, 1450s, 1436s, 1378s, 1356w, 1339w, 1317s, 1289m, 1258m, 1205s, 1144s, 1111w, 1099w, 1061m, 1026m, 998w, 877wm, 745w, 724m, 692m cm^{-1}. Anal. Calcd for $U_2C_{54}H_{84}N_6Se$: C, 46.32; H, 6.28; N, 6.23. Found: C, 47.26; H, 5.55; N, 5.47. Elemental analyses were consistently off because of the difficulty of removing Ph_3P.

$(C_5Me_5)_2$(hpp)U($=$NSiMe$_3$), 6. In an argon-filled glovebox, Me_3SiN_3 (39 μL, 0.29 mmol) was added via syringe to a stirred solution of $(C_5Me_5)_2$(hpp)U, **4**, (157 mg, 0.24 mmol) in benzene (8 mL). After 12 h, the volatiles were removed under reduced pressure, and the resulting black solid was washed with hexanes and dried under vacuum to give dark black **6** (146 mg, 82%). Purple X-ray quality crystals of **6** were grown from a concentrated toluene/hexane solution at −35 °C. ^{1}H NMR (C_6D_6) δ 5.22 (s, $\Delta\nu_{1/2} = 78$ Hz, 9H, $\mathrm{Si}\mathit{Me}_3$), 3.33 (s, $\Delta\nu_{1/2} = 17$ Hz, 2H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), 3.04 (s, $\Delta\nu_{1/2} = 7$ Hz, 2H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), 2.57 (s, $\Delta\nu_{1/2} = 11$ Hz, 30H, $\mathrm{C_5}\mathit{Me}_5$), −2.01 (s, $\Delta\nu_{1/2} = 9$ Hz, 2H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), −4.37 (s, $\Delta\nu_{1/2} = 23$ Hz, 2H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), −8.21 (s, $\Delta\nu_{1/2} = 24$ Hz, 2H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$), −16.91 (s, $\Delta\nu_{1/2} = 15$ Hz, 2H, $\mathrm{C_7}\mathit{H}_{12}\mathrm{N_3}$). ^{13}C NMR ($C_6D_6$) δ 52.8 ($\mathit{C}_7\mathrm{H_{12}N_3}$), 40.9 ($\mathit{C}_7\mathrm{H_{12}N_3}$), −9.8 ($\mathit{C}_7\mathrm{H_{12}N_3}$), −18.6 ($\mathrm{C_5}\mathit{Me}_5$), −34.3 ($\mathit{C}_7\mathrm{H_{12}N_3}$), −37.7 ($\mathrm{Si}\mathit{Me}_3$), −41.8 ($\mathit{C}_7\mathrm{H_{12}N_3}$), −55.9 ($\mathit{C}_7\mathrm{H_{12}N_3}$). IR: 2956s, 2905s, 2854s, 2724w, 1638m, 1612m, 1542s, 1503w, 1476w, 1442s, 1376s, 1319s, 1294m, 1259m, 1242m, 1199s, 1145w, 1113w, 1067m, 1023m, 937m, 882w, 832w, 804w, 744w, 706m, 672w cm^{-1}. Anal. Calcd for $UC_{30}H_{51}N_4Si$: C, 49.09; H, 7.00; N, 7.63. Found: C, 48.99; H, 6.22; N, 8.02.

X-ray Data Collection, Structure Determination, and Refinement. X-ray crystallographic information on **2**, **3**, **5**, and **6** is summarized in Table 1.

Results

$(C_5Me_5)_2$(hpp)UMe, 1. Following the method successfully used to make (hpp)$^-$ complexes of lanthanide metallocenes in eq 1, the deprotonation of Hhpp with the uranium metallocene, $(C_5Me_5)_2UMe_2$[11] was examined. As shown in eq 2, one methyl group reacts to form methane and the uranium (hpp)$^-$ complex, $(C_5Me_5)_2$(hpp)UMe, **1**.



Complex **1** was characterized by NMR and IR spectroscopy, as well as by elemental analysis. The structure of **1** was determined by X-ray crystallography, Figure 1, but

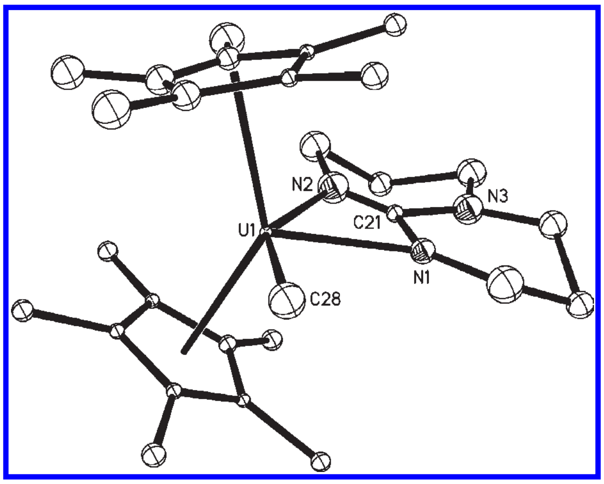


Figure 1. Thermal ellipsoid plot of $(C_5Me_5)_2$(hpp)UMe, **1**, drawn at the 10% probability level. Hydrogen atoms have been excluded for clarity.

