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Crystal Structures of $(MeC_5H_4)_4U_2(\mu\text{-}NR)_2$. Unsymmetrical Bridging, R = Ph, and Symmetrical Bridging, R = $SiMe_3$, Organoimide Ligands in Organoactinide Compounds

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Abstract: The tetravalent uranium complexes with bridging organoimide ligands, $(MeC_5H_4)_4U_2(\mu\text{-}NR)_2$, have been prepared by the valence conproportionation reaction of $(MeC_5H_4)_3U{\cdot}thf$ and $(MeC_5H_4)_3UNR$. X-ray crystallographic study of R = Ph and $SiMe_3$ shows that the NPh group asymmetrically bridges the two uranium fragments, whereas the $NSiMe_3$ group symmetrically bridges the two uranium fragments. Crystals of $(MeC_5H_4)_4U_2(NPh)_2$ are monoclinic, $P2_1/n$, with $a = 14.738$ (3) Å, $b = 9.933$ (2) Å, $c = 10.612$ (2) Å, $\beta = 102.11$ (2)° at 23 °C. For $Z = 2$ (dimers) the calculated density is 2.13 g/cm^3. The structure was refined by full-matrix least-squares to a conventional R factor of 0.029 [1600 data, $F^2 > 2\sigma(F^2)$]. Crystals of $(MeC_5H_4)_4U_2(NSiMe_3)_2$ also are monoclinic, $P2_1/n$, with $a = 15.761$ (6) Å, $b = 9.389$ (4) Å, $c = 11.052$ (4) Å, $\beta = 101.36$ (3)° at 23 °C. For $Z = 2$ (dimers) the calculated density is 2.00 g/cm^3. The structure was refined by full-matrix least-squares to a conventional R factor of 0.023 [2544 data, $F^2 > 2\sigma(F^2)$]. Both complexes are dimers in which the two $(MeC_5H_4)_2U$ fragments are bridged by the organoimide group so that an inversion center is located in the center of the U_2N_2 ring. The bridging U-N distances are 2.156 (8) and 2.315 (8) Å in the NPh complex and 2.217 (4) and 2.230 (4) Å in the $NSiMe_3$ complex.

The trivalent uranium metallocenes, $(RC_5H_4)_3U$, have been found to be versatile one- and two-electron-transfer reagents toward a variety of organic molecules.[1] These reactions are of general interest since they yield new and unusual molecular structures and reaction types in organo-f-element chemistry. In the course of our synthetic studies we discovered that $(RC_5H_4)_3U$ reacts with dioxygen to give the unusual valence disproportionation product $(RC_5H_4)_4U$ in ca. 15% yield. This reaction involves, in a phenomenological though not in a mechanistic sense, oxidation of uranium by one unit and scavenging a cyclopentadienide ligand from some source.[1c] The reaction reflects the thermodynamic stability of U(IV) and the small kinetic barriers to ligand exchange in these paramagnetic 5f-metal centers. Since U(IV) is thermodynamically stable with respect to U(III) or U(V) in aqueous solution,[2] it was of interest to examine the reaction of a U(III)

$$\mathrm{U(III)} \xrightarrow{+0.63\ \mathrm{V}} \mathrm{U(IV)} \xleftarrow{+0.58\ \mathrm{V}} \mathrm{U(V)}$$

and a U(V) metallocene to see if they would undergo irreversible electron and ligand exchange to give U(IV) metallocenes. Extrapolation of aqueous solution redox potentials to metallocenes in hydrocarbon solution is only a guide to the important thermodynamic result that U(IV) is stable relative to U(III) and U(V). Uranium(IV) metallocenes are thermodynamically stable relative to their U(III) analogues since the reduction potential of $(Me_5C_5)_2UCl_2$ in MeCN and $(MeC_5H_4)_3UCl$ in thf is -1.30 and -1.52 V relative to SCE, respectively, though no information is available on pentavalent uranium metallocenes.[3] In this paper we describe the reaction of $(MeC_5H_4)_3UNR$ with $(MeC_5H_4)_3U$(thf) to give $(MeC_5H_4)_4U_2(NR)_2$, i.e., $\mathrm{U(V)} + \mathrm{U(III)} \rightarrow 2\mathrm{U(IV)}$.

Synthetic Studies. Stirring an equimolar mixture of $(MeC_5H_4)_3UNPh$[1a] and $(MeC_5H_4)_3U$(thf) in tetrahydrofuran for 24 h gives two uranium(IV) containing products as judged by ^1H NMR spectroscopy. The two red products could be separated by fractional crystallization from diethyl ether since one of the compounds is very soluble in that solvent and the other compound crystallized on cooling a concentrated solution to -20 °C. The red crystals, mp 167-170 °C, from diethyl ether have the molecular formula $(MeC_5H_4)_4U_2(NPh)_2$. The ^1H and ^{13}C NMR spectrum (see Experimental Section for details) shows that the MeC_5H_4 rings are equivalent at all temperatures, and the narrow line widths, ca. 1-2 Hz at half-height, are consistent with tetravalent uranium.[1b] The precise molecular structure is shown in Figure 1.

