Preparation of Actinide Phosphinidene Complexes: Steric Control of Reactivity

David S. J. Arney, R. Chris Schnabel, Brian C. Scott, and Carol J. Burns*

Chemical Science and Technology Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Received January 23, 1996

It has long been recognized that chemical reactivity of d-transition metal complexes containing terminal imido, oxo, and alkylidene ligands (as well as their heavier homologues) is governed to a large extent by the degree of metal−ligand multiple bonding.[1] Recent studies of early transition metal imido complexes[2] demonstrate that these ligands can act as nucleophiles in synthetic transformations, probably as a result of a reduced degree of metal−ligand multiple bonding.[1a,3] We have been investigating the preparation and reactivity of tetravalent actinide complexes containing imido ligands,[4] in the hopes of gaining an understanding of the role metal 6d- and 5f-orbitals play in metal−ligand multiple bonding. We have found in some cases that these species are less reactive than expected based on their similarity to Group 4 d-transition metal analogs, suggesting that the actinide centers can play a significant role in stabilizing nitrogen 2p-lone pair electron density.

We have recently undertaken the investigation of phosphinidene analogs of these complexes, both in order to expand our understanding of the role of the actinide-based orbitals in metal−ligand multiple bonding and in the hopes of enhancing the reactivity of the multiply-bonded functional group. In general, phosphinidene complexes are expected to have weaker metal−ligand $d\pi-p\pi$ bonding than imido complexes. The extent of metal−phosphorus multiple bonding is governed by competition between the phosphinidene fragment and the ancillary ligands for interaction with metal orbitals of π-symmetry.[5] While there are still relatively few transition metal phosphinidene complexes available for examination,[6] this feature of the electronic structure appears to be manifested in some cases in “bent” phosphinidene ligands and enhanced reactivity. Clearly it is of interest to examine actinide analogs, in order to determine if the 6d- and 5f-orbitals are at all effective in stabilizing electron density at the phosphorus through π-type interactions.

We report herein that synthetic routes previously employed in the production of uranium organoimido complexes of the actinides have now been extended to the preparation of phosphinidene analogs. No terminal phosphinidene complex of an actinide has previously been isolated. The large ionic radii exhibited by the actinide ions make it difficult to introduce sufficient steric stabilization of a terminal “PR” ligand. Indeed, the only previously reported example of an actinide phosphinidene complex is $[(\eta^5\text{-}C_5Me_5)_2U(OMe)]_2(\mu\text{-}PH)$,[7] in which the phosphinidene ligand is capable of bridging even the relatively sterically hindered “$(\eta^5\text{-}C_5Me_5)_2U$” moieties.

Elimination reactions are most often employed in the production of terminal phosphinidene complexes of the d-transition metals.[6] In general, the terminal disposition of the phosphinidene ligand is stabilized by substantial phosphorus-to-metal π-donation; in some instances, the steric bulk of the ancillary ligands undoubtedly serves to inhibit oligomerization.

Utilizing a combination of bulky substituents on the phosphinidene and stabilization by an additional coordinated Lewis base, a terminal phosphinidene complex of uranium may be successfully isolated. Reaction of $KPH\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2$ with $(\eta^5\text{-}C_5Me_5)_2UMeCl$ at room temperature in toluene in the presence of trimethylphosphine oxide yields the complex $(\eta^5\text{-}C_5Me_5)_2U({=}P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)(O{=}PMe_3)$ as black crystals in 62% yield (eq 1).[8] In the absence of added base, intractable product mixtures result, possibly due to reduction of the metal center or reaction of the phosphinidene ligand formed with solvent or ancillary ligand.[9] This reactivity stands in contrast to the stability of the uranium(IV) organoimido analogs, which are similarly produced by intramolecular elimination reactions.[4] The arylimido complexes may be isolated as base-free monomers; they do not exhibit the reactivity evident in zirconium organoimido chemistry.[2]

$$(\eta^5\text{-}C_5Me_5)_2UMeCl + KPH\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2 \xrightarrow[\text{12 h, RT}]{OPMe_3} \underset{(\mathbf{1})}{(\eta^5\text{-}C_5Me_5)_2U(P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)(OPMe_3)} \quad (1)$$

The phosphine oxide adduct has been structurally characterized (Figure 1). The coordination geometry about the uranium atom is essentially tetrahedral, with a O−U−P angle of 95.1(2)°. The uranium−oxygen (phosphine oxide) distance is 2.370(5) Å, and the U−O−P(1) angle is 157.5(4)°; the bending of this angle from linear is unusual among phosphine oxide adducts of U(IV).[10] The most interesting feature of the complex is the

---

[1] (a) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988. (c) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

[2] (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (b) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (c) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708. (d) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753. (e) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705. (f) Cundari, T. R. *Organometallics* **1993**, *12*, 4971. (g) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179. (h) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2669.