Table 1. X-ray Data Collection Parameters for $(C_5Me_5)_2$(hpp)UCl, **2**, $(C_5Me_5)_2$(hpp)UN$_3$, **3**, $[(C_5Me_5)_2$(hpp)U$]_2$(μ-Se), **5**, and $(C_5Me_5)_2$(hpp)U($=$NSiMe$_3$), **6**

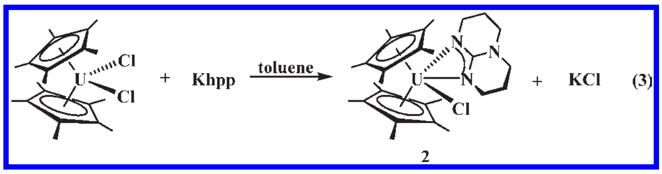
	2	3	5	6
empirical formula	$C_{27}H_{42}N_3ClU$	$C_{27}H_{42}N_6U$	$C_{54}H_{84}N_6SeU_2$	$C_{30}H_{51}N_4SiU$
formula weight	682.12	688.70	1372.29	733.87
temperature (K)	100(2)	153(2)	103(2)	143(2)
crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.8192(6)	11.3246(6)	15.2203(6)	10.7804(7)
b (Å)	17.3674(12)	20.1621(11)	16.9397(7)	15.5317(11)
c (Å)	17.2120(12)	11.8247(6)	19.8735(8)	17.9557(12)
α (deg)	90	90	90	90
β (deg)	92.9160(10)	94.8080(10)	90	90
γ (deg)	90	90	90	90
volume Å^3	2632.9(3)	2690.4(2)	5123.9(4)	3006.5(4)
Z	4	4	4	4
ρ_{calcd} (mg/m^3)	1.721	1.700	1.779	1.621
μ (mm^{-1})	6.286	6.059	7.065	5.464
R1^a ($I > 2.0\sigma(I)$)	0.0199	0.0154	0.0199	0.0174
wR2^b (all data)	0.0501	0.0401	0.0470	0.0423

^{a}R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. ^{b}wR2 $= [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

the quality of the X-ray data does not allow a detailed discussion of the bond distances. The structure of **1** suggests why it does not react with excess Hhpp: there is no apparent room to place a second $(hpp)^-$ ligand around uranium. The methyl group in **1** is also unreactive in σ bond metathesis reactions with PhSSPh[14] and H_2 at 25 °C.[11]

The IR spectrum of **1** contains a C−N stretch at 1603 cm^{-1}, and complexes **2**−**6**, presented below, have analogous C−N stretches at 1607, 1618, 1645, 1604, and 1612 cm^{-1}, respectively.[15] The ^1H NMR spectrum of **1** has six independent resonances attributable to the $(hpp)^-$ ligand. Three are at low field, 26.20, 8.31, and 2.65 ppm, and three are at high field, −8.40, −18.39, and −30.0 ppm. The U^{4+} complexes **2** and **3**, described below, display a similar pattern. The $(hpp)^-$ resonances in **1** are significantly shifted from the 3.07−1.56 ppm range of diamagnetic $(C_5Me_5)_2Y(hpp)$.[6] The ^1H NMR resonances for the $(C_5Me_5)^-$ methyl groups and the U−Me of **1**, −1.72 and −219.70 ppm, respectively, are shifted from the starting material $(C_5Me_5)_2UMe_2$, 5.03 and −124.00 ppm,[11] respectively.

$(C_5Me_5)_2(hpp)UCl$, 2. The preparation of uranium metallocene $(hpp)^-$ complexes via ionic metathesis reactions was examined with the actinide metallocene dichloride, $(C_5Me_5)_2UCl_2$.[11] As shown in eq 3, this complex reacts with Khpp, prepared from Hhpp and $K[N(SiMe_3)_2]$, to form the chloride analogue of **1**, namely, $(C_5Me_5)_2(hpp)UCl$, **2**. Complex **2** was characterized by the same methods used for **1**, and its X-ray crystal structure is shown in Figure 2. Structural details are discussed below. Like **1**, complex **2** did not react further with additional $(hpp)^-$ reagent to form a bis(hpp) product.