The other product in the reaction, the compound that is very soluble in diethyl ether and which may be crystallized from hexane, mp 120-122 °C, is the phenylamide, $Cp_3UN(H)(Ph)$. This formulation is consistent with the elemental analysis and the mass spectrum which shows the highest mass peak at 567 and the ^1H NMR spectrum which is given in the Experimental Section as well as independent synthesis. The phenylamide is also isolated in the reaction of $(MeC_5H_4)_3U$(thf) with phenylazide. The origin of this substance is under investigation.[4]

Reaction of the trimethylsilylimido compound, $(MeC_5H_4)_3UNSiMe_3$,[1a] and $(MeC_5H_4)_3U$(thf) also undergo the valence disproportionation and ligand redistribution reaction in tetrahydrofuran. Again two U(IV) products are formed, but in this case they cannot be separated by fractional crystallization though the red polyfacial crystals and red plates could be separated manually. The elemental analysis and mass spectrum ($M^+ = 554$) suggest that the polyfacial crystals are $(MeC_5H_4)_4U$.[5] The red plates which show an M^+ in the mass spectrum at 983 are consistent with the composition $(MeC_5H_4)_4U_2(NSiMe_3)_2$. The precise structure of the latter compound was determined by X-ray crystallography and an ORTEP diagram is shown in Figure 3. The rather complex nature of the reactions described above precludes any meaningful discussion of reaction pathway. Studies directed toward synthesis of larger quantities of these new materials in pure form is in progress so that the reaction chemistry and physical properties of these bimetallic complexes can be explored.[4]

Structural Studies. The positional parameters for $(MeC_5H_4)_4U_2(\mu\text{-}NPh)_2$ and $(MeC_5H_4)_4U_2(\mu\text{-}SiMe_3)_2$ are in

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(1) (a) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514-516. (b) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1986**, *25*, 1756-1760, 1761-1765. (c) Brennan, J. G.; Andersen, R. A.; Zalkin, A., to be submitted for publication.

(2) Johnson, D. A. *Some Thermodynamic Aspects of Inorganic Chemistry*, 2nd ed.; Cambridge University Press: Cambridge, England, 1982; p 169.

(3) (a) Finke, R. G.; Gaughan, G.; Voegeli, R. *J. Organomet. Chem.* **1982**, *229*, 179-184. (b) Gaughan, G. Ph.D. Thesis, University of Oregon, 1973.

(4) Rosen, R. K., work in progress.

(5) (a) Fischer, E. O.; Hristidu, Y. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962**, *17B*, 275. (b) Bursten, B. E.; Casarin, M.; DiBella, S.; Fang, A.; Fragala, I. L. *Inorg. Chem.* **1985**, *24*, 2169-2173.

0002-7863/88/1510-4554$01.50/0

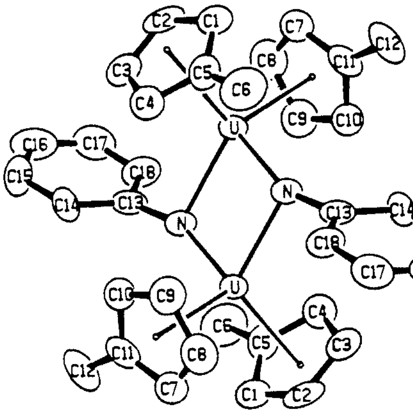

Figure 1. ORTEP drawing of $(\mathrm{MeC_5H_4})_4\mathrm{U_2}(\mathrm{NPh})_2$; thermal ellipsoids at 50% probability level.

Table I. Positional Parameters with Estimated Standard Deviations for $(\mathrm{MeC_5H_4})_4\mathrm{U_2}(\mathrm{NPh})_2$

atom	*x*	*y*	*z*
U	0.46931 (3)	0.43589 (4)	0.64111 (4)
N	0.5116 (6)	0.6289 (8)	0.5455 (8)
C(1)	0.5687 (9)	0.2532 (14)	0.8130 (12)
C(2)	0.5650 (10)	0.3717 (15)	0.8866 (11)
C(3)	0.6171 (10)	0.4693 (13)	0.8447 (12)
C(4)	0.6550 (8)	0.4143 (13)	0.7447 (12)
C(5)	0.6248 (8)	0.2791 (13)	0.7234 (12)
C(6)	0.6522 (10)	0.1820 (15)	0.6315 (13)
C(7)	0.3442 (9)	0.3000 (18)	0.7573 (13)
C(8)	0.3155 (9)	0.4321 (20)	0.7502 (14)
C(9)	0.2812 (8)	0.4647 (16)	0.6216 (13)
C(10)	0.2909 (8)	0.3475 (14)	0.5480 (12)
C(11)	0.3298 (9)	0.2446 (13)	0.6346 (13)
C(12)	0.3559 (10)	0.1022 (12)	0.5975 (15)
C(13)	0.5169 (8)	0.7156 (12)	0.6512 (10)
C(14)	0.5978 (8)	0.7832 (12)	0.7109 (11)
C(15)	0.6022 (11)	0.8552 (13)	0.8253 (13)
C(16)	0.5232 (12)	0.8614 (13)	0.8799 (13)
C(17)	0.4433 (11)	0.7994 (14)	0.8219 (14)
C(18)	0.4376 (8)	0.7323 (12)	0.7086 (11)
H(1)	0.530 (6)	0.193 (10)	0.809 (8)
H(2)	0.532 (9)	0.382 (13)	0.945 (13)
H(3)	0.623 (8)	0.551 (12)	0.873 (11)
H(4)	0.695 (6)	0.476 (9)	0.712 (8)
H(5)	0.370 (12)	0.236 (19)	0.807 (16)
H(6)	0.317 (8)	0.481 (12)	0.815 (11)
H(7)	0.259 (6)	0.553 (11)	0.590 (9)
H(8)	0.273 (6)	0.334 (9)	0.449 (9)
H(9)	0.667 (6)	0.783 (10)	0.675 (8)
H(10)	0.676 (11)	0.924 (17)	0.852 (16)
H(11)	0.508 (8)	0.914 (11)	0.954 (11)
H(12)	0.391 (6)	0.819 (9)	0.848 (8)
H(13)	0.359 (10)	0.691 (14)	0.646 (12)

