Challenging the Metallocene Dominance in Actinide Chemistry with a Soft PNP Pincer Ligand: New Uranium Structures and Reactivity Patterns**

Thibault Cantat, Christopher R. Graves, Brian L. Scott, and Jaqueline L. Kiplinger*

Cyclopentadienyl-based ligand sets, in particular the bis(pentamethylcyclopentadienyl) ligand, are enormously successful frameworks in actinide chemistry and no alternative has proved as fruitful to date.^[1] However, the bis(C₅Me₅) framework suffers from inconvenient drawbacks such as the chronic release of the (C₅Me₅)₂ dimer upon oxidation of " $[(C_5Me_5)_2U]$ " complexes.^[2] Inspired by the ability of ligands that combine both hard and soft coordination environments to stabilize highly reactive functional groups (such as alkylidenes, imides, and phosphinidenes) on transition metals and lanthanides,^[3] we have extended this strategy to the actinides by using the monoanionic bis[2-(diisopropylphosphino)-4-methylphenyl]amido (PNP) ligand. Compared to the C₅Me₅ ligand, which only displays η^5 -coordination to uranium,^[4] this soft PNP pincer ligand adopts a variety of coordination modes that range from κ^2 -(*P*,*N*) to κ^3 -(*P*,*N*,*P'*) and provides more steric crowding and greater electronic density at the metal center.^[5] By capitalizing on this versatility, we now demonstrate by using $[(PNP)_2U(I)]$ (1) and $[(C_5Me_5)_2U(I)(thf)]$ (2) that the PNP ligand not only promotes unprecedented reactivity patterns for low-valent uranium but also supports new structures for the actinide series that are not available with the C₅Me₅ ligand framework.

Trivalent [(C_5Me_5)₂U(I)(thf)] (2) in the presence of Na/Hg amalgam or KC₈, a classic uranium(II) synthetic equivalent, is known to provide up to four reducing equivalents.^[6] As such, initial studies with **1** were targeted toward establishing the capacity of the bis(PNP) platform to support low-valent uranium chemistry [Eq. (1)]. Treatment of a cold (-35° C) solution of **1** and KC₈ in toluene with hexachloroethane resulted in an immediate color change from deep green to bright red and formation of the known uranium(IV) [(PNP)₂UCl₂] complex^[5]; following workup the yield of the isolated product was 96%. These observations clearly demonstrate that the PNP ligand can indeed support low-valent



uranium with the $1/KC_8$ system able to function as a new uranium(II) synthon.

The ability of the bis(PNP) platform to promote new uranium chemistry was validated by comparing the reactions of $1/KC_8$ and $2/KC_8$ with diphenyldiazomethane. Reaction of $1/KC_8$ with Ph₂C=N₂ afforded the hydrazonido complex 4, which was isolated in 98% yield [Eq. (2)]. To the best of our



knowledge, complex **4** represents the first example of an actinide hydrazonido $[\eta^2 - (N,N')=N-N=CR_2]^{2-}$ complex and the first example of such a ligand stabilized by a single metal ion.^[7] Figure 1 shows the molecular structure of complex **4**, which reveals that the $[\eta^2 - (N,N')=N-N=CPh_2]^{2-}$ ligand is stabilized by both a short U=N double bond (U(1)-N(4) = 2.097(5) Å) and an additional U–N dative interaction (U(1)-N(3) = 2.370(5) Å). The U=N linkage is substantially shorter than a uranium(IV)-amide bond (ca. 2.3 Å) and compares well with the few structurally characterized U^{IV} complexes that contain an imido functional group (1.95 Å).^[8]

The hydrazonido $[\eta^2 - (N,N')=N-N=CPh_2]^{2-}$ ligand is formed by the two-electron reduction of diphenyldiazomethane. The N–N bond of the reduced Ph₂C=N₂ unit (N(3)– N(4) 1.359(7) Å) is substantially elongated compared to that in uncomplexed diazoalkanes (1.12–1.13 Å)^[9] and is slightly longer than that reported for the $[\eta^2 - (N,N')-N-N=CPh_2]^$ ligand in $[(tBuArO)_3(tacn)U\{\eta^2 - (N,N')-N-N=CPh_2\}]$ (1.338(5) Å; tacn = 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane).^[10] In fact, the N(3)–N(4) bond distance in **4** is longer than those observed for the imido ligands in $[(C_5Me_5)_2U(=N-N=CPh_2)(=N-2,4,6-tBu_3-C_6H_2)]$