(3)

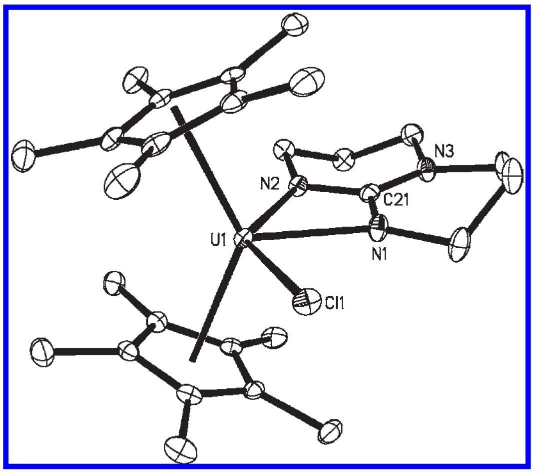


Figure 2. Thermal ellipsoid plot of $(C_5Me_5)_2(hpp)UCl$, **2**, drawn at the 50% probability level. Hydrogen atoms have been excluded for clarity.

$(C_5Me_5)_2(hpp)UN_3$, 3. Although the chloride in **2** does not react with Khpp, it is reactive with less sterically bulky reagents. The reaction with NaN_3 was examined because of an interest in making uranium complexes rich in nitrogen.[16] As shown in eq 4, **2** reacts with NaN_3 to form the tetravalent uranium guanidinate azide complex, $(C_5Me_5)_2(hpp)UN_3$, **3**.

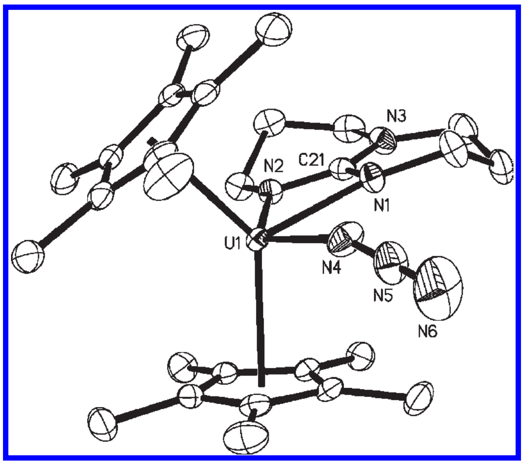
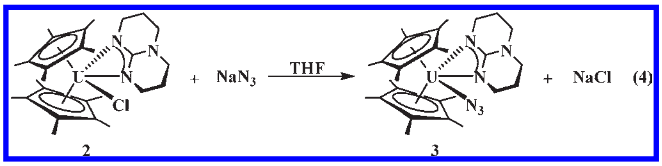


Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_2(hpp)UN_3$, **3**, drawn at the 50% probability level. Hydrogen atoms have been excluded for clarity.



(4)

Complex **3** was characterized by NMR and IR spectroscopy and by elemental analysis and X-ray crystallography, Figure 3. The infrared spectrum of **3** contains a strong absorption at 2076 cm^{-1} corresponding to the coordinated $(N_3)^-$ anion that is similar to the 2073 cm^{-1} absorption observed for the terminal azide ligands in $[(C_5Me_5)_2UN_3(\mu\text{-}N_3)]_3$.[17]

$(C_5Me_5)_2(hpp)U$, 4. The synthesis of a trivalent uranium $(hpp)^-$ complex was examined by studying the reaction of the U^{3+} precursor $[(C_5Me_5)_2U][BPh_4]$[12] with Khpp, eq 5. $(C_5Me_5)_2(hpp)U$, **4**, was obtained as the first U^{3+} guanidinate complex and characterized

---

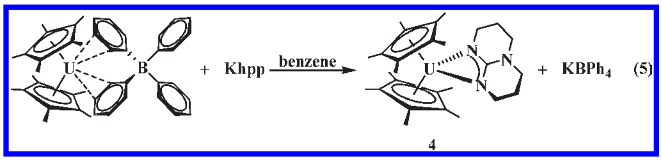
(14) Evans, W. J.; Miller, K. A.; Ziller, J. W.; DiPasquale, A. G.; Heroux, K. J.; Rheingold, A. L. *Organometallics* **2007**, *26*, 4287–4293.

(15) Wilkins, J. D. *J. Organomet. Chem.* **1974**, *80*, 349–355.

(16) (a) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Science* **2005**, *309*, 1835–1838. (b) Evans, W. J.; Miller, K. A.; Ziller, J. W.; Greaves, J. *Inorg. Chem.* **2007**, *46*, 8008–8018. (c) Nocton, G.; Pecaut, J.; Mazzanti, M. *Angew Chem., Int. Ed.* **2008**, *47*, 3040–3042. (d) Korobkov, I.; Gambarotta, S.; Yap Glenn, P. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 3433–3436. (e) Black, L.; Miserque, F.; Gouder, T.; Havela, L.; Rebizant, J.; Wastin, F. *J. Alloys Compd.* **2001**, *315*, 36–41. (f) Thetford, R.; Mignanelli, M. *J. Nucl. Mater.* **2003**, *320*, 44–53. (g) Crawford, M. J.; Ellern, A.; Mayer, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 7874–7878. (h) Fox, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 5716. (i) Fortier, S.; Guang, W.; Hayton, T. W.; U(IV) and U(V) Azide Complexes Supported by Amide or Aryloxide Ligands. *Dalton Trans.* [Online early access]. DOI: 10.1039/b909879h. Published Online: July 24, 2009. http://www.rsc.org/ publishing/journals/DT/article.asp?doi=b909879h (accessed Oct 27, **2009**).