Table II. Positional Parameters with Estimated Standard Deviations for $(\mathrm{MeC_5H_4})_4\mathrm{U_2}(\mathrm{NSiMe_3})_2$

atom	*x*	*y*	*z*
U	0.42876 (1)	0.42371 (2)	0.58416 (2)
N	0.55124 (26)	0.5461 (4)	0.6084 (4)
Si	0.61269 (10)	0.62019 (18)	0.74075 (15)
C(1)	0.3775 (4)	0.1575 (7)	0.6607 (7)
C(2)	0.4031 (5)	0.1360 (7)	0.5493 (8)
C(3)	0.4899 (5)	0.1584 (6)	0.5675 (7)
C(4)	0.5208 (4)	0.1946 (7)	0.6910 (7)
C(5)	0.4502 (4)	0.1934 (6)	0.7517 (6)
C(6)	0.4520 (7)	0.2115 (12)	0.8856 (8)
C(7)	0.3539 (4)	0.6727 (7)	0.6418 (7)
C(8)	0.3656 (4)	0.5935 (8)	0.7509 (7)
C(9)	0.3056 (4)	0.4795 (8)	0.7286 (7)
C(10)	0.2571 (3)	0.4883 (7)	0.6088 (6)
C(11)	0.2888 (4)	0.6083 (7)	0.5530 (7)
C(12)	0.1834 (5)	0.3954 (9)	0.5552 (8)
C(13)	0.5730 (5)	0.7988 (7)	0.7789 (7)
C(14)	0.7276 (5)	0.6419 (11)	0.7264 (9)
C(15)	0.6164 (6)	0.5079 (10)	0.8810 (7)
H(1)	0.3185 (16)	0.153 (7)	0.680 (4)
H(2)	0.3580 (24)	0.101 (6)	0.477 (3)
H(3)	0.5331 (23)	0.140 (7)	0.514 (4)
H(4)	0.5815 (14)	0.203 (6)	0.735 (3)
H(5)	0.374 (4)	0.780 (8)	0.619 (6)
H(6)	0.399 (5)	0.610 (9)	0.833 (8)
H(7)	0.297 (4)	0.412 (6)	0.783 (6)
H(8)	0.272 (4)	0.649 (7)	0.472 (6)
H(9)	0.477 (6)	0.126 (6)	0.936 (8)
H(10)	0.3901 (22)	0.216 (11)	0.896 (8)
H(11)	0.495 (5)	0.283 (8)	0.928 (9)
H(12)	0.133 (3)	0.408 (7)	0.597 (5)
H(13)	0.195 (5)	0.292 (3)	0.546 (7)
H(14)	0.162 (4)	0.435 (7)	0.469 (3)
H(15)	0.5128 (21)	0.793 (8)	0.798 (6)
H(16)	0.572 (4)	0.866 (5)	0.709 (4)
H(17)	0.611 (4)	0.838 (7)	0.854 (3)
H(18)	0.734 (6)	0.705 (6)	0.657 (4)
H(19)	0.750 (4)	0.545 (3)	0.716 (6)
H(20)	0.761 (4)	0.683 (7)	0.805 (4)
H(21)	0.654 (5)	0.560 (9)	0.950 (6)
H(22)	0.647 (5)	0.422 (6)	0.860 (10)
H(23)	0.5594 (24)	0.485 (9)	0.900 (7)

Table III. Selected Distances (Å) in $(\mathrm{MeC_5H_4})_4\mathrm{U_2}(\mathrm{NPh})_2$ and $(\mathrm{MeC_5H_4})_4\mathrm{U_2}(\mathrm{NSiMe_3})_2$

$(\mathrm{MeC_5H_4})_4\mathrm{U_2}(\mathrm{NPh})_2$		$(\mathrm{MeC_5H_4})_4\mathrm{U_2}(\mathrm{NSiMe_3})_2$	
atoms	dist	atoms	dist
U–C(1)	2.765 (12)	U–C(1)	2.808 (6)
U–C(2)	2.764 (11)	U–C(2)	2.747 (7)
U–C(3)	2.747 (13)	U–C(3)	2.690 (6)
U–C(4)	2.736 (11)	U–C(4)	2.729 (6)
U–C(5)	2.756 (12)	U–C(5)	2.823 (6)
U–C(7)	2.775 (12)	U–C(7)	2.749 (6)
U–C(8)	2.754 (11)	U–C(8)	2.765 (7)
U–C(9)	2.751 (11)	U–C(9)	2.795 (6)
U–C(10)	2.752 (11)	U–C(10)	2.838 (5)
U–C(11)	2.790 (11)	U–C(11)	2.772 (6)
U–C(13)	2.862 (12)		
U–N	2.315 (8)	U–N	2.217 (4)
U–N′[a]	2.156 (8)	U–N′	2.230 (4)
N–C(13)	1.404 (13)	N–Si	1.733 (4)
U–U′	3.542 (1)	U–U′	3.493 (1)
N–N′	2.733 (17)	N–N′	2.753 (8)
$\mathrm{Cp_1}$[b]–U	2.481	$\mathrm{Cp_1}$–U	2.493
$\mathrm{Cp_2}$–U	2.495	$\mathrm{Cp_2}$–U	2.513
U–C(av)	2.759 ± 0.015	U–C(av)	2.77 ± 0.05

[a] The primes are related to the nonprimes by inversion. [b] $\mathrm{Cp_1}$ and $\mathrm{Cp_2}$ represent the centers of the cyclopentadienyl rings consisting of C(1)–C(5) and C(7)–C(11), respectively.

Tables I and II, respectively. Bond lengths and bond angles are in Tables III and IV, and crystal data are in Table V. The ORTEP diagrams for the bridging phenylimide are in Figures 1 and 2. Two views are shown so that the orientation of the *N*-phenyl group relative to the $\mathrm{U_2N_2}$ unit and the $\mathrm{MeC_5H_4}$ rings is easily seen. Figure 3 is an ORTEP view of the bridging trimethylsilylimide. The two complexes crystallize in the monoclinic crystal system in space group $P2_1/n$, and the unit cell dimensions and volumes are nearly identical. Both molecules have idealized C_{2h} symmetry with the inversion center located in the center of the $\mathrm{U_2N_2}$ ring.

