Inorganic Chemistry

Article

Reaction Chemistry of the U^{3+} Metallocene Amidinate (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr]U Including the Isolation of a Uranium Complex of a Monodentate Acetate

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The reductive chemistry of U^{3+} in the metallocene amidinate coordination environment of (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N,N$'$]U, **1**, has been explored. Two equivalents of **1** react with PhSSPh and 2,2$'$-dithiopyridine (pySSpy) to produce (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N,N$'$]U(SPh), **2**, and (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N,N$'$]U(Spy), **3**, respectively. Complexes **2** and **3** can also be synthesized through insertion of ^{i}PrN=C=N^{i}Pr into the methyl group in (C$_5$Me$_5$)$_2$UMe(SPh) and (C$_5$Me$_5$)$_2$UMe(Spy), **4**, respectively. Complex **1** readily reduces the Cu^{1+} reagents, CuBr, CuI, and CuO$_2$CMe, to produce the corresponding (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N,N$'$]UX complexes (X = Br, **5**; I, **6**; O$_2$CMe, **7**). X-ray crystallography established complex **7** as the first f element complex containing a *mono*dentate acetate anion. Complex **7** can also be obtained by reaction of (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N,N$'$]UMe with CO$_2$ at 80 psi. In contrast to the reactions above, **1** reduces TlC$_5$H$_5$ with the unusual loss of (C$_5$Me$_5$)$^-$ to form (C$_5$Me$_5$)(C$_5$H$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N,N$'$]U, **8**.

Introduction

Recent studies of carbodiimide insertion with the actinide metallocene dialkyl complexes (C$_5$Me$_5$)$_2$AnMe$_2$ (An = U, Th) have produced monoalkyl products (C$_5$Me$_5$)$_2$[^{i}PrNC-(Me)N^{i}Pr-κ^2N,N$'$]AnMe,[1] eq 1, that contain an ancillary ligand set, {(C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr]}$^{3-}$, alternative to the
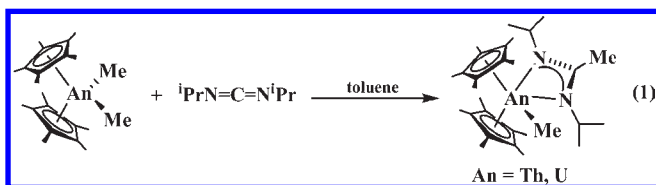
heavily studied (C$_5$Me$_5$)$_2$$^{2-}$ organoactinide coordination environment. This ligand set allows for examination of U-element bond reactivity in a metallocene complex with one "action" ligand, X or R, rather than the two found in (C$_5$Me$_5$)$_2$AnX$_2$ and (C$_5$Me$_5$)$_2$AnR$_2$ complexes.[2]

Complexes of U^{4+} with this heteroleptic cyclopentadienyl amidinate ligand set were found to undergo reduction to form the U^{3+} complex, (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N,N$'$]U, **1**. Specifically, {(C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N,N$'$]U}{BPh$_3$Me}

reacts with KC$_5$Me$_5$ to form **1**.[3] Complex **1** provides an opportunity to explore reductive U^{3+} chemistry[4] with a new ligand set and to expand the range of uranium compounds with {(C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr]}$^{3-}$ ligation. Representative reactions of the reductive chemistry of **1** with inorganic substrates are reported here including the isolation of the first *mono*dentate acetate complex of uranium and an unusual (C$_5$Me$_5$)$^-$ displacement reaction.[5] As emphasized in several recent reviews,[6] exploration of new coordination environments and identification of new coordination modes and reactivity patterns are essential to fully defining the fundamental chemistry of the actinides.

Experimental Section

The syntheses and manipulations described below were conducted with rigorous exclusion of air and water using

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Schlenk, vacuum line, and glovebox techniques. All reactions were conducted in a Vacuum Atmospheres inert-atmosphere (Ar) glovebox free of coordinating solvents. Solvents were sparged with UHP argon, dried by passage through columns containing Q-5 and molecular sieves, and delivered directly to the glovebox through stainless steel tubing. All reactions were conducted in an Ar glovebox free of coordinating solvents. Benzene-d_6 (Cambridge Isotope Laboratories) was dried over NaK alloy and benzophenone, degassed by three freeze−pump−thaw cycles, and vacuum transferred before use. $(C_5Me_5)_2[^iPrNC(Me)N^iPr-\kappa^2N,N']U$, **1**,[3] $(C_5Me_5)_2[^iPrNC(Me)N^iPr-\kappa^2N,N']UMe$,[1] and $(C_5Me_5)_2UMe(SPh)$[7] were prepared as previously described. 2,2′-Dithiodipyridine, CuSPh, CuBr, CuI, CuO_2CMe (Aldrich) and cyclopentadienylthallium (Strem, 99% sublimed) were used as received. $^iPrN=C=N^iPr$ (Aldrich) was dried over molecular sieves and degassed by three freeze−pump−thaw cycles. PhSSPh (Aldrich) was sublimed prior to use. CO_2 (Airgas) was used as received. NMR experiments were conducted with Bruker 400 and 500 MHz spectrometers. Because of the paramagnetism of uranium, only resonances that could be unambiguously assigned are reported.[8] Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany) or with a Perkin-Elmer 2400 CHN elemental analyzer.

Synthesis of $(C_5Me_5)_2[^iPrNC(Me)N^iPr-\kappa^2N,N']U(SPh)$, 2. Method A. PhSSPh (29 mg, 0.13 mmol) was added to a stirred solution of **1** (175 mg, 0.269 mmol) in hexanes (6 mL). After 12 h, the solvent was removed, and **2** was isolated as a red powder (163 mg, 80%). Crystals suitable for X-ray diffraction were grown from a saturated pentane/toluene solution at −35 °C. ^1H NMR (C_6D_6, 298 K): δ 13.0 (s, 6H, CHMe_2), 9.4 (s, 1H, CHMe$_2$), 5.3 (s, 30H, C_5Me_5), 1.3 (s, 3H, Me), 0.4 (s, 1H, CHMe$_2$). IR: 3058s, 2980s, 1648w, 1578 m, 1489 m, 1435 m, 1342s, 1196s, 1141s, 1084s, 1058 m, 1024s, 789s, 737s cm^{-1}. Anal. Calcd. for $C_{34}H_{52}N_2SU$: C, 53.81; H, 6.91; N, 3.69. Found: C, 53.81; H, 7.14, N, 3.19.