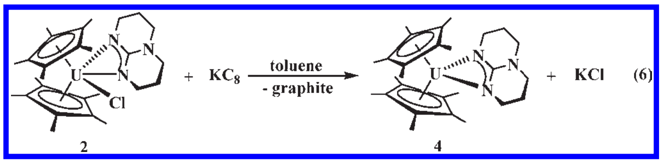
(17) Evans, W., J.; Miller, K., A.; Ziller, J., W.; Greaves, J. *Inorg. Chem.* **2007**, *46*, 8008–8018.

by NMR and IR spectroscopy and by elemental analysis.

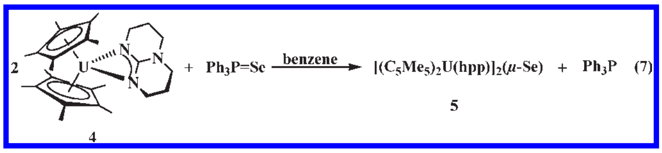


The ^{1}H NMR spectrum of complex **4** contains only three independent resonances attributable to the (hpp)$^-$ ligand at 0.28, −3.10, and −20.17 ppm, which is consistent with a symmetric structure as shown in eq 5. The 4.70 ppm resonance for the $(C_5Me_5)^-$ methyl groups of the starting material $[(C_5Me_5)_2U][BPh_4]$[12] shifts to −12.87 ppm in **4**.

Complex **4** can also be synthesized from the reaction of **2** with KC_8, eq 6. Since $(C_5Me_5)_2UCl_2$ is easier to access than $[(C_5Me_5)_2U][BPh_4]$, eq 6 is preferable to eq 5.



$[(C_5Me_5)_2(hpp)U]_2(\mu\text{-Se})$, 5. The reductive capacity of **4** can be used as another route to U^{4+} (hpp)$^-$ complexes. As shown in eq 7, **4** reduces $Ph_3P{=}Se$ to yield the tetravalent uranium complex, $[(C_5Me_5)_2(hpp)U]_2(\mu\text{-Se})$, **5**, Figure 4. The most common reduction reactions of trivalent uranium complexes are the reactions involving the one electron U^{4+}/U^{3+} redox couple, as shown in this reaction.[18] Like **2** and **3**, complex **5** has six (hpp)$^-$ ^{1}H NMR resonances with a wide spread of chemical shifts. The high solubility of **5** in arenes made it difficult to separate from the PPh_3 byproduct, but in one case X-ray quality crystals were obtainable that allowed the structure to be determined.



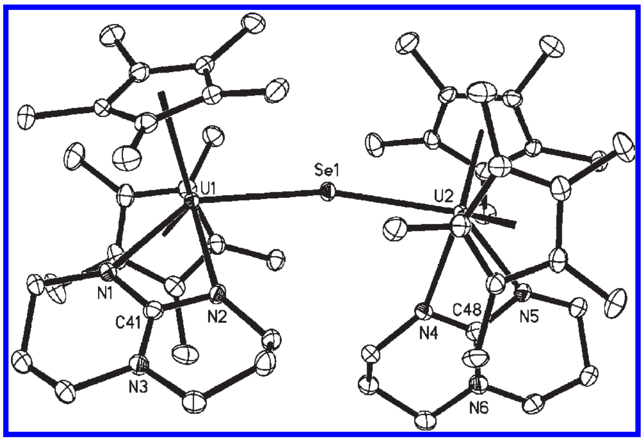


Figure 4. Thermal ellipsoid plot of $[(C_5Me_5)_2(hpp)U]_2(\mu\text{-Se})$, **5**, drawn at the 50% probability level. Hydrogen atoms have been excluded for clarity.