The substituted-cyclopentadienyl uranium portion of both molecules is very similar. The averaged U–C(Cp) distance in the phenylimide is 2.76 ± 0.02 Å, the U–ring centroid distance is 2.49 Å, and the ring centroid–U–ring centroid angle is 118°. In the trimethylsilylimide, the averaged U–C(Cp) distance is 2.77 ± 0.05 Å, the U–ring centroid distance is 2.50 Å, and the ring centroid–U–ring centroid angle is 120°. These parameters are in the range found in cyclopentadienyl and substituted cyclopentadienyl compounds of the type $(\mathrm{RC_5H_4})_3\mathrm{UX}$[1,6] and $(\mathrm{R}_n\mathrm{C_5H}_{5-n})_2\mathrm{U(X)(Y)}$[7] where X and Y are anionic ligands.

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[6] Raymond, K. N.; Eigenbrot, C. W. *Acc. Chem. Res.* **1980**, *13*, 276–280.

Table IV. Selected Angles (Å) in $(MeC_5H_4)_4U_2(NPh)_2$ and $(Me_2C_5H_4)_4U_2(NSiMe_3)_2$

$(MeC_5H_4)_4U_2(NPh)_2$		$(MeC_5H_4)_4U_2(NSiMe_3)_2$	
atoms	angle	atoms	angle
N–U–N′[a]	75.2 (4)	N–U–N′	76.48 (12)
U–N–U′	104.7 (4)	U–N–U′	103.52 (16)
U–N–C(13)	97.6 (6)	U–N–Si	129.71 (23)
U′–N–C(13)	157.1 (7)	U′–N–Si	126.42 (22)
Cp_1[b]–U–Cp_2	118.4	Cp_1–U–Cp_2	119.7
Cp_1–U–N	108.0	Cp_1–U–N	114.1
Cp_1–U–N′	107.2	Cp_1–U–N′	110.0
Cp_2–U–N	129.6	Cp_2–U–N	110.1
Cp_2–U–N′	107.0	Cp_2–U–N′	118.7

[a] The primes are related to the nonprimes by inversion. [b] Cp_1 and Cp_2 represent the centers of the cyclopentadienyl rings consisting of C(1)–C(5) and C(7)–C(11), respectively.

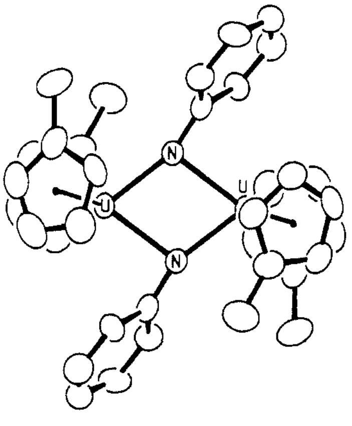

Figure 2. ORTEP drawing of $(MeC_5H_4)_4U_2(NPh)_2$ down a line connecting the cyclopentadienyl centers.

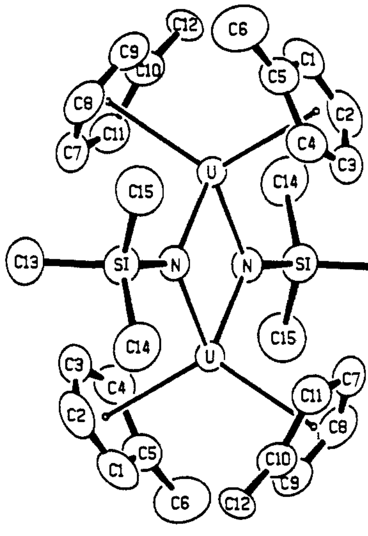

Figure 3. ORTEP drawing of $(MeC_5H_4)_4U_2(NSiMe_3)_2$; thermal ellipsoids at 50% probability level.

Table V. Crystallographic Summary and Data Processing for $(MeC_5H_4)_4U_2(NPh)_2$ and $(MeC_5H_4)_4U_2(NSiMe_3)_2$

	$(MeC_5H_4)_4U_2(NPh)_2$	$(MeC_5H_4)_4U_2(NSiMe_3)_2$
a, Å[a]	14.738 (3)	15.761 (6)
b, Å	9.933 (2)	9.389 (4)
c, Å	10.612 (2)	11.052 (4)
β, deg	102.11 (2)	101.36 (3)
cryst syst	monoclinic	
space group	$P2_1/n$	
equiv positions	$\pm(x, y, z); \pm(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)$	
reflcn rules	$h0l{:}h+l = 2n$; $0k0{:}k = 2n$	
vol, Å³	1518.9	1603.4
d(calcd), g/cm³	2.131	2.003
Z	2	2
temp (°C)	23	23
empirical formula	$C_{36}H_{38}N_2U_2$	$C_{30}H_{46}N_2Si_2U_2$
f(000)	904	904
fw	974.79	966.95
color	red	red
diffractometer	modified Picker FACS-1	
scan type	θ–2θ	
X-ray	Mo Kα (graphite monochromated)	
wavelength ($K\alpha_1$, $K\alpha_2$), Å	70930, 0.71359	
cryst size (mm)	0.04 × 0.24 × 0.14	0.08 × 0.10 × 0.32
μ, cm⁻¹	101.2	96.6
abs corr range	1.71–2.17	1.94–2.90
cryst decay corr range	0.99–1.01	0.98–1.02
2θ limits, deg	4–50	4–55
hkl limits	*h* – 17, 17; *k* – 2, 11; *l* – 12, 2	*h* – 20, 19; *k*0, 12; *l* – 14, 14
scan width, deg	1.8 + 0.693 × tan(θ)	1.8 + 0.693 × tan(θ)
no. of stds	3	3
interval of stds	250	250
no. scan data	5375	7410
no. unique reflcns	2689	3709
R_{int}[b]	0.051	0.029
no. non-zero wtd data	1600 ($F^2 > 2\sigma$)	2544 ($F^2 > 2\sigma$)
p[c]	0.035	0.030
extinction k[d]	5.2×10^{-7}	9.3×10^{-8}
max % extinction corr	10.0	4.8
no. parameters	233	255
R (non-zero wtd data)[e]	0.029	0.023
R_w[f]	0.029	0.024
R (all data)	0.082	0.051
goodness-of-fit[g]	0.98	1.00
max shift/esd in least-square	0.04	0.03
max/min in diff map (e/Å³)	1.9, –2.2	1.2, –0.9