Method B. Complex **2** can also be prepared by addition of $^iPrN=C=N^iPr$ (35 μL, 0.23 mmol) to a stirred solution of $(C_5Me_5)_2UMe(SPh)$ (160 mg, 0.225 mmol) in hexanes (8 mL). After 1 h, the solvent was removed under vacuum to yield **2** as a microcrystalline red solid (181 mg, 94%).

Method C. Reaction of **1** (20 mg, 0.031 mmol) with CuSPh (6 mg, 0.03 mmol) in an NMR tube showed the quantitative conversion to **2** by ^1H NMR spectroscopy.

$(C_5Me_5)_2[^iPrNC(Me)N^iPr-\kappa^2N,N']U(Spy)$, 3. Method A. 2,2′-Dithiodipyridine (18 mg, 0.082 mmol) was added to a stirred solution of **1** (97 mg, 0.149 mmol) in methylcyclohexane (10 mL). The color turned from green-brown to orange. After 12 h, the solvent was removed under vacuum to yield an orange oil. Crystallization from a saturated pentane solution at −35 °C gave orange crystals of **3** (74 mg, 66%). ^1H NMR (C_6D_6, 298 K): δ 28.4 (s, 1H, py), 12.3 (s, 30H, C_5Me_5), 4.8 (t, 1H, py), 4.0 (s, 1H, CHMe$_2$), −7.6 (s, 1H, py), −9.7 (s, 3H, Me). IR: 2963s, 1585s, 1543 m, 1513 m, 1443s, 1413s, 1378s, 1260 m, 1195s, 1137s, 1087 m, 785s, 756s, 729s cm^{-1}. Anal. Calcd for $C_{33}H_{51}N_3SU$: C, 52.44; H, 6.80; N, 5.56. Found: C, 52.15; H, 6.87; N, 5.96.

Method B. Complex **3** can also be prepared from $(C_5Me_5)_2$-UMe(Spy), **4**, described below. In an NMR tube, 15 mg of **4** and 5 μL of $^iPrN=C=N^iPr$ were combined. The quantitative conversion of **4** to **3** was observed by ^1H NMR spectroscopy.

$(C_5Me_5)_2UMe(Spy)$, 4. After addition of pySSpy (165 mg, 0.749 mmol) to a stirred solution of $(C_5Me_5)_2UMe_2$ (203 mg, 0.377 mmol) in toluene (10 mL), the solution was allowed to stir

for 16 h. The solvent was then removed under vacuum to yield a red-orange oil. Upon crystallization from a saturated hexanes solution, **4** was obtained as orange crystals suitable for X-ray diffraction (175 mg, 85%). ^1H NMR (C_6D_6, 298 K): δ 15.1 (s, 3H, Me), 8.2 (d, 1H, py), 7.4 (d, 1H, py), 6.8 (t, 1H, py), 6.3 (t, 1H, py), 2.8 (s, 15H, C_5Me_5), 1.8 (s, 15H, C_5Me_5). Anal. Calcd for $C_{26}H_{37}NSU$: C, 49.28; H, 5.89; N, 2.21. Found: C, 49.52; H, 5.99; N, 2.13.

$(C_5Me_5)_2[^iPrNC(Me)N^iPr-\kappa^2N,N']UBr$, 5,[9] from 1 and CuBr. In an NMR tube, CuBr (6 mg, 0.04 mmol) was added to a solution of **1** (20 mg, 0.031 mmol) in C_6D_6 (0.5 mL). After 3 h, the ^1H NMR resonances corresponding to **1** disappeared, and the previously characterized **5** was the only observable product with the formation of a dark precipitate. ^1H NMR (C_6D_6, 298 K): δ 5.8 (s, 30H, C_5Me_5), −5.1 (s, 3H, Me). IR: 2931s, 2893s, 1642 m, 1476s, 1442s, 1418s, 1383s, 1347s, 1339s, 1203s, 1143s, 1126s, 1047 m, 1019 m, 993s, 790 m cm^{-1}. Anal. Calcd for $C_{28}H_{47}N_2BrU$: C, 46.09; H, 6.49; N, 3.84. Found: C, 46.15; H, 6.68; N, 3.76.

$(C_5Me_5)_2[^iPrNC(Me)N^iPr-\kappa^2N,N']UI$, 6,[9] from 1 and CuI. In an NMR tube, CuI (6 mg, 0.03 mmol) was added to a solution of **1** (20 mg, 0.031 mmol) in C_6D_6 (0.5 mL). Over 3 h, the ^1H NMR resonances corresponding to **1** disappeared, and the previously characterized **6** was the only observable product with the formation of a dark precipitate. ^1H NMR (C_6D_6, 298 K): δ 8.3 (s, 30H, C_5Me_5), −4.8 (s, 3H, Me). IR: 2927s, 2896s, 2720 m, 1638w, 1494s, 1436s, 1414s, 1379s, 1359s, 1349s, 1195s, 1140s, 1126s, 1055 m, 1018 m, 1000 m, 808w, 790 m cm^{-1}. Anal. Calcd for $C_{28}H_{47}N_2IU$: C, 43.30; H, 6.10; N, 3.61; I, 16.34; U, 30.65. Found: C, 43.73; H, 5.68; N, 3.34; I, 16.03; U, 30.84.