[3] (a) Morrison, D. L.; Wigley, D. E. *Inorg. Chem.* **1995**, *34*, 2610. (b) Morrison, D. L.; Wigley, D. E. *J. Chem. Soc., Chem. Commun.* **1995**, 79. (c) Huber, S. R.; Baldwin, T. C.; Wigley, D. E. *Organometallics* **1993**, *12*, 91.

[4] (a) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448. (b) Arney, D. S. J.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 10068.

[5] For discussions of bonding in phosphinidene complexes, see: (a) Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. (b) Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81.

[6] (a) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282. (b) Bohra, P.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *Polyhedron* **1989**, *8*, 1884. (c) Cowley, A. H.; Pellerin, B.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 6734. (d) Hou, Z.; Stephan. D. W. *J. Am. Chem. Soc.* **1992**, *114*, 10088. (e) Hou, Z.; Breen, D. W.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158. (f) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 756. (g) Bonanno, J. B.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1994**, *116*, 11159.

[7] Duttera, M. R.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2907.

[8] $(\eta^5\text{-}C_5Me_5)_2U(P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)(OPMe_3)$ (**1**): ^1H NMR (250 MHz, C_6D_6) ∂ 6.47(s, arene H’s, 2H), 1.31 (s, C_5Me_5, 30 H), −1.90, −6.31 (s, *t*-Bu (*ortho*), 18 H), −12.07 (bs, *t*-Bu (*para*), 9H), −23.31 (d, $OPMe_3$, J_{PH} = 13 Hz); ^{31}P NMR (300 MHz, C_6D_6) ∂ 71.06 (bs, $P(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$), −59.84 (m, $OPMe_3$); IR (KBr pellet, cm^{-1}) 2966, 2905, 2867, 2369, 2341, 1586, 1363, 1411, 1128, 946, 857. Anal. Calcd for $C_{41}H_{68}P_2OU$: C, 56.15; H, 7.82. Found: C, 55.50; H, 7.92.

[9] Precedent exists in the literature for both reduction of uranium(IV) by phosphide ligands and intramolecular C−H activation by reactive metal phosphinidene complexes: (a) Blake, P. C.; Hey, E.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Organomet. Chem.* **1988**, *353*, 307. (b) Champion, D. H.; Cowley, A. H. Polyhedron **1985**, *4*, 1791. (c) Arif, A. M.; Cowley, A. H.; Nunn, C. M.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1987**, 994. See also ref 11d.

[10] (a) Bombieri, G.; Forsellini, E.; Day, J. P.; Azeez, W. I. *J. Chem. Soc., Dalton Trans.* **1978**, 677. (b) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1986**, *25*, 1761. (c) Bombieri, G.; Brown, D.; Mealli, C. *J. Chem. Soc., Dalton Trans.* **1976**, 2025. (d) Alcock, N. W.; Roberts, M. M.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1982**, 25. (e) Cotton, A.; Marler, D. O.; Schwotzer, W. *Acta Crystallogr.* **1984**, *C40*, 1186.

S0002-7863(96)00221-1 CCC: $12.00

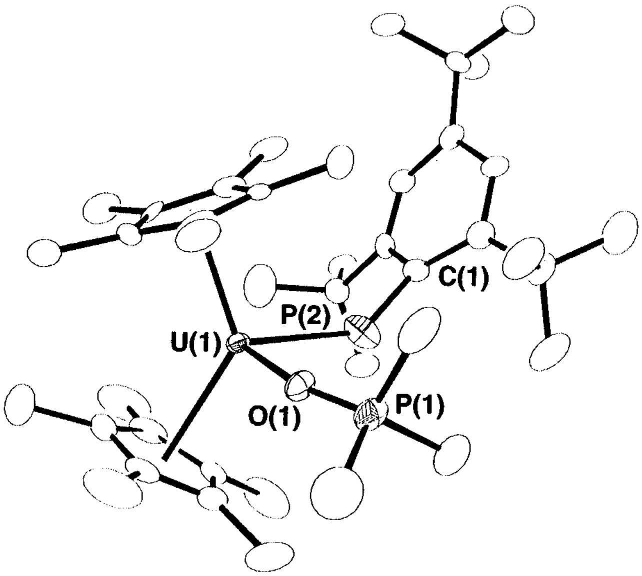

Figure 1. ORTEP drawing of $(\eta^5\text{-}C_5Me_5)_2U(P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)(OPMe_3)$ (**1**), with atoms shown as 50% probability ellipsoids. Selected distances (Å) and angles (deg) for **2**: U(1)−P(2) = 2.562(3), U(1)−O(1) = 2.370(5), U(1)−P(2)−C(1) = 143.7(3), O−U(1)−P(2) = 95.1(2), U(1)−O(1)−P(1) = 157.5(4), Cp(centroid)−U(1)−Cp(centroid) = 131.4.