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 18 reflections (**1**), 20 reflections (**2**) for $20 < 2\theta < 30$. [b] R_{int} = agreement factor between equivalent or multiply measured reflections: $= \sum_i\sum_j[F^2(hkl)_j - \langle F^2(hkl)\rangle_i]/\sum_i\langle F^2(hkl)\rangle_i$. [c] In the least-squares, the assigned weights to the data are $1.0/[\sigma(F)]^2$ and were derived from $\sigma(F)^2 = [S^2 + (pF^2)^2]$, where S^2 is the variance due to counting statistics and *p* is assigned a value that adjusts the weights of the stronger reflections such that their weighted residuals are comparable to those of the weak ones. [d] Simple extinction correction has the form $(F\text{obsd})_{corr} = (1 + kI)F\text{obsd}$, where *I* is the uncorrected intensity and *F*obsd is the observed scattering amplitude. [e] $R = \sum(|F\text{obsd}| - |F\text{calcd}|)/\sum|F\text{obsd}|$. [f] $R_w = ([\sum w(|F\text{obsd}| - |F\text{calcd}))^2/\sum wF\text{obsd}^2])^{1/2}$. [g] σ_1 = error in observation of unit weight $= ([\sum(w(|F\text{obsd}| - |F\text{calcd}|)^2)/(\text{no} - \text{nv})])^{1/2}$, where no is the number of observations and nv is the number of variables.

The nature of the bridging organoimido portion in the two molecules is vastly different. In the case of the trimethylsilylimide, the $NSiMe_3$ group nearly symmetrically bridges the two uranium centers, whereas the phenylimide group asymmetrically bridges the two $(MeC_5H_4)_2U$ fragments.

The most straightforward complex is $(MeC_5H_4)_4U_2(\mu\text{-}SiMe_3)_2$. The two independent U–N distances of 2.217 (4) and 2.230 (4) Å, the averaged value is 2.224 ± 0.003 Å, are equal to within 3σ. The U_2N_2 unit is planar, and the UNU′ and NUN′ angles are 103.5 (2)° and 76.5 (4)°, respectively. The two independent UNSi angles are 129.7 (2)° and 126.4 (2)°, so the N–Si vector is nearly a perpendicular bisector of the U_2N_2 ring plane. There are no structures of compounds in which two uranium atoms are bridged by organoimide groups and only a few in which two uraniums are bridged by dialkylamide groups. In $U_2(NEt_2)_6(\mu\text{-}NEt_2)_2$ the nonequivalent distances (one is axial and one is equatorial in an idealized trigonal bipyramid) are 2.46 (1) and 2.57 (1) Å.[8a] In the trimeric and tetrameric complexes $[U(MeNCH_2CH_2NMe)_2]_{3,4}$

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(7) (a) Duttera, M. R.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2907–2912. (b) Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1082–1084.

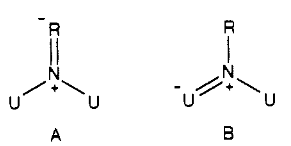
the bridging U–N distances range from 2.37 (2) to 2.60 (2) Å.[8b] Detailed comparison among these structures cannot be made other than to note that a U–N(sp^2-hybridized) distance should be ca. 0.10 Å shorter than a U–N(sp^3-hybridized) distance.[9]

The geometry about the bridging phenylimide group is much more asymmetric than that found in the isomorphous trimethylsilylimide complex. The two independent U–N distances of 2.156 (8) and 2.315 (8) Å are clearly unequal, though the averaged distance of 2.236 ± 0.040 Å is close to that found for the equivalent distance in the bridging silylimide. The U_2N_2 unit is planar, and the UNU′ and NUN′ angles are 104.7 (4)° and 75.2 (4)°, respectively, within 1° of those found in the bridging silylimide. The two independent U–N–C(13) angles of 97.6 (6)° and 157.1 (7)° are unequal, though the averaged U–N–C angle of 127° is again similar to the UNSi angle found in the silylimide. Accordingly the phenyl group is displaced from the perpendicular bisector of the U_2N_2 ring plane by 37°. The phenyl group is neither perpendicular to nor coplanar with the U_2N ring plane; the dihedral angle formed by intersection of the U_2N_2 and NC-(13,14,18) planes is 58°. The structural result of the opened U–N–C(Ph) angle is that C(18) and C(13) of the phenyl ring are close to the uranium atom. The U···C(18) and U···C(13) contact distances are 3.09 (1) and 3.49 (1) Å, respectively. These distances are longer than the uranium–aryl distance in Cp_3U(*p*-tolyl) of 2.51 (2) Å,[10a] but they are similar to some of the uranium or thorium to benzyl contact distances found in $(Me_5C_5)Th(CH_2Ph)_3$,[10b] $(PhCH_2)_4Th$(dmpe), $(PhCH_2)_3MeU$(dmpe),[10c] and in the η^6-arene complexes $(PhH)U(AlCl_4)_3$,[10d] $(Me_6C_6)_2U_2Cl_7(AlCl_4)$, $(Me_6C_6)_2U_3Cl_{12}$,[10e] and $(Me_6C_6)_3U_3Cl_5(AlCl_4)_4$.[10f]

The geometrical effects of terminal alkyl or aryl imides, RN^{2-}, and the isoelectronic O^{2-} and N^{3-} compounds of the d-block transition series have been rationalized in terms of a structural trans influence.[11] In mononuclear compounds the bond length of the group trans to the organoimide group is usually long relative to equivalent bonds trans to other ligands of lesser trans influence. A similar trans influence has been observed in binuclear compounds in which bridging anionic ligands are trans or nearly trans to terminal organoimide groups.[12] The structural data are useful for constructing a trans influence series since two types of M–X bond lengths can be compared within one molecule. The data show that organoimide groups can lengthen trans bonds by up to 0.2 Å.