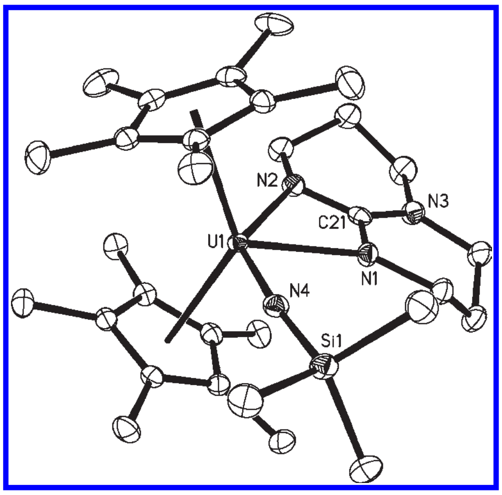
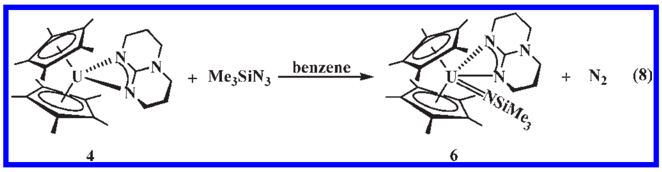


Figure 5. Thermal ellipsoid plot of $(C_5Me_5)_2(hpp)U({=}NSiMe_3)$, **6**, drawn at the 50% probability level. Hydrogen atoms have been excluded for clarity.

$(C_5Me_5)_2(hpp)U({=}NSiMe_3)$, 6. Complex **4** effects a two-electron reduction with Me_3SiN_3 to form the U^{5+} imido complex, $(C_5Me_5)_2(hpp)U({=}NSiMe_3)$, **6**, eq 8, Figure 5. The ^{1}H NMR spectrum of **6** has six (hpp)$^-$ resonances like **2**, **3**, and **5**, but the chemical shifts extend over a narrower range, from 3.33 to −16.91 ppm, for this $5f^1$ complex.[19] Formation of the metallocene U^{5+} monoimido complexes, $(C_5H_4Me)_3U({=}NR)$[20] (R = Ph, $SiMe_3$) and $[C_5H_3(SiMe_3)_2]_2UCl({=}NSiMe_3)$,[21] from the U^{3+} reagents, $(C_5H_4Me)_3U(THF)$[20] and $\{[C_5H_3(SiMe_3)_2]_2UCl\}_2$,[21] respectively, by the reduction of the corresponding RN_3 reagent has been previously reported.



X-ray Structures. Complexes **2**, **3**, **5**, and **6** each have a nine-coordinate uranium metal center ligated by two pentamethylcyclopentadienyl ligands, a chelating (hpp)$^-$ ligand, and an additional anionic ligand, X, [X = **2**, Cl^-; **3**, N_3^-; **5**, Se^{2-}; **6**, $(NSiMe_3)^{2-}$], Figures 2−5. As shown in Table 2, these complexes have similar metrical parameters for the $[(C_5Me_5)_2(hpp)U]^{n+}$ components regardless of the oxidation state of uranium.

In complexes **2**, **3**, **5**, and **6**, the (hpp)$^-$ ligand interacts with the uranium metal centers primarily through two nitrogen atoms with 2.330(2)−2.472(2) Å U−N distances. The U−C(hpp) distances in complexes **2** [2.835(3) Å], **3** [2.830(2) Å], **5** [2.859(3) and 2.872(3) Å], and **6** [2.864(2) Å] are significantly longer. Within a complex, the U−N(hpp) bond lengths differ by

---

[18] Evans, W. J.; Kozimor, S. A. *Coord. Chem. Rev.* **2006**, *250*, 911–935.

[19] Graves, C. R.; Vaughn, A. E.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.* **2008**, *47*, 11879–11891.

[20] Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514–516.

[21] Blake, P. C.; Lappert, M. F.; Taylor, R. G.; Atwood, J. L.; Zhang, H. *Inorg. Chim. Acta* **1987**, *139*, 13–20.

Table 2. Bond Distances (Å) and Angles (deg) in $(C_5Me_5)_2$(hpp)UCl, **2**, $(C_5Me_5)_2$(hpp)UN_3, **3**, $[(C_5Me_5)_2$(hpp)U$]_2$(μ-Se), **5**, and$(C_5Me_5)_2$(hpp)U(=$NSiMe_3$), **6**