phosphinidene ligand. The U−P distance is 2.562(3) Å, and the angle about the phosphorus atom is 143.7(3)°. This bond distance is significantly shorter than those found in the bridging phosphinidene complex $[(\eta^5\text{-}C_5Me_5)_2U(OMe)]_2(\mu\text{-}PH)$ (U−P = 2.743(1) Å)[7] or in tetravalent actinide phosphide complexes (e.g. U−P = 2.789(4) Å in $(\eta^5\text{-}C_5Me_5)_2UCl[P(SiMe_3)_2]$).[11] The nonlinear angle about the phosphorus is not unprecedented; angles about terminal phosphinidene ligand in d-transition metal chemistry range from 110.2(4)° to near linear.[6] It has been speculated that the bent angles in these complexes are a compromise between the linear geometries preferred to maximize phosphorus−metal π-overlap and the bent geometries inherently preferred by heavier main group elements.[5b,6g] It has been suggested that in some instances this bending mode is rather “soft”, i.e. little energy is required to bend the ligand.[12] This leaves open the possibility that intermolecular packing forces may play a role in determining the geometry of the complex.

The apparent instability of the base-free phosphinidene complex certainly implies a reactive functional group. The question remains whether this reactivity is a consequence of a decreased metal−ligand bond order, a more sterically accessible multiply-bound functional group (longer U−P bond), or a combination of both of these influences. In an attempt to further reduce the steric constraints of the metal center, the elimination chemistry has been extended to the known chelating metallocene system $[(R_4C_5)_2(\mu\text{-}SiMe_2)]UX_2$ (R = Me, H).[13]

Rather than producing an even more reactive phosphinidene species, use of chelating ligand set resulted in the isolation from toluene of a base free complex of the formula “$[(\eta^5\text{-}R_4C_5)_2(\mu\text{-}SiMe_2)]U(P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)$” (eq 2).[14] Solution molecular

$$[(\eta^5\text{-Cp})_2(\mu\text{-SiMe}_2)]\text{UMe}_2 + \text{H}_2\text{P-2,4,6-}t\text{-Bu}_3\text{C}_6\text{H}_2 \xrightarrow{\text{6 d, 45 °C}}$$

$$0.5\{[(\eta^5\text{-Cp})_2(\mu\text{-SiMe}_2)]\text{U}(\mu\text{-P-2,4,6-}t\text{-Bu}_3\text{C}_6\text{H}_2)\}_2$$

$$(\mathbf{2a}, 52\%; \mathbf{2b}, 73\%)$$

$$(\mathbf{a}\text{: } (\eta^5\text{-Cp})_2 = (\eta^5\text{-Me}_4\text{C}_5)_2; \mathbf{b}\text{: } (\eta^5\text{-Cp})_2 = (\eta^5\text{-Me}_4\text{C}_5)(\eta^5\text{-H}_4\text{C}_5) \qquad (2)$$

weight determinations[15] suggest that the unusual stability of the molecule may be attributed to stabilization of the phosphinidene group in the bridging position of a dimeric complex. Any inherent energy difference between a complex containing two U−P “bridge” bonds and a U═P moiety may be overcome; the dimer may be readily disrupted by the addition of an equivalent of phosphine oxide as a Lewis base, yielding a product that may be formulated on the basis of NMR spectroscopy as the analog of compound **1**.[16]

In summary, the first terminal phosphinidene complex of an f-element has been isolated. The structural features of the complex suggest a model of bonding which is similar to that proposed for some transition metal phosphinidine complexes, in which (while a metal−ligand multiple is clearly evident) a bent phosphinidene results when both ligand π-electron pairs are not strongly stabilized by interaction with metal-based orbitals.[6g] Evidence suggests that the base-free phosphinidene complexes are more reactive than their previously characterized imido analogs. Phosphinidene functional groups may be stabilized against further reaction, however, either by imposition of additional ligands at the metal center or by relaxation of the steric constraints introduced by the ancillary ligands so that dimerization is feasible.

Acknowledgment. We acknowledge the Division of Chemical Sciences, Office of Energy Research, U.S. Department of Energy, and the LANL Laboratory Directed Research and Development Program for support. We wish to thank Dr. John Watkin and Dr. Steven Grumbine for the loan of experimental equipment. We also thank Prof. Thomas Cundari for helpful discussions.