$(C_5Me_5)_2[^iPrNC(Me)N^iPr-\kappa^2N,N']U(O_2CMe)$, 7. Method A. CuO_2CMe (34 mg, 0.28 mmol) was added to a stirred solution of **1** (123 mg, 0.189 mmol) in toluene (8 mL). After 16 h, insoluble material was removed by centrifugation, and the solvent was removed under vacuum to yield **7** as a red-brown oil. Upon extraction with hexanes and removal of solvent, **7** was obtained as a red-brown powder (114 mg, 85%). Crystals suitable for X-ray crystallography were grown from a saturated pentane/toluene solution at −35 °C. ^1H NMR (C_6D_6, 298 K): δ 32.0 (s, 3H, Me), 27.9 (s, 6H, CHMe_2), 3.9 (s, 1H, CHMe$_2$), 0.04 (s, 30H, C_5Me_5), −9.8 (s, 3H, Me), −19.7 (s, 6H, CHMe_2). IR: 2955s, 2859s, 1657s, 1584s, 1514s, 1436 m, 1419s, 1376s, 1356s, 1197s, 1130s, 1007 m, 922 m, 791 m, 677 m cm^{-1}. Anal. Calcd for $C_{30}H_{50}N_2O_2U$: C, 52.37; H, 8.05; N, 3.70. Found: C, 51.93; H, 7.94; N, 3.88.

Method B. In a glovebox, $(C_5Me_5)_2[(^iPr)NC(Me)N(^iPr)]UMe$ (150 mg, 0.226 mmol) was dissolved in toluene (5 mL) and placed into a Fischer−Porter vessel. The reaction vessel was attached to a high pressure line and CO_2 (80 psi) was introduced. Over 24 h, the color of the mixture changed from yellow-brown to orange. The reaction vessel was transferred to a glovebox where the solvent removed under vacuum to yield **7** (identified by ^1H NMR spectroscopy) as an orange microcrystalline solid in quantitative yield.

$(C_5Me_5)(C_5H_5)[^iPrNC(Me)N^iPr-\kappa^2N,N']U$, 8. TlC$_5H_5$ (48 mg, 0.31 mmol) was added to a stirred solution of **1** (98 mg, 0.15 mmol) in toluene (8 mL). The solution turned from green to red after several minutes. After 12 h, insoluble material was removed by centrifugation, and the solvent was removed under vacuum to yield **8** as a red powder (80 mg, 82%). Crystals suitable for X-ray crystallography were grown from a saturated toluene solution at −35 °C. ^1H NMR (C_6D_6, 298 K): δ 4.5 (s, 6H, CHMe_2), 2.3 (s, 6H, CHMe_2), 2.2 (s, 15H, C_5Me_5), −11.3 (s, 10H, C_5H_5). IR: 2971s, 1469s, 1440 m, 1377s, 1359s, 1199s, 1142s, 1060 m, 1011s, 995s, 903w, 791s, 716s, 693s cm^{-1}. Anal. Calcd for $C_{28}H_{42}N_2U$: C, 52.17; H, 6.37; N, 4.21. Found: C, 52.38; H, 6.49; N, 4.10.

X-ray Data Collection, Structure Solution, and Refinement for 2−4, 7, and 8. This information is available in the Supporting

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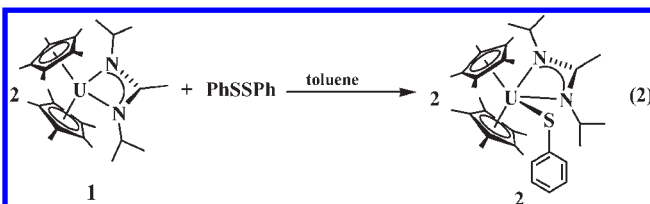**Table 1.** X-ray Data Collection Parameters for Complexes **2–4**, **7**, and **8**

	2	**3**	**4**	**7**	**8**
empirical formula	$C_{34}H_{52}N_2SU$	$C_{33}H_{51}N_3SU \cdot 1/2(C_7H_8)$	$C_{26}H_{37}NSU$	$C_{30}H_{50}N_2O_2U$	$C_{28}H_{42}N_2U$
formula weight	758.87	805.93	633.66	708.75	644.67
temperature (K)	103(2)	103(2)	153(2)	143(2)	103(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P2_1$	$P2_1/n$	$P\bar{1}$
a (Å)	11.5156(6)	34.4356(18)	8.343(3)	9.5795(6)	8.2845(4)
b (Å)	17.1703(9)	12.3473(7)	15.068(5)	17.4341(11)	11.1001(6)
c (Å)	16.0926(8)	16.1941(9)	9.730(3)	17.8520(11)	14.2310(7)
α (deg)	90	90	90	90	81.9930(5)
β (deg)	90.2320(10)	90.6820(10)	96.247(4)	101.4380(10)	76.1897(5)
γ (deg)	90	90	90	90	81.9746(6)
volume Å^3	3181.9(3)	6885.0(7)	1216.0(7)	2992(9)	1250.72(11)
Z	4	8	2	4	2
ρ_{calcd} (Mg/m^3)	1.584	1.555	1.731	1.611	1.712
μ (mm^{-1})	5.191	4.804	6.772	5.582	6.506
R1 [$I > 2.0\sigma(I)$]^a	0.0295	0.0181	0.0431	0.0240	0.0166
wR2 (all data)^a	0.0622	0.0468	0.1111	0.0604	0.0427

^{a} Definitions: wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, R1 = $\sum ||F_o| - |F_c||/\sum |F_o|$.
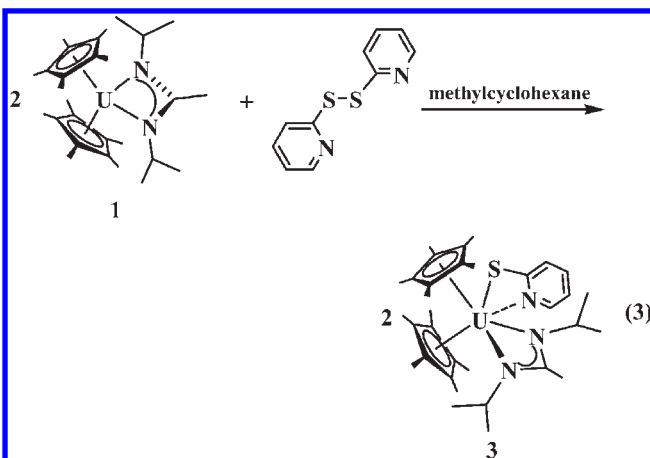
Information. Selected X-ray collection parameters are found in Table 1.