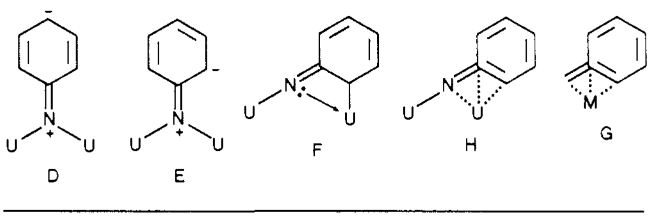
A substantial number of compounds with bridging organoimides is known.[12c,d,i,13] In the majority of these structures, in which the coordination about the metal is not tetrahedral nor pseudotetrahedral, the metal-to-bridging organoimide bond lengths are symmetric unless the identity of the ligands that are trans or nearly trans to the bridging organoimide are not identical. In molecules in which the metals are in pseudotetrahedral coordination the metal–bridging imide distances are symmetrical unless the terminal ligands are not identical.[14] The geometrical differences have been rationalized in terms of second-order Jahn–Teller effects[13c] or the competition for population of metal π-orbitals by the ligands that surround the metal atoms.[13a] These explanations are not applicable in the case of the two uranium complexes described in this paper since the ligand environment around each uranium atom is identical in each case. This requires that the identity of the organic group on the bridging imide ligand plays the dominant role in the origin of the distortion. In the rationalization that follows we assume that steric and packing effects do not play a dominant role. With this cautionary note we offer the following as a reasonable rationalization of the molecular distortion.

The bonding in the $U_2(\mu\text{-}NSiMe_3)$ group can be described by the three resonance structures A, B, and C ($R = SiMe_3$). These



resonance forms account for the planarity at nitrogen since the lone pair can π-bond to either silicon or uranium. The trimethylsilyl and $(MeC_5H_4)_2U$ fragments have empty π-symmetry orbitals available for bonding. It is impossible to get information about the extent of U–N π-bonding on the basis of comparative X-ray crystallography since these molecules are unique. It is easier to get some qualitative information on the extent of N–Si π-bonding. The N–Si distances vary from 1.64 Å in K(dioxane)$_2N(SiMe_3)_2$ in which N–Si π-bonding is thought to be extensive[15a] to 1.81 Å in $(Me_3Si)_2N_2$ in which π-bonding is thought to be minimal.[15b] The N–Si bond distance in the uranium compound of 1.725 (6) Å is consistent with some degree of π-bonding and resonance structure A appears to be important. The importance of resonance forms B and C, which show uranium–nitrogen π-bonds, is controversial; the primary issue being what is a short bond.[1,16]

The unsymmetrical U–N–C bond angles and U–N bond lengths in the phenylimide may be rationalized in the following way. As in the trimethylsilylimide, resonance structures B and C (R = Ph) are used to illustrate U–N single and double bonds. In addition, the phenyl group can delocalize negative charge to the ring ortho and para positions, symbolized by resonance structures D and E (only one given). The resonance structure E can be written with a direct U–C bond which makes the U–N–C angles and U–N bond lengths unequal, as shown in F. The resonance structures



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[8] (a) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M.; Templeton, L. K. *Inorg. Chem.* **1976**, *15*, 2498–2502. (b) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 599–603; 1858–1861.

[9] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1967; p 246.

[10] (a) Perego, G.; Cesari, M.; Farina, F.; Lugli, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 3034–3037. (b) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692–4693. (c) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293–298. (d) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* **1971**, *5*, 439–444. (e) Campbell, G. C.; Cotton, F. A.; Haw, J. F.; Schwotzer, W. *Organometallics* **1986**, *5*, 274–279. (f) Cotton, F. A.; Schwotzer, W.; Simpson, C. Q. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 637–639.

[11] (a) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459–517; **1972**, *8*, 369–396. (b) Nugent, W. A.; Haymore, B. L. *Ibid.* **1980**, *31*, 123–175. (c) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413–486. (d) Wheeler, R. A.; Whangbo, M.-H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222–2236.

[12] (a) Strähle, J.; Baernighausen, K. *Z. Anorg. Allg. Chem.* **1968**, *357*, 325–337. (b) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 103–104. (c) Bradley, D. C.; Jelfs, A. N.; Short, R. L. *Polyhedron* **1983**, *2*, 849–852. (d) Bradley, D. C.; Errington, R. J.; Hursthouse, M. B.; Nielson, A. J.; Short, R. L. *Ibid.* **1983**, *2*, 843. (e) Bates, P. A.; Nielson, A. J.; Waters, J. M. *Ibid.* **1985**, *4*, 1391–1401. (f) Nielson, A. J.; Waters, J. M. *Ibid.* **1982**, *1*, 561–562. (g) Jones, T. C.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Chem. Commun.* **1984**, 205–206. (h) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Vura, G. B. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1069–1072. (i) Chisholm, M. H.; Foltings, K.; Huffman, J. C.; Kirkpatrick, C. C.; Raterman, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 1305–1306. (j) Cotton, F. A.; Shamshoun, E. S. *Ibid.* **1984**, *106*, 3222–3225. (k) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Ibid.* **1984**, *106*, 4749–4751.