Supporting Information Available: Tables of final atomic coordinates and isotropic displacement information, including hydrogen atom locations, anisotropic displacement parameters, complete bond lengths, and bond angles, for compound **1**; complete atomic numbering scheme and unit cell diagram (showing disordered molecule of solvation) for **1** (13 pages). Ordering information is given on any current masthead page.

JA960221Y

---

(11) (a) Ritchey, J. M.; Zozulin, A. J.; Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 501. (b) Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Salazar, K. V.; Paine, R. T.; Moody, D. C. *Organometallics* **1986**, *5*, 90. (c) Paolucci, G.; Rossetto, G.; Zanella, P.; Fischer, R. D. *J. Organomet. Chem.* **1985**, *284*, 213. (d) Hall, S. W.; Huffman, J. C.; Miller, M. M.; Avens, L. R.; Burns, C. J.; Arney, D. S. J.; England, A. F.; Sattelberger, A. P. *Organometallics* **1993**, *12*, 752.

(12) T. R. Cundari, personal communication.

(13) (a) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828. (b) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558. (c) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, J.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (d) Schnabel, R. C.; Burns, C. J.; Scott, B. C. Manuscript in preparation.

(14) $\{[(\eta^5\text{-}Me_4C_5)_2(\mu\text{-}SiMe_2)]U(\mu\text{-}P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2$ (**2a**): ^1H NMR (300 MHz, C_6D_6) ∂ 13.48 (s, arene H’s, 2H), 2.54 (s, *t*-Bu (*ortho*), 18H), 1.22 (s, *t*-Bu(*para*), 9H), −24.44 (s, C_5Me_4, 24H), −43.62 (s, Me_2Si, 6H); ^{31}P NMR (300 MHz, C_6D_6) ∂ −79.20; $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6) ∂ −79.20 (bs, $P(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$); IR (KBr pellet, cm^{-1}) 2960, 2904, 2865, 2341, 1594, 1450, 1244, 852, 805, 744, 732. Anal. Calcd for $C_{38}H_{59}SiPU$: C, 56.14; H, 7.32. Found: C, 55.89; H, 7.28. $\{[(\eta^5\text{-}Me_4C_5)(\eta^5\text{-}H_4C_5)(\mu\text{-}SiMe_2)]U(\mu\text{-}P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2$ (**2b**): ^1H NMR (300 MHz, C_6D_6) ∂ 19.70 (s, C_5H_4, 2H), 14.33, 10.90 (s, Me_2Si, 6H), 9.16 (s, C_5Me_4, 6H), 5.85 (s, *t*-Bu (*ortho*), 18H), −2.74 (s, C_5H_4, 2H), −20.06 (s, C_5Me_4, 6H), −22.99 (s, *t*-Bu (*para*), 9H); $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6) ∂ −72.22 bs, $P(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$); IR (KBr pellet, cm^{-1}) 2961, 2904, 2865, 2229, 1595, 1454, 1361, 1248, 830, 807, 786. Anal. Calcd for $C_{34}H_{51}SiPU$: C, 53.96; H, 6.79. Found: C, 54.16; H, 6.73.

(15) The molecular weight of **2b** was determined using a Signer-type isopiestic molecular weight apparatus (*The Manipulation of Air-Sensitive Compounds, 2nd ed.*; Shriver, D. F.; Drezdzon, M. A., Eds.; Wiley Interscience: New York, 1986). Weight determined: 1570 amu (expected molecular weight for dimer = 1513.75 amu).

(16) Reaction of **2a** with $OPMe_3$. An NMR tube was charged with 22 mg of **2a** and 1.1 equiv of $OPMe_3$, and the mixture was dissolved in 0.5 mL of C_6D_6. After 2 h, resonances assignable to $[(\eta^5\text{-}Me_4C_5)_2(\mu\text{-}SiMe_2)]U(\mu\text{-}P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)(OPMe_3)$ replaced the resonances assignable to **2a**. ^1H NMR (300 MHz, C_6D_6): ∂ 20.71 (s, arene H’s, 2H), 10.02 (s, Me_2Si, 6H), 9.79 (s, C_5Me_4, 6H), 2.01 (s, *t*-Bu (ortho), 18H), 1.60 (s, *t*-Bu (para), 9H), 1.32 (s, C_5Me_4, 6H), −6.94 (s, C_5Me_4, 6H), −22.53 (s, $OPMe_3$, 9H), −47.88 (s, C_5Me_4, 6H). $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6): ∂ 60.38 (bs, $P\text{-}2,4,6,\text{-}t\text{-}Bu_3C_6H_2$), −3.84 (m, $OPMe_3$).