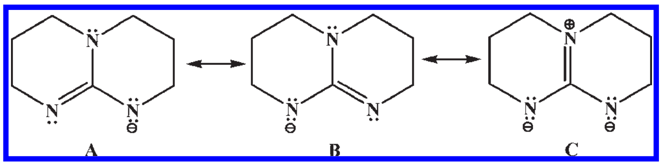
	2	**3**	**5**[c]	**6**
U(1)−(C_5Me_5 ring centroid)	2.449, 2.534	2.481, 2.486	2.529, 2.538, 2.521, 2.531	2.518, 2.531
U(1)−C(C_5Me_5) avg	2.77(2)	2.76(3)	2.80(2), 2.80(7)	2.80(4)
U(1)−N(1)	2.346(2)	2.330(2)	2.465(2), 2.472(2)	2.343(2)
U(1)−N(2)	2.395(2)	2.412(2)	2.343(2), 2.349(2)	2.459(2)
U(1)−C(21)	2.835	2.829(2)	2.859(3), 2.872(3)	2.864(2)
U(1)−X	2.6623(8)[a]	2.316(2)[b]	2.8476(3), 2.8570(3)[d]	1.969(2)[b]
N(1)−C(21)	1.340(4)	1.345(3)	1.321(3), 1.322(4)	1.352(3)
N(2)−C(21)	1.349(4)	1.340(3)	1.353(3), 1.357(4)	1.333(3)
N(3)−C(21)	1.359(4)	1.356(3)	1.369(3), 1.360(4)	1.361(3)
Cnt1−U(1)−Cnt2[e]	130.9	135.1	129.0, 127.2	132.0
N(1)−C(21)−N(2)	112.5(3)	113.1(2)	113.4(2), 113.2(3)	112.8(2)
N(1)−U(1)−N(2)	56.26(9)	56.35(6)	55.32(7), 55.21(8)	55.47(7)
U(1)−N(1)−C(21)	96.7(2)	97.0(1)	93.1(1), 93.5(2)	98.0(1)
U(1)−N(2)−C(21)	94.3(2)	93.4(1)	97.7(2), 98.0(9)	93.3(1)
N(1)−U(1)−X	77.50(7)[a]	78.71(6)[b]	136.15(5), 135.81(6)[e]	82.24(7)[b]

[a] X = Cl(1). [b] X = N(4). [c] Corresponding bond lengths and angles in bimetallic **5**. [d] X = Se(1). [e] Cnt1 and Cnt2 = centroids of the two $(C_5Me_5)^-$ ligands.

0.05−0.12 Å. This difference in metal to atom bond distances is common for f element allyl complexes[22] and has been observed previously in uranium amidinate complexes.[23] In all cases, the U−N(hpp) distances adjacent to the anionic X ligands are shorter than those further from X. The same trend was observed in $(C_5Me_5)_2$U(C≡CPh)[(^{i}Pr)NC(C≡CPh)N(^{i}Pr)-κ^2N,N'],[23] UCl[(Me_3Si)-NC(Ar)N($SiMe_3$)-$\kappa^2N,N'$$]_3$,[24] and UCl[CyNC(Me)NCy-$\kappa^2N,N'$$]_3$.[25] In addition, U−N(hpp) bond lengths are within the 2.330(1)−2.491(3) Å range found in the polymetallic uranium structures involving the chelating bridging $\{[(CyHN)(CyN)C{=}N\text{-}]_2\}^{2-}$ ligands.[7] The U−N(hpp) distances are also longer than the 2.237(3) Å U−N distance in the U^{4+} metallocene chloride complex, $(C_5Me_5)_2$-UCl[NH(C_6H_4Cl-4)].[26]

The set of N(1), N(2), N(3), C(21), and U(1) atoms in **2**, **3**, **5**, and **6** are coplanar within 0.037, 0.023, 0.059, and 0.026, and 0.057 Å, respectively. The C(21)−N(1), C(21)−N(2), and C(21)−N(3) bond lengths fall in the narrow range, 1.321(3)−1.369(3) Å, and are shorter than the average distance expected for a C−N single bond (1.469 Å) but longer than that expected for a C−N double bond (1.303 Å).[27] This indicates delocalization of the negative charge of the monoanionic $(hpp)^-$ ligand. The Δ_{CN} values that have been used to evaluate this delocalization,[28] that is, the difference in N(1)−C(21) and N(2)−C(21) bond lengths are 0.009, 0.005, 0.032, and 0.035, and 0.019 Å for **2**, **3**, **5**, and **6**, respectively. These also support a delocalized bonding arrangement, since fully delocalized systems should have Δ_{CN} = 0.[28] The previously characterized lanthanide guanidinate complexes $(C_5Me_5)_2$(hpp)Ln (Ln = Ce, Sm, Y) have Δ_{CN} values of 0.003, 0.000, and 0.004 Å, respectively.[6]

Scheme 1



The resonance forms for the $(hpp)^-$ ligand are shown in Scheme 1. An indication of the relative contributions which these resonance forms make to the coordinated $(hpp)^-$ ligand can be provided by a comparison of the C−N bond lengths within the CN_3 unit. The Δ'_{CN} values, previously defined by Coles and Hitchcock[28] as the difference between the average C−N(amidine) and C−N(amide) bond lengths, for **2**, **3**, **5**, and **6** are −0.014, −0.035, −0.032, and −0.020, and −0.018 Å, respectively, and indicate only a small contribution of the zwitterionic resonance form **C** to the overall bonding. Similarly, small values were observed for $(C_5Me_5)_2$(hpp)Ln (Ln = Ce, Sm, Y), namely, −0.018, −0.031, and −0.031 Å, respectively.[6] Therefore, the $(hpp)^-$ ligand coordinates in these complexes mainly as a 1,3-diazallyl ligand and there is little contribution from the zwitterionic resonance form **C** that can stabilize high oxidation state transition metals.[2,8]