 ^[*] Dr. T. Cantat, Dr. C. R. Graves, Dr. B. L. Scott, Dr. J. L. Kiplinger Los Alamos National Laboratory Mail Stop J514, Los Alamos, NM 87545 (USA) Fax: (+1) 505-667-9905 E-mail: Kiplinger@lanl.gov

^[**] We acknowledge LANL (Director's PD Fellowships to T.C. and C.R.G.), G.T. Seaborg Institute for Transactinium Science (PD Fellowship to C.R.G.), and the Heavy Element Chemistry Program, Division of Chemical Sciences, Office of Basic Energy Sciences for financial support of this work. We thank Anthony Mancinco for the design of the inside cover art.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200806115.



Figure 1. Molecular structure of complexes **4** (a) and **5** (b) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms and methyl groups on the PNP ligands are omitted for clarity. Selected bond distances [Å] and angles [°] for **4**: U(1)–N(3) 2.375(5), U(1)–N(4) 2.097(5), N(3)–N(4) 1.359(7), N(3)–C(53) 1.302(8). For **5**: U(1)–N(1) 1.999(4), U(1)–N(3) 2.018(4), N(1)–N(2) 1.315(6), N(3)–N(4) 1.324(5), N(2)–C(21) 1.314(6), N(4)–C(34) 1.305(6); N(3)-U(1)-N(1) 103.26(16).

(1.308(8) Å)^[11] and in **5** (1.315(6), 1.324(5) Å, see below). This bond lengthening is accompanied by a shortening of the C=N bond from 1.32–1.33 Å in uncomplexed diazoalkanes^[9] to 1.302(8) Å for C(53)–N(3) in 4. The same shortening is observed in $[(C_5Me_5)_2U(=N-N=CPh_2)(=N-2,4,6-tBu_3-C_6H_2)]$ (1.310(10) Å)^[11] and in 5 (1.314(6), 1.305(6) Å), but not for the radical anion ligand in $[(tBuArO)_3(tacn)U{\eta^2-(N,N')-N-$ N-CPh₂] (1.333(6) Å), as expected for a $[\eta^2 - (N,N') - N - N]$ CPh_2 ⁻ radical anion compared to a $[\eta^2 - (N,N') = N - N = CPh_2]^2$ dianion.^[10] Finally, the coordination sphere of the uranium(IV) center^[12] in **4** is completed by two PNP ligands in κ^3 -(P,N,P') and κ^2 -(P,N) coordination modes.^[13] This is the first example of such a coordination environment for the bis(PNP) framework and illustrates the flexibility of this ligand set to accommodate various electronic and steric environments which are needed to enable new reactivity patterns for uranium.

Indeed, different chemistry is observed in the reaction of $2/KC_8$ and $Ph_2C=N_2$, which gives the bis(imido) uranium(VI) complex 5 in 94% yield of isolated product; two equivalents of the oxidant are needed for the completion of the reaction [Eq. (3)]. The molecular structure of 5 features two imido



ligands obtained by the formal two electron reduction of each diphenyldiazomethane (Figure 1). As noted for **4**, this reduction results in a significant lengthening of the N–N bonds and a shortening of the C=N bonds of the diazoalkane. The U=N double bonds are characterized by short U–N bond distances (U(1)-N(1)=1.999(4), U(1)-N(3)=2.018(4) Å), which are in agreement with those found in the related $[(C_5Me_5)_2U(=N-1)]$

 $N=CPh_2$)(=N-2,4,6-*t*Bu₃-C₆H₂)]^[11] and other [(C₅Me₅)₂U^{VI}] bis(imido) complexes (average U=N = 1.98 Å).^[14]

The mechanisms of these two transformations were probed to determine the origin of the difference in reactivity between the [(PNP)₂U(I)] (1) and [(C₅Me₅)₂U(I)(thf)] (2) systems. Compound 2 is known to be a two-electron reductant and the active species in the reductive cleavage of azobenzene (to give [(C₅Me₅)₂U(=NPh)₂]) and the reductive coupling of diphenylacetylene (to give [(C₅Me₅)₂U{ κ^2 -(*C*,*C*')-CPh=CPh-CPh=CPh].^[6] In the absence of KC₈ or Na/Hg amalgam, complex 2 reacts with one equivalent of Ph₂C=N₂ to produce 0.5 equivalents of 5 and 0.5 equivalents of [(C₅Me₅)₂U(I)₂] (6) [Eq. (4)].