Results

RSSR Reactions. PhSSPh is one of the substrates examined with new f element reducing agents since the S−S bond is readily reduced ($E = -1.7$ vs SCE)[10] and the (SPh)$^-$ ligands formed on reduction frequently form isolable complexes.[11] Two equivalents of **1** reduce PhSSPh to produce the U^{4+} complex (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N,N′]U(SPh), **2**, eq 2. Complex **2** was characterized by analytical and spectroscopic methods, but did not initially

crystallize to allow identification by X-ray crystallography. To provide an extra coordination option, the pyridyl (py) analogue, pySSpy, was treated with **1** and (C$_5$Me$_5$)$_2$[^{i}PrNC-(Me)N^{i}Pr-κ^2N,N′]U(Spy), **3**, was isolated, eq 3.

Subsequently, both **2** and **3** were obtained in crystalline form suitable for X-ray crystallography, Figures 1 and 2. Hence, the (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr]}$^{3-}$ ligand set can
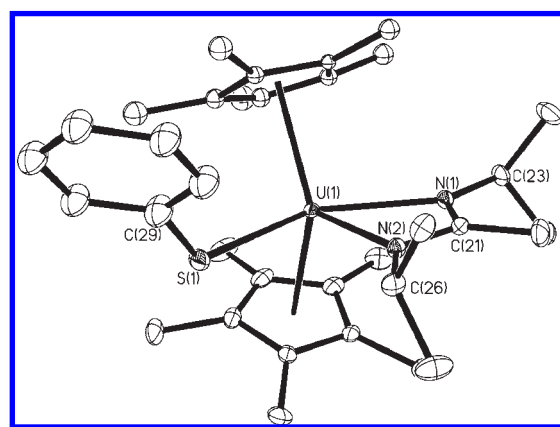

Figure 1. Thermal ellipsoid plot of (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr-κ^2N, N′]U(SPh), **2**, shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

accommodate both a mono- and bidentate arylsulfide ligand. Table 2 compares the metrical parameters of these closely related complexes.

Complex **2** displays U−(C$_5$Me$_5$ ring centroid) distances of 2.510 and 2.515 Å that are between the 2.498 and 2.500 Å distances in (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr]UI[9] and the 2.527 and 2.538 Å in (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr]UMe.[1] The 2.7665(9) Å U−S bond is longer than the 2.7060(14) Å distance in (C$_5$Me$_5$)$_2$UMe(SPh)[7] and the 2.6845(7) and 2.6967(7) Å lengths in (C$_5$Me$_4$H)$_2$U(SPh)$_2$[12] as might be expected since the [^{i}PrNC(Me)N^{i}Pr]$^-$ ligand is larger than (Me)$^-$ and (SPh)$^-$.

In complex **3**, the 2.565 and 2.608 Å U−(C$_5$Me$_5$ ring centroid) distances are longer than those in **2** and in any previously characterized U^{4+} metallocene amidinate complexes.[1,3,9] This is consistent with the increased coordination number. Interestingly, the 2.408(1) and 2.510(1) Å U−N (amidinate) bond distances and

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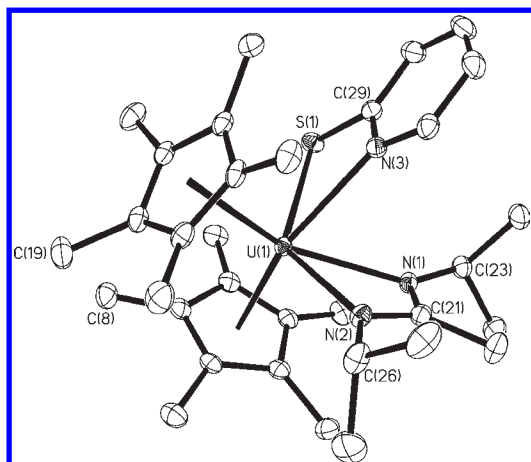
Figure 2. Thermal ellipsoid plot of $(C_5Me_5)_2[^iPrNC(Me)N^iPr$-$\kappa^2N$, $N']U(Spy)$, **3**, shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $(C_5Me_5)_2[^iPrNC$-$(Me)N^iPr$-$\kappa^2N,N']U(SPh)$, **2**, and $(C_5Me_5)_2[^iPrNC(Me)N^iPr$-$\kappa^2N,N']U(Spy)$, **3**

bond distance/angle	2	3
U(1)−(C$_5$Me$_5$ ring centroid)	2.510, 2.515	2.565, 2.608
U(1)−N(1)	2.482(3)	2.510(2)
U(1)−N(2)	2.380(3)	2.408(2)
U(1)−C(21)	2.902(3)	2.926(2)
U(1)−N(3)		2.572(2)
U(1)−S(1)	2.7665(9)	2.7997(6)
(C$_5$Me$_5$ ring centroid)−U(1)−(C$_5$Me$_5$ ring centroid)	129.7	118.7
(C$_5$Me$_5$ ring centroid)−U(1)−N(1)	101.1, 100.1	93.4, 146.2
(C$_5$Me$_5$ ring centroid)−U(1)−N(2)	122.3, 108.9	109.0, 101.9
(C$_5$Me$_5$ ring centroid)−U(1)−N(3)		146.4, 89.1
(C$_5$Me$_5$ ring centroid)−U(1)−S(1)	91.2, 102.4	95.3, 101.7
U(1)−S(1)−C(29)	126.46(18)	84.24(8)
N(1)−U(1)−N(2)	54.41(10)	53.84(6)