In $[(C_5Me_5)_2$(hpp)UX$]_y$ [y = 1, X = Cl^-, **2**; N_3^-, **3**; $(NSiMe_3)^{2-}$, **6**; y = 2, X = Se^{2-}, **5**], the U−X bond lengths are within the expected ranges. For example, in **2** the 2.6623(8) Å U(1)−Cl(1) bond length is similar to the corresponding 2.696(2) Å bond distance in $(C_5Me_5)_2U(C_3H_4N_2)Cl_2$,[29] equivalent to that in $(C_5Me_5)_2$U[(CH_2)(CH_2)P(Ph)Me]Cl [2.658(2) Å],[30] and slightly longer than the 2.583(6) Å U−Cl distance in $(C_5Me_5)_2UCl_2$.[31] In **3**, the 2.316(2) Å U(1)−N(4) bond length is within the range for the terminal U−N(azido) distances in $(Bu_4N_3)_3[U(N_3)_7]$[32] [2.323(6)−2.431(7) Å], [η^5-1,2,4-(Me_3C$)_3C_5H_2]_2U(N_3)_2$ [2.219(6) and 2.244(6) Å],[33] and

---

(22) Evans, W. J.; Kozimor, S. A.; Brady, J. C.; Davis, B. L.; Nyce, G. W.; Seibel, C. A.; Ziller, J. W.; Doedens, R. J. *Organometallics* **2005**, *24*, 2269–2278.

(23) Evans, W. J.; Walensky, J. R.; Ziller, J. W.; Rheingold, A. L. *Organometallics* **2009**, *28*, 3350–3357.

(24) Wedler, M.; Knoesel, F.; Noltemeyer, M.; Edelmann, F. T.; Behrens, U. *J. Organomet. Chem.* **1990**, *388*, 21–45.

(25) Villiers, C.; Thuery, P.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2004**, 4624–4632.

(26) Peters, R. G.; Scott, B. L.; Burns, C. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *C55*, 1482–1483.

(27) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987**, S1–S19.

(28) Coles, M. P.; Hitchcock, P. B. *Organometallics* **2003**, *22*, 5201–5211.

(29) Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653–2660.

(30) Cramer, R. E.; Roth, S.; Edelmann, F.; Bruck, M. A.; Cohn, K. C.; Gilje, J. W. *Organometallics* **1989**, *8*, 1192–1199.

(31) Spirlet, M. R.; Rebizant, J.; Apostolidis, C.; Kanellakopulos, B. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *C48*, 2135–2137.

(32) Crawford, M. J.; Ellern, A.; Mayer, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 7874–7878.

(33) Zi, G.; Jia, L.; Werkema, E. L.; Walter, M. D.; Gottfriedsen, J. P.; Andersen, R. A. *Organometallics* **2005**, *24*, 4251–4264.

$[(C_5Me_5)_2UN_3(\mu\text{-}N_3)]_3$ [2.258(14), 2.273(14), and 2.283(14)].[17] The 1.193(3) and 1.151(3) Å N−N bond distances within the azide ligand are almost equivalent and within the 1.124−1.216 Å range reported for the N=N distances in azides.[27]

The 2.8476(3) Å U(1)−Se(1) and 2.8570(3) Å U(2)−Se(1) bond lengths in **5** are close to the corresponding 2.8432(7) Å U−Se bond length in $(C_5Me_5)_2UMe(SePh)$[14] and within the 2.849(1)−3.056(1) Å range in $[U(SePh)_2(\mu_2\text{-}SePh)_2(CH_3CN)_2]_2$.[34] The U−Se distances in **5** are significantly longer than those in $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}Se)$[35] [2.779(1) and 2.782 (1) Å] and $[(C_5Me_5)_2Yb]_2(\mu\text{-}Se)$[36] [2.621(1) Å] when the difference in ionic radii[37] are considered: nine-coordinate U^{4+}, 1.05 Å; seven-coordinate Yb^{3+}, 0.925 Å; eight-coordinate Sm^{3+}, 1.079 Å. A U−Se bond distance of 2.7 Å would be expected based on the lanthanide structures. The reason for this difference is not obvious since the M−Se−M angles in these lanthanide complexes, 169.7(1) and 171.09(6)°, respectively, are similar to the 167.20(1)° U(1)−Se(1)−U(2) angle in **5**.

The 1.969(2) Å U(1)−N(4) bond length in **6** is comparable to the 1.957(5)−1.976(4) Å U−N(imido) bond lengths in the metallocene monoimido complexes $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)X$ where X = OTf, I, SPh, Cl, Br, F synthesized by a one electron oxidation from U^{4+} precursors.[9,38] The nearly linear U(1)−N(4)−Si(1) angle [173.64(12)°] in **6** is close to the 168.3(5)−172.2(9)° range found in the latter $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)X$ complexes.