[13] (a) Alcock, N. W.; Pierce-Butler, M.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1976**, 707–713. (b) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1759–1760. (c) Thorn, D. L.; Nugent, W. A.; Harlow, R. L. *Ibid.* **1981**, *103*, 357–363.

[14] (a) Wiberg, N.; Häring, W. H.; Schubert, U. *Chem. Ber.* **1978**, *111*, 2708–2715. (b) Wiberg, N.; Häring, H. W.; Schubert, U. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1365–1369. (c) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030–2032. (d) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 1015–1017. (e) Vroegop, C. T.; Teuben, J. H.; van Bolhuis, F.; van der Linden, J. G. M. *Ibid.* **1983**, 550–552.

[15] (a) Domingos, A. M.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 517–519. (b) Veith, M.; Bärnighausen, *Ibid.* **1974**, *B30*, 1806–1813.

[16] Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 1853–1854; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 912–913.

(D and E) show the similarity of the phenylimide dianion to the isoelectronic benzyl anion and the former may be called the azabenzyl dianion in recognition of this similarity. There are several examples of a benzyl group acting as a terminal η^3-benzyl, G,[10b,c,17] and it is our contention that the bond angles and bond lengths in the bridging phenylimide portion of $(MeC_5H_4)_4U_2(\mu\text{-}NPh)_2$ may be rationalized by postulating that the imide is acting as a bridging, η^3-azabenzyl group, μ, η^3-NPh as shown in H.

It is difficult to get bond length data to justify C–N π-bonding in the phenylimide bridge, since the bond lengths in azobenzenes range from 1.423 (3) Å to 1.464 (7) Å and from 1.392 (6) Å to 1.360 (5) Å in anilines.[19] In the anionic complexes, $Li(OEt_2)\text{-}NPhC(CMe_3)(=CH_2)$[20a] and (14-crown-4)$LiNPh_2$,[20b] the C–N distance is 1.380 (1) Å and 1.389 (5) Å, respectively. In the phenylimide, the C–N distance is 1.40 (1) Å which is not significantly different from the other C–N bond lengths.

Experimental Section

All operations were done under nitrogen. Microanalyses were performed by the microanalytical laboratory of this department. The ^1H and ^{13}C NMR spectra were measured at 89.56 MHz and 22.50 MHz, respectively, on a JEOL-FX90Q instrument. Chemical shifts are reported in δ units relative to tetramethylsilane with positive values to high frequency. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 580 instrument. Mass spectra were obtained on a AEI-MS-12 machine equipped with a direct inlet by using electron ionization.

$(MeC_5H_4)_3UNSiMe_3$. Trimethylsilyl azide (0.20 mL, 1.4 mmol) was added to $(MeC_5H_4)_3U{\cdot}thf$[1b] (0.79 g, 1.4 mmol) in diethyl ether (20 mL). Gas evolution was evident though the color of the solution stayed deep red. The solution was stirred for 12 h, and the diethyl ether was removed under reduced pressure. The red solid was dissolved in hexane (30 mL), the solution was filtered, and the filtrate was cooled to −80 °C. Red crystals (0.26 g, 32%), mp 132–140 °C, were collected and dried under reduced pressure: the mass spectrum contained a M^+ at 562; IR 1238 m, 1035 w, 979 s, 830 m, 763 m, 745 w, 720 w cm^{-1}; ^1H NMR (C_6D_6, +36 °C) 6.72 ($\nu_{1/2}$ = 11 Hz, 9 H), 3.03 ($\nu_{1/2}$ = 10 Hz, 9 H), −1.96 ($\nu_{1/2}$ = 37 Hz, 6 H), −10.4 ($\nu_{1/2}$ = 29 Hz, 6 H); $^{13}C\{^1H\}$ NMR (C_6D_6, +36 °C) 121, 117, 101, 73.3, −2.28. The first three and last resonances are due to the MeC_5H_4 carbons. Anal. Calcd for $C_{21}H_{30}NSiU$: C, 44.8; H, 5.38; N, 2.49. Found: C, 45.2; H, 5.39; N, 2.30.

$(MeC_5H_4)_3UNPh$. Phenyl azide (0.30 g, 2.5 mmol) was added to $(MeC_5H_4)_3U{\cdot}thf$ (1.40 g, 2.53 mmol) in diethyl ether (30 mL). Gas evolution was immediate, and the color of the solution turned from red to violet. The solution was stirred for 2 h, and the diethyl ether was removed under reduced pressure. The solid residue was extracted with hexane (50 mL), the extract was filtered, and the filtrate was cooled to −20 °C. The red needles were recrystallized repeatedly, usually 3–5 times to free the phenylimide from $(MeC_5H_4)_3UN(H)(Ph)$, see below. The final yield of $(MeC_5H_4)_3UNPh$, mp 108–110 °C, was 0.22 g, 15%: the mass spectrum gave an M^+ at 566; IR 1580 w, 1571 w, 1555 w, 1259 s, 1157 w, 1149 w, 1062 w, 1045 w, 1030 w, 1018 w, 990 w, 970 w, 925 w, 904 m, 890 w, 860 w, 845 m, 777 s, 757 s, 720 m, 689 m, 600 w, 531 w, 330 m, 230 m cm^{-1}; ^1H NMR (C_6D_6, +32 °C) 18.5 ($\nu_{1/2}$ = 15 Hz, 2 H), 4.20 ($\nu_{1/2}$ = 2 Hz, t, J = 7 Hz, 1 H), 3.67 ($\nu_{1/2}$ = 19 Hz, 9 H), −2.40 ($\nu_{1/2}$ = 8 Hz, 2 H), −3.39 ($\nu_{1/2}$ = 45 Hz, 6 H), −10.8 ($\nu_{1/2}$ = 45 Hz, 6 H); $^{13}C\{^1H\}$ NMR (C_6D_6, +32 °C). The MeC_5H_4 carbons appear at 118, 99.3, 82.0, and −3.9, the phenyl carbons appear at 123, 97.6, and 108, and the ipso carbon resonance is not observed. Anal. Calcd for $C_{24}H_{26}NU$: C, 50.9; H, 4.63; N, 2.47. Found: C, 50.0; H, 4.72; N, 2.13. The $(MeC_5H_4)_3UN(H)(Ph)$ was isolated from the mother liquor in ca. 10% yield, mp 120–122 °C: the mass spectrum contained an M^+ at 567; ^1H NMR (C_6D_6, 31 °C) 4.13 (9 H, $\mathit{Me}C_5H_4$), −1.03 (6 H, $MeC_5\mathit{H}_4$), −1.92 (1 H, t, *p*-NPh), −3.04 (2 H, *o*- or *m*- of NPh), −18.16 (6 H, $MeC_5\mathit{H}_4$), −32.81 (2 H, *o*- or *m*- of NPh), −158.1 (1 H, N*H*Ph). The line width of the resonances is ca. 1–2 Hz consistent with the tetravalent formulation. Anal. Calcd for $C_{23}H_{27}NU$: C, 50.8; H, 4.79; N, 2.46. Found: C, 50.9; H, 4.63; N, 2.01. An authentic sample of the phenylamide has been prepared by reaction of $(MeC_5H_4)_3UMe$ and aniline.[4]