$$[(C_5Me_5)_2U(I)(thf)] + Ph_2C=N_2 \xrightarrow{\text{toluene}} 0.5 \ \mathbf{5} + 0.5 [(C_5Me_5)_2U(I)]_2 \ \mathbf{(4)}$$
2 6

Similarly, in the absence of KC₈, addition of Ph₂C=N₂ to one equivalent of **1** yielded a 50:50 mixture of $4/(\text{PNP})_2\text{U}(\text{I})_2$ (7) to leave 0.5 equivalents of Ph₂C=N₂ unreacted [Eq. (5)].^[15]

$$[(PNP)_2U(I)] + Ph_2C=N_2 \xrightarrow{\text{toluene}} 0.5 \ 4 + 0.5 \ [(PNP)_2U(I)]_2 \quad (5)$$
1
7

The combination of these observations suggests that the active species are the uranium(III) complexes **1** and **2**, which can accomplish the two-electron reduction of the substrate. As such, the role of the exogenous reductant (KC₈) is merely to regenerate the active uranium(III) species by reducing **6** to **2** and **7** to **1**. The difference in the observed reactivity is likely to arise from the different redox behavior of the uranium(IV) complexes obtained by reaction with the diphenyldiazomethane oxidant (that is, $[(C_5Me_5)_2U=N-N=CPh_2]$ versus (PNP)₂U[η^2 -(*N*,*N'*)=N-N=CPh₂] (**4**)).

To determine whether the reduction chemistry with **1** was limited to the formation of uranium(IV) complexes, its reaction with stronger oxidants was explored. A dramatic distinction between PNP and C_5Me_5 as supporting ligands is seen in the reactivity of **1** and **2** with pyridine-*N*-oxide. Addition of one equivalent of pyridine-*N*-oxide to a solution of **1** in toluene led to the complete consumption of pyridine-*N*-oxide and formation of pyridine, 0.5 equivalents of **7**, and 0.5 equivalents of the new uranium(VI) complex **8**, which showed that two equivalents of the oxidant had reacted. In fact, reaction of **1**/KC₈ with two equivalents of pyridine-*N*oxide smoothly produced complex **8** as the only uranium complex, which was isolated in 85% yield [Eq. (6)]. This



Angew. Chem. Int. Ed. 2009, 48, 3681-3684

transformation decisively illustrates the ability of **1** to act as a four-electron reductant and to support uranium(VI).

Single-crystal X-ray diffraction confirmed that **8** consists of a uranyl moiety supported by two PNP ligands in κ^3 -(*P*,*N*,*P'*) and κ^2 -(*P*,*N*) coordination modes (Figure 2), which



Figure 2. Molecular structure of complex 8 with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms and methyl groups are omitted for clarity. Selected bond distances [Å] and angles [°]: U(1)-P(1) 3.066(3), U(1)-P(3) 3.017(3), U(1)-P(4) 2.984(3), U(1)-O(1) 1.791(6), U(1)-O(2) 1.808(6), U(1)-N(1) 2.405(7), U(1)-N(2) 2.402(8); O(1)-U(1)-O(2) 177.0(3).

makes it the first uranyl phosphine complex. The U-P bond lengths in 8 (U(1)-P(1) = 3.066(3), U(1)-P(3) = 3.017(3),U(1)-P(4) = 2.984(3) Å) compare well with those reported $[U(I)_2 (= NtBu)_2 (thf) (PMe_3)_2]$ for (U-P=3.075(3),3.042(2) Å).^[16] The uranium-oxo bond lengths are short, with U(1)–O(1) = 1.791(6) Å and U(1)–O(2) = 1.808(6) Å, which is typical for uranyl complexes.^[17] It is noteworthy that the formation of 8 represents only the second rational synthesis of a uranyl fragment from a low-valent uranium precursor; the other reported example relies on the oxidation $[U(I)_3(thf)_3]$ using pyridine-N-oxide to of form $[UO_2(I)_2(py)_3]$.^[18]

Finally, for purposes of comparison, the same reaction using $2/KC_8$ instead of **1** was found to produce the dimer $(C_5Me_5)_2$ as the only C_5Me_5 -containing compound [Eq. (7)].