2.7997(6) Å U−S bond length in **3** are not dissimilar to the distances seen in **2**: 2.380(3)/2.482(3) Å and 2.7996(9) Å, respectively. Two other U^{4+} complexes bearing the thio-pyridine ligand are known, U(Spy)$_4$(THF)[8] and [U{(SiMe$_2$NPh)$_3$-tacn}(Spy)],[13] but comparisons are more complicated since they are not metallocenes. The 2.572(1) Å U−N(3) bond in **3** is similar to the 2.504-(2)−2.575(2) Å U−N(py) analogues in these compounds as is the 2.7997(6) Å U−S distance (2.8222(8)−2.880(2) Å in the other compounds).

Since complex **3** exhibited long U−(C$_5$Me$_5$ ring centroid) distances compared to the other metallocene amidinate complexes, the displacements of the methyl groups from the plane of the (C$_5$Me$_5$)$^-$ ligand were measured. Displacements of this type have been used as a calibration of steric crowding in f element complexes.[14] Displacements of 0.27, 0.21, 0.43, 0.11, and 0.22 Å were found for C(6)−C(10), and values of 0.28, 0.33, 0.12, 0.52, and 0.32 Å were measured for C(16)−C(20), respectively. The 0.52 Å value measured for C(19), Figure 3, is in the range of extreme values displayed by sterically crowded (C$_5$Me$_5$)$_3$M complexes
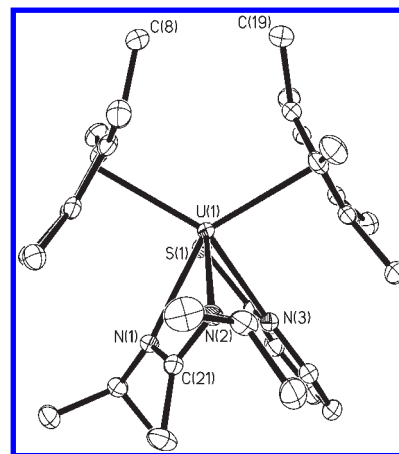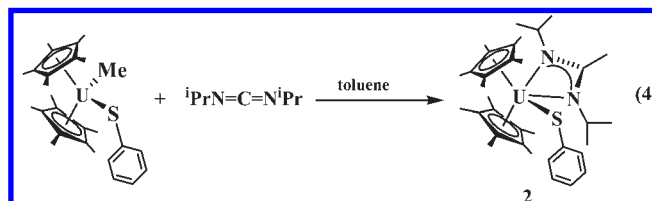

Figure 3. Two methyl groups with the greatest displacement from the cyclopentadienyl ring plane, C(8) and C(19), in complex **3** are shown. Thermal ellipsoids are shown at the 50% probability level.
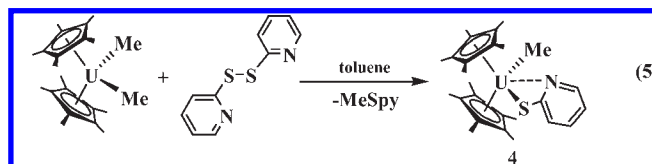
that display unusual (C$_5$Me$_5$)$^-$ reactivity like sterically induced reduction (SIR).[14,15]

Although **3** has a methyl group with an extreme displacement, it does not display unusual (C$_5$Me$_5$)$^-$ reactivity. For example, it does not reduce phenazine even at 100 °C in toluene. This is consistent with the finding that the sterically crowded complexes that have SIR reactivity are globally crowded at all the ligand sites.[16]

Since **2** could be formed by insertion of $^iPrN=C=N^iPr$ into the methyl group of the U^{4+} complex, (C$_5$Me$_5$)$_2$-UMe(SPh),[7] this reaction was examined and a second route to **2** was identified, eq 4. To determine if **3** could also form via insertion of a carbodiimide, the necessary

precursor, (C$_5$Me$_5$)$_2$UMe(Spy), **4**, was synthesized by the reaction of (C$_5$Me$_5$)$_2$UMe$_2$ with pySSpy, eq 5. The byproduct of this σ bond metathesis reaction, MeSpy,

was identified by ^{1}H NMR spectroscopy.[17] The structure of **4** was established by X-ray crystallography, Figure 4, although the data were not of high enough quality for a detailed discussion. As shown in eq 6, insertion of a carbodiimide into the U−Me bond in **4** is also successful and forms **3**. Hence, the extra coordination of the pyridyl

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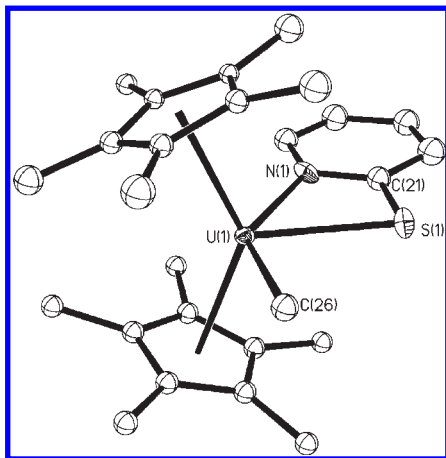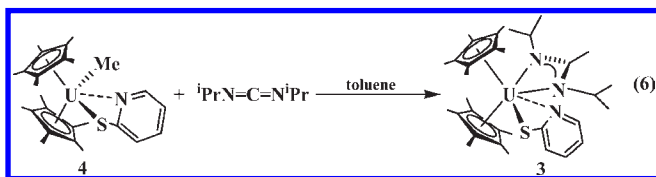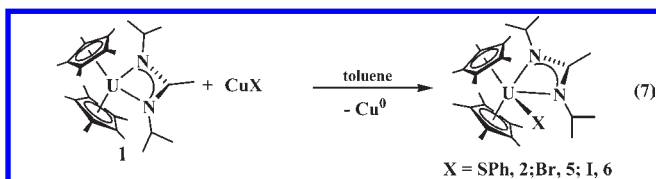
Figure 4. Thermal ellipsoid plot of $(C_5Me_5)_2UMe(Spy)$, **4**, shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

substituent in **4** versus $(C_5Me_5)_2UMe(SPh)$ did not prevent this insertion from occurring.