Discussion

The $(hpp)^-$ ligand can be conveniently incorporated into U^{4+} metallocenes both by deprotonation of Hhpp, eq 2, and by ionic metathesis with Khpp, eq 3. Once the heteroleptic $\{(C_5Me_5)_2(hpp)\}^{3-}$ ligand combination was attached to uranium in $(C_5Me_5)_2(hpp)UMe$, **1**, and $(C_5Me_5)_2(hpp)UCl$, **2**, further reaction of the remaining methyl and chloride ligands with Hhpp and Khpp, respectively, did not occur. Presumably the size of the $(hpp)^-$ ligand allows only one $(hpp)^-$ ligand to be attached to a bis(pentamethylcyclopentadienyl) metallocene. In general, reduced reactivity is observed for the methyl group in **1**. Hence reagents such as PhSSPh and H_2 that commonly react with U^{4+} methyl bonds[11,14] do not react with **1**. This suggests that the $\{(C_5Me_5)_2(hpp)\}^{3-}$ ligand combination may be useful in protecting the remaining coordination site and stabilizing highly reactive U-ligand moieties. Complex **2** does exhibit substitution reactivity with $(N_3)^-$, and this provides a synthetic route to other U^{4+} $\{(C_5Me_5)_2(hpp)\}^{3-}$ complexes. Since the cylindrical azide reacts, but $(hpp)^-$ does not, it is possible that this heteroleptic ancillary ligand set could be used for size selective reactions.

Tetravalent $\{(C_5Me_5)_2(hpp)\}^{3-}$ uranium complexes can also be accessed using the U^{3+} reagent $(C_5Me_5)_2(hpp)U$, **4**. Since **4** can be obtained from **2**, this provides an alternative synthesis when substitution by ionic metathesis is not successful. The reaction of **4** with $Ph_3P{=}Se$ to make a bimetallic $(\mu\text{-}Se)^{2-}$ complex is reminiscent of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Yb$ reactions.[35,36] Hence, the $\{(C_5Me_5)_2(hpp)\}^{3-}$ ligation in **4** may provide a neutral U^{3+} equivalent of divalent lanthanide metallocenes. The structure of **5** suggest that this uranium system may generate bridged structures more sterically crowded that those generated from the divalent lanthanides. Attempts to generate pentavalent $(C_5Me_5)_2(hpp)USe$ from **4** and 1 equiv of $Ph_3P{=}Se$ gave only **5**. Trivalent **4** can be used, however, to obtain U^{5+} complexes as shown in the reaction with Me_3SiN_3, eq 8.

Structural details on **2** and **3** indicate little contribution from the zwitterionic form of $(hpp)^-$, **C** in Scheme 1, that helps stabilize higher oxidation states. Hence, formation of the U^{5+} imido complex, $(C_5Me_5)_2(hpp)U(=NSiMe_3)$, **6**, represents "normal" uranium metallocene reactivity. Likewise, it was not particularly difficult to access the U^{3+} complex **4**, and it did not appear to have unusually powerful reductive capacity. The similarity of the structural parameters in pentavalent **6** and in tetravalent **2**, **3**, and **5**, also suggests that there is no significant contribution of the $(hpp)^-$ resonance form **C**. Hence, the $(hpp)^-$ ligand in these uranium metallocenes is functioning primarily as a monoanionic bidentate nitrogen donor ligand.

Conclusion

The $(hpp)^-$ ligand can be readily incorporated into metallocene complexes of U^{3+}, U^{4+}, and U^{5+}. This provides the trianionic ligand combination, $\{(C_5Me_5)_2(hpp)\}^{3-}$, with which to ligate uranium. In contrast to the heavily studied $\{(C_5Me_5)_2\}^{2-}$ ligand combination which generates U^{4+} and U^{5+} complexes with two additional ligands, this heteroleptic group of ancillary ligands may provide a good option for exploration of U^{4+}- and U^{5+}-ligand reaction chemistry with a single action ligand.[39]

Acknowledgment. We thank the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy for support. This research was facilitated in part by a National Physical Science Consortium Fellowship and by stipend support from Los Alamos National Laboratory (to E.M.). We thank Michael K. Takase for assistance with X-ray crystallography.

Supporting Information Available: X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles for complexes **2**, **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(34) Gaunt, A. J.; Scott, B. L.; Neu, M. P. *Inorg. Chem.* **2006**, *45*, 7401–7407.

(35) Evans, W. J.; Rabe, G. W.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1994**, *33*, 2719–2726.

(36) Berg, D. J.; Burns, C. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865–1870.

(37) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(38) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272–5285.

(39) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2005.