This finding implies the generation of an unstable hexavalent $(C_5Me_5)_2U(=O)_2$ complex that is reduced by the $C_5Me_5^-$ ligand to produce $(C_5Me_5)_2$ and uranium oxides.^[2a,8] In contrast, the stability of **8** reinforces the hypothesis that the PNP ligand, as a better donor and a more flexible ligand than C_5Me_5 , can support structures that are simply not accessible with the bis (C_5Me_5) ligand framework.

In conclusion, the work presented here demonstrates that the PNP ligand is capable of supporting not only low-valent uranium but also high-valent species and represents an exciting alternative for promoting reaction chemistry and structural motifs at uranium that are simply not available for the C_5Me_5 ligand set. As evidenced by the formation of the uranyl complex **8**, the PNP ligand is able to support U^{VI} and efforts are now directed towards exploiting systems such as 4 as entries to actinide metallanitrene and nitride chemistry.^[19]

Received: December 15, 2008 Published online: February 16, 2009

Keywords: actinides · hydrazonido compounds · metallocenes · N,P ligands · uranium

- a) T. J. Marks, A. Streitwieser in *The Chemistry of the Actinide Elements, Vol. 2* (Eds.: J. J. Katz, G. T. Seaborg, L. R. Morss), Chapman and Hall, New York, **1986**, pp. 1547–1587; b) C. J. Burns, M. S. Eisen in *The Chemistry of the Actinide and Transactinide Elements, Vol. 5* (Eds.: L. R. Morss, N. M. Edelstein, J. Fuger), Springer, Dordrecht, **2006**, pp. 2799–2910.
- [2] For key references on the decomposition of low-valent uranium-bis(C₅Me₅) complexes in oxidation reactions, see: a) P. B. Duval, C. J. Burns, D. L. Clark, D. E. Morris, B. L. Scott, J. D. Thompson, E. L. Werkema, L. Jia, R. A. Andersen, *Angew. Chem.* 2001, *113*, 3461–3465; *Angew. Chem. Int. Ed.* 2001, *40*, 3357–3361; b) J. Maynadie, J.-C. Berthet, P. Thuery, M. Ephritikhine, *Chem. Commun.* 2007, 486–488.
- [3] a) O. V. Ozerov in *The Chemistry of Pincer Compounds* (Eds.: D. Morales-Morales, C. Jensen), Elsevier Science, Amsterdam, 2007, p. 287; b) J. D. Masuda, K. C. Jantunen, O. V. Ozerov, K. J. T. Noonan, D. P. Gates, B. L. Scott, J. L. Kiplinger, *J. Am. Chem. Soc.* 2008, *130*, 2408–2409; c) J. Scott, F. Basuli, A. R. Fout, J. C. Huffman, D. J. Mindiola, *Angew. Chem.* 2008, *120*, 8630–8633; *Angew. Chem. Int. Ed.* 2008, *47*, 8502–8505.
- [4] Actinide-bis(C₅Me₅) complexes adopt a bent metallocene structural motif, with the exception of a few recent examples of uranium linear metallocene complexes, see: a) A. Maynadié, J. C. Berthet, P. Thuery, M. Ephritikhine, J. Am. Chem. Soc. 2006, 128, 1082–1083; b) J. Maynadié, N. Barros, J.-C. Berthet, P. Thuery, L. Maron, M. Ephritikhine, Angew. Chem. 2007, 119, 2056–2058; Angew. Chem. Int. Ed. 2007, 46, 2010–2012.
- [5] T. Cantat, B. L. Scott, O. V. Ozerov, D. E. Morris, J. L. Kiplinger, *Inorg. Chem.* 2009, 48, 2114–2127.
- [6] a) B. P. Warner, B. L. Scott, C. J. Burns, Angew. Chem. 1998, 110, 1005–1007; Angew. Chem. Int. Ed. 1998, 37, 959–960; b) J. M. Manriquez, P. J. Fagan, T. J. Marks, S. H. Vollmer, C. S. Day, V. W. Day, J. Am. Chem. Soc. 1979, 101, 5075–5078; c) P. J. Fagan, J. M. Manriquez, T. J. Marks, C. S. Day, S. H. Vollmer, V. W. Day, Organometallics 1982, 1, 170–180.
- [7] Hydrazonido [η²-(*N*,*N*')-N-N=CR₂]²⁻ complexes are only known for the transition metals, in these complexes the ligand is always bridging. For representative examples, see: a) L. K. Bell, W. A. Herrmann, G. W. Kriechbaum, H. Pfisterer, M. L. Ziegler, *J. Organomet. Chem.* 1982, 240, 381–393; b) S. Gambarotta, C. Floriani, A. Chiesivilla, C. Guastini, *J. Am. Chem. Soc.* 1983, 105, 7295–7301; c) D. Nucciarone, N. J. Taylor, A. J. Carty, *Organometallics* 1986, 5, 2565–2567; d) W. A. Herrmann, B. Menjon, E. Herdtweck, *Organometallics* 1991, 10, 2134–2141; e) V. Tabernero, T. Cuenca, E. Herdtweck, *J. Organomet. Chem.* 2002, 663, 173–182; f) R. J. Wright, M. Brynda, J. C. Fettinger, A. R. Betzer, P. P. Power, *J. Am. Chem. Soc.* 2006, 128, 12498–12509.
- [8] a) D. S. J. Arney, C. J. Burns, J. Am. Chem. Soc. 1995, 117, 9448–9460; b) C. R. Graves, P. Yang, S. A. Kozimor, A. E. Vaughn, D. L. Clark, S. D. Conradson, E. J. Schelter, B. L. Scott, J. D. Thompson, P. J. Hay, D. E. Morris, J. L. Kiplinger, J. Am. Chem. Soc. 2008, 130, 5272–5285.