$$\text{(6)}$$

4   **3**

Attempts to reduce $1,3,5,7\text{-}C_8H_8$ ($E = -1.85$ V and -1.9 V vs SCE),[18] with **1** were unsuccessful even at 100 °C in toluene. Although the reductions of PhSSPh ($E = -1.7$ V vs SCE)[9] and pySSpy were facile, complex **1** showed no reactivity with phenazine ($E = -0.36$ V vs SCE),[19] benzaldehyde azine,[20] and benzophenone.[21]

Reactions of **1** with copper salts were also of interest since Kiplinger and co-workers recently showed that it was possible to convert U^{3+} precursors to U^{4+} halides and pseudohalides.[22] Complex **1** reacts similarly with CuSPh, CuBr, and CuI to form **2**, $(C_5Me_5)_2[^iPrNC(Me)-N^iPr\text{-}\kappa^2N,N']UBr$, **5**,[9] and $(C_5Me_5)_2[^iPrNC(Me)N^iPr\text{-}\kappa^2N,N']UI$, **6**,[9] eq 7, respectively. Complexes **5** and **6** were previously synthesized by reaction of $(C_5Me_5)_2[^iPrNC(Me)N^iPr\text{-}\kappa^2N,N']UMe$ with CuBr and CuI, respectively.[9] The previous synthesis is a more facile route to **5** and **6** than eq 7, since $(C_5Me_5)_2[^iPrNC(Me)N^iPr\text{-}\kappa^2N,N']UMe$ is directly obtainable from $(C_5Me_5)_2UMe_2$, eq 1.[1]

$$\text{(7)}$$

1   X = SPh, **2**; Br, **5**; I, **6**

The reaction of **1** with copper acetate provided the desired result. Complex **1** reacts with CuO_2CMe to make the expected acetate complex, $(C_5Me_5)_2[^iPrNC(Me)N^iPr\text{-}$
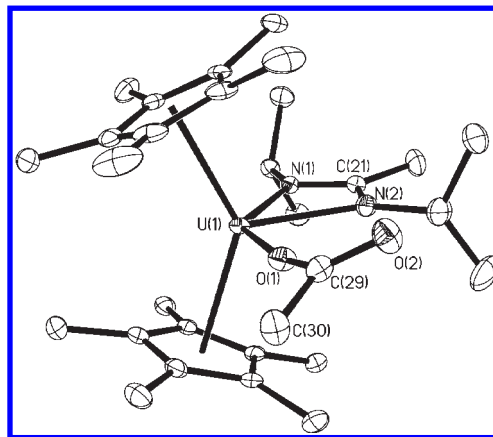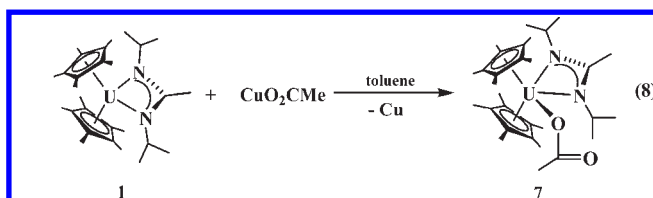

Figure 5. Thermal ellipsoid plot of $(C_5Me_5)_2[^iPrNC(Me)N^iPr\text{-}\kappa^2N,N']U(O_2CMe)$, **7**, shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

$\kappa^2N,N']U(O_2CMe)$, **7**, eq 8, but X-ray crystallography showed that the acetate attached to uranium in a monodentate

$$\text{(8)}$$

1   **7**

coordination mode, $(C_5Me_5)_2[^iPrNC(Me)N^iPr\text{-}\kappa^2N,N']\text{-}U(\eta^1\text{-}O_2CMe)$, **7**, Figure 5. Although monodentate acetate coordination has been observed in transition metal complexes,[23] this is a new mode of acetate binding in f element chemistry where the large, highly charged, electropositive metals would be expected to interact with both acetate oxygen atoms. Given the flexibility in the coordination sphere exhibited by complexes **2** and **3**, it is surprising that this small bite angle chelate did not form a bidentate complex.

Just as **2** and **3** could be made from $^iPrN=C=N^iPr$ insertion reactions, **7** can also be obtained via CO_2 insertion, eq 9. Since $(C_5Me_5)_2[^iPrNC(Me)N^iPr\text{-}\kappa^2N,N']UMe$ is a precursor to **1**, eq 9 is a more efficient way to form **7**.

$$\text{(9)}$$

7
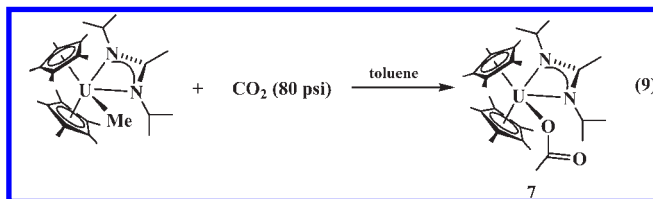
Only one other U^{4+} acetate structure was found in the literature, $[HB(3,5\text{-}Me_2Pz)_3]U(O_2CMe)_3$,[24] although many UO_2^{2+} acetate structures are known.[25] The U−(C_5Me_5 ring centroid) distances of 2.495 and 2.504 Å and

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Table 3. Selected Bond Lengths [Å] and Angles [deg] for $(C_5Me_5)_2[^iPrNC(Me)$-N^iPr-$\kappa^2 N,N']U(O_2CMe)$, **7**

bond distance/angle	7
U(1)−(C$_5$Me$_5$ ring centroid)	2.495, 2.504
U(1)−N(1)	2.503(3)
U(1)−N(2)	2.370(3)
U(1)−C(21)	2.895(3)
U(1)−O(1)	2.213(2)
(C$_5$Me$_5$ ring centroid)−U(1)−(C$_5$Me$_5$ ring centroid)	135.4
(C$_5$Me$_5$ ring centroid)−U(1)−N(1)	99.8, 99.2
(C$_5$Me$_5$ ring centroid)−U(1)−N(2)	112.9, 111.0
(C$_5$Me$_5$ ring centroid)−U(1)−O(1)	95.9, 96.2
N(1)−U(1)−O(1)	138.18(9)
N(2)−U(1)−O(1)	83.72(10)
N(1)−U(1)−N(2)	54.46(9)

the U−N(1) and U−N(2) distances of 2.503(3) and 2.370(3) Å in **7** (Table 3) are not unusual: they are similar to those observed in **2** (2.482(3) and 2.380(3) Å) and **6** (2.480(3) and 2.371(4) Å). The 2.213(2) Å U−O(1) bond is similar to the 2.117(9) Å of the U−O(OH) bond in $(C_5Me_5)_2UCl(OH)(HNSPh_2)$,[26] but much shorter than the average U−O(acetate) bond distance of 2.41(1) Å in $[HB(3,5-Me_2Pz)_3]U(O_2CMe)_3$,[24] in which the acetates are coordinated in a bidentate fashion. The 1.302(4) and 1.221(4) Å bond distances for C(29)−O(1) and C(29)−O-(2), respectively, show the localization in the acetate ligand. Examining the crystal packing in the unit cell, a 2.55 Å distance was found between the uncoordinated oxygen of the acetate ligand and a hydrogen atom on a nearby $(C_5Me_5)^-$ ligand of an adjacent molecule (see Figure 1 in Supporting Information). This distance is much less than the sum of the covalent radii of oxygen and hydrogen.[27,28]

The reaction of **1** with TlC$_5$H$_5$ was examined to determine if an unsubstituted cyclopentadienyl ligand could coordinate along with the $\{(C_5Me_5)_2[^iPrNC(Me)N^iPr]\}^{3-}$ ligand set. Previously, it had been shown that $(C_5Me_5)^-$ was too large to add to actinide complexes with this ligation and led to an unexpected C−H bond, eq 10, and reduction reactivity.[3] As shown in eq 11, an unexpected $(C_5Me_5)^-$ displacement occurred to form

(10)

(11)
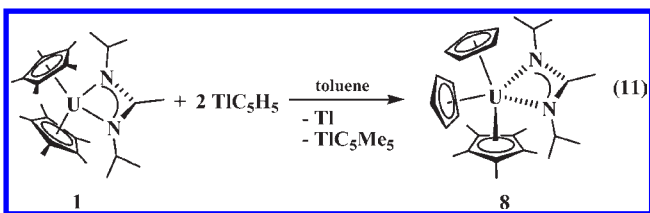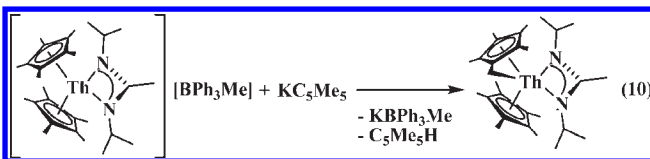
$(C_5Me_5)(C_5H_5)_2[^iPrNC(Me)N^iPr$-$\kappa^2 N,N']U$, **8**. Attempts to react just 1 equiv of TlC$_5$H$_5$ with **1** only gave a 50%

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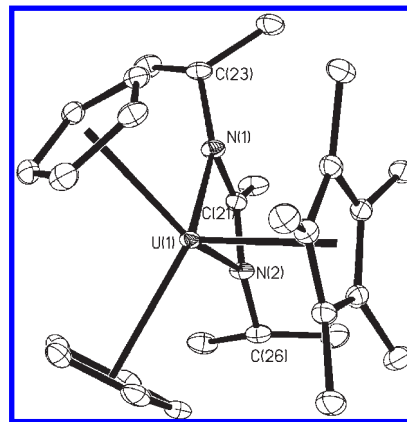
Figure 6. Thermal ellipsoid plot of $(C_5Me_5)(C_5H_5)_2[^iPrNC(Me)N^iPr$-$\kappa^2 N,N']U$, **8**, shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Lengths [Å] and Angles [deg] for $(C_5Me_5)(C_5H_5)_2$-$[^iPrNC(Me)N^iPr$-$\kappa^2 N,N']U$, **8**

bond distance/angle	7
U(1)−(C$_5$Me$_5$ ring centroid)	2.565
U(1)−(C$_5$H$_5$ ring centroid)	2.581, 2.591
U(1)−N(1)	2.480(2)
U(1)−N(2)	2.502(2)
U(1)−C(21)	2.950(2)
(C$_5$Me$_5$ ring centroid)−U(1)−(C$_5$H$_5$ ring centroid)	114.1, 112.6
(C$_5$H$_5$ ring centroid)−U(1)−(C$_5$H$_5$ ring centroid)	105.2
(C$_5$Me$_5$ ring centroid)−U(1)−N(1)	101.9
(C$_5$Me$_5$ ring centroid)−U(1)−N(2)	94.2
(C$_5$H$_5$ ring centroid)−U(1)−N(1)	130.9, 89.3
(C$_5$H$_5$ ring centroid)−U(1)−N(2)	90.5, 138.6
N(1)−U(1)−N(2)	53.37(6)

yield of **8** with starting material remaining. Interestingly, this same $[(C_5Me_5)(C_5H_5)_2U]^{1+}$ unit is obtained cleanly from $(C_5Me_5)U(CH_2Ph)_3$ and cyclopentadiene.[29] Complex **8** was identified by X-ray crystallography, Figure 6. The ^1H NMR spectrum of **8** showed the presence of TlC$_5$Me$_5$ (δ 2.28 ppm in C$_6$D$_6$) as a byproduct.[30]