Communications

- [9] S. Patai, *The Chemistry of Diazonium and Diazo Groups, Parts 1 and 2*, Wiley, New York, **1978**.
- [10] O. P. Lam, P. L. Feng, F. W. Heinemann, J. M. O'Connor, K. Meyer, J. Am. Chem. Soc. 2008, 130, 2806–2816.
- [11] J. L. Kiplinger, D. E. Morris, B. L. Scott, C. J. Burns, Chem. Commun. 2002, 30-31.
- [12] The solution magnetic moment of **4** was determined in C_6D_6 (2.99 μ_B) by using Evans' method and confirmed the U^{IV} oxidation state of the metal center. M. L. Naklicki, C. A. White, L. L. Plante, C. E. B. Evans, R. J. Crutchley, *Inorg. Chem.* **1998**, *37*, 1880–1885.
- [13] Retention of the κ^3 -(*P*,*N*,*P'*) and κ^2 -(*P*,*N*) coordination modes for the two PNP ligands in **4** in solution was demonstrated by using ¹H and ³¹P NMR spectroscopy.
- [14] A Cambridge Structural Database search identified four bis-(C₅Me₅)-uranium(VI) imido structures with an average U=N bond length of 1.98 Å (range 0.09 Å). For specific references, see: a) [(C₅Me₅)₂U(=NPh)₂], U-N = 1.952(7) Å: D. S. J. Arney, C. J. Burns, D. C. Smith, J. Am. Chem. Soc. **1992**, 114, 10068-

10069; b) $[(C_5Me_5)_2U(=NAd)_2]$ (Ad = 1-adamantyl), U-N = 1.94(2), 1.96(2) Å: reference [6a]; c) $[(C_5Me_5)_2U(=O)(=N-2,6-iPr_2C_6H_3)]$, U-N = 1.988(4) Å: D. S. J. Arney, C. J. Burns, J. Am. Chem. Soc. **1993**, 115, 9840–9841; d) $[(C_5Me_5)_2U(=N-N=CPh_2)(=N-2,4,6-tBu_3-C_6H_2)]$, U-N = 2.031(6), 1.987(5) Å: reference [11].

- [15] Complex 7 was independently synthesized (isolated in 100% yield) by oxidation of 1 with iodine. See the Supporting Information for further details.
- [16] T. W. Hayton, J. M. Boncella, B. L. Scott, E. R. Batista, P. J. Hay, J. Am. Chem. Soc. 2006, 128, 10549–10559.
- [17] J. J. Katz, L. R. Morss, G. T. Seaborg, Summary and Comparative Aspects of the Actinide Elements, Chapman & Hall, London, 1986.
- [18] L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2006, 128, 7152–7153.
- [19] D. J. Mindiola, Angew. Chem. 2008, 120, 1580-1583; Angew. Chem. Int. Ed. 2008, 47, 1557-1559.