The U−(C$_5$Me$_5$ ring centroid) distance of 2.565 Å in **8** (Table 4) is identical to that of the smaller of the two centroid distances in **3**, but **8** has methyl displacements (0.22−0.36 Å) in the sterically normal range. The 2.480(2) and 2.502(2) Å U−N bond lengths are also similar to those in **3** (2.408(2) and 2.510(2) Å). The average U−C-(C$_5$H$_5$) distances of 2.84(1) and 2.86(1) Å are significantly longer than those in $(C_5Me_5)(C_5H_5)_2U(CH_2C_6H_5)$ (2.74(1) and 2.75(1) Å),[29] $(C_5H_5)_3UCl$ (2.74(1) Å),[31] and $(C_5Me_5)_2(C_5H_5)UMe$ (2.76(1) Å).[16] The (C$_5$H$_5$ ring centroid)−U−(C$_5$H$_5$ ring centroid) angle of 105.2° is smaller than the 113.8° in $(C_5Me_5)(C_5H_5)_2U(CH_2C_6H_5)$ as well.

Discussion

$(C_5Me_5)_2[^iPrNC(Me)N^iPr]U$, **1**, readily reduces disulfide substrates to make tetravalent $(C_5Me_5)_2[^iPrNC(Me)N^iPr]$-$U(SR)$ complexes, **2** and **3**, eq 2 and 3. Complex **1** also reduces copper halides to produce $(C_5Me_5)_2[^iPrNC(Me)N^iPr]UX$

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species, **5** and **6**, eq 7, as is typical for trivalent uranium metallocenes.[22] Complex **1** does not react with phenazine,[32] benzaldehyde azine,[20] benzophenone,[21] and cyclooctatetrene,[33] substrates generally reducible with low-valent f element metallocenes. It is possible that steric crowding from the amidinate ligand may prevent coordination of these substrates that could inhibit electron transfer if an inner sphere electron mechanism is involved. However, the sterically crowded trivalent uranium complex $(C_5Me_5)_3U$ is known to reduce C_8H_8,[34] and $(C_5Me_5)_3U$ is known to reduce first via U^{3+} in some cases.[35] Moderation of reactivity with the $\{(C_5Me_5)_2[^iPrNC(Me)N^iPr]\}^{3-}$ ligand set has previously been observed with U^{4+} alkyl complexes,[9] and was explained on the basis of steric protection. It is possible that these three ancillary ligands can protect U^{3+} as well as U^{4+} alkyls.

The formation of the monohapto acetate complex, $(C_5Me_5)_2[(^iPr)NC(Me)N(^iPr)]U(O_2CMe)$ **7**, eq 8, demonstrates the type of steric variation that can be achieved with the $\{(C_5Me_5)_2[^iPrNC(Me)N^iPr]\}^{3-}$ ligand set. Clearly, coordination modes of common ions can be changed just by adding an amidinate to a metallocene coordination environment. Since coordination chemistry is used to control speciation in f element separation chemistry,[36] it is important to remember that unusual coordination modes may be accessible in the presence of the certain collections of ligands as shown in **7**.

Interestingly, although this heteroleptic ligand set leads to a monohapto acetate ligand, it can accommodate both monodentate $(SPh)^-$ and bidentate $(Spy)^-$ ligation in **2** and **3**, respectively. An electronic argument can be made for the difference between the thiopyridyl and acetate ligands. Since acetate is a hard-donor ligand, it may satisfy the uranium center in a monodentate binding mode while the softer sulfur ligand requires the binding to the harder nitrogen donor atom in the pyridyl substituent.

The formation of $(C_5Me_5)(C_5H_5)_2[(^iPr)NC(Me)N(^iPr)]U$, **8**, eq 11, is another unusual result from this heteroleptic ligand set, since a usually inert $(C_5Me_5)^-$ ligand is displaced from uranium. If this reaction initially involves U^{3+} reduction of Tl^{1+}, an intermediate such as "$(C_5Me_5)_2(C_5H_5)U[^iPrNC(Me)N^iPr]$" could be envisioned. If the cyclopentadienyl ligands are pentahapto, this would be expected to be extremely crowded and could lose $(C_5Me_5)^-$ as previously observed in the reaction of the sterically crowded $[(C_5Me_5)_2U]_2(C_6H_6)$ with $[N(SiMe_3)_2]^-$.[5a] The isolation of **8** suggests that several combinations of amidinate and cyclopentadienyl ligands of various substitutions should be accessible.

Conclusion

The heteroleptic ligand set $\{(C_5Me_5)_2[(^iPr)NC(Me)N(^iPr)]\}^{3-}$ provides an alternative coordination environment with which to explore U^{3+} chemistry. $(C_5Me_5)_2[^iPrNC(Me)N^iPr]U$, **1**, displays selective reductive chemistry that appears to be dependent on the specific substrate. Selective chemistry is also observed in terms of the types of coordination modes accessible with these ancillary ligands. This ligand set can accommodate variable coordination modes with $(SPh)^-$ and $(Spy)^-$ ligands, but enforces an unusual $(\eta^1\text{-}O_2CMe)$ binding mode with acetate. The $(C_5Me_5)_2[^iPrNC(Me)N^iPr]U$ unit appears to be sufficiently sterically saturated that addition of ligands such as $(C_5H_5)^-$ can lead to unusual $(C_5Me_5)^-$ diplacement.

Supporting Information Available: X-ray diffraction details (CIF) and X-ray data collection, structure, solution, and refinement of compounds **2**−**4**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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