$(MeC_5H_4)_4U_2(\mu\text{-}NSiMe_3)_2$. A mixture of $(MeC_5H_4)_3U{\cdot}thf$ (0.50 g, 0.91 mmol) and $(MeC_5H_4)_3UNSiMe_3$ (0.50 g, 0.92 mmol) was dissolved in tetrahydrofuran (20 mL), and the solution was stirred for 24 h. The tetrahydrofuran was removed, and the red residue was extracted with diethyl ether (20 mL). Cooling the extract to −80 °C yielded crystals in two distinct habitats, thin plates and polyfaced cubes. The plates gave an M^+ at 983 in the mass spectrum and were shown to be the bridging silylimide by X-ray crystallography. The other crystals gave a mass peak at 554 in the mass spectrum, consistent with formulation $(MeC_5H_4)_4U$. Better synthetic methods are under study.[4]

$(MeC_5H_4)_4U_2(\mu\text{-}NPh)_2$. A mixture of $(MeC_5H_4)_3U{\cdot}thf$ (0.51 g, 0.93 mmol) and $(MeC_5H_4)_3UNPh$ (0.52 g, 0.92 mmol) was dissolved in tetrahydrofuran (20 mL), and the solution was stirred for 24 h. The tetrahydrofuran was removed under reduced pressure, and the red residue was dissolved in diethyl ether (25 mL) and cooled (−20 °C). The red solid was collected and dried under reduced pressure. Yield was 0.17 g, 38%, mp 167–170 °C: the mass spectrum gave an M^+ at 974; ^1H NMR (C_6D_6, 31 °C) 3.16 (4 H, $MeC_5\mathit{H}_4$), −1.32 (4 H, $MeC_5\mathit{H}_4$), −10.55 (6 H, $\mathit{Me}C_5H_4$), −4.46 (2 H, *o*- or *m*-N*Ph*), −57.99 (2 H, *o*- or *m*-N*Ph*), −5.89 (1 H, t, *p*-N*Ph*); ^{13}C NMR (C_6D_6, 31 °C) 214.9 (d), 207.3 (s), 203.5 (d), 156.1 (d), 130.1 (s), 86.7 (d), −38.53 (q); IR 1590 w, 1575 m, 1550 w, 1260 s, 1163 w, 1148 w, 1068 w, 1030 m, 1017 w, 990 w, 970 w, 925 w, 865 m, 820 m, 750 s, 613 m, 600 s, 538 m, 498 m, 383 m, 330 m, 235 m cm^{-1}. Anal. Calcd for $C_{36}H_{38}N_2U_2$: C, 44.4; H, 3.92; N, 2.87. Found: C, 44.0; H, 3.84; N, 2.42. The mother liquor contained resonances in the ^1H NMR spectrum due to $(MeC_5H_4)_3UN(H)(Ph)$.

X-ray Crystallography. Crystals were sealed inside quartz capillaries because of their sensitivity to the atmosphere. The structures were solved by Patterson and Fourier methods. Anisotropic thermal parameters were assigned to all the non-hydrogen atoms. In $(MeC_5H_4)_4U_2(NPh)_2$ the non-methyl hydrogen atoms were included in the full-matrix least-squares refinements; the methyl hydrogen atoms were omitted. In $(MeC_5H_4)_4U_2(NSiMe_3)_2$ all of the hydrogen atoms were included but refined with distance restraints.[21] Atomic scattering factors for all atoms were derived from values in ref 22. Experimental details of the data collection and the least-squares refinements are tabulated in Table V.

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Registry No. $(MeC_5H_4)_3U{\cdot}thf$, 78869-46-2; $(MeC_5H_4)_3UNSiMe_3$, 94202-28-5; $(MeC_5H_4)_3UNPh$, 94161-46-3; $(MeC_5H_4)_3UN(H)(Ph)$, 114533-66-3; $(MeC_5H_4)_3UMe$, 114533-67-4; $(MeC_5H_4)_4U_2(\mu\text{-}NSiMe_3)_2$, 114533-68-5; $(MeC_5H_4)_4U$, 96481-60-6; $(MeC_5H_4)_4U_2(\mu\text{-}NPh)_2$, 114533-69-6.

Supplementary Material Available: Listings of thermal parameters, distance restraints on H atoms, additional interatomic distances (C–C, C–H, Si–C) and angles, least-squares planes, and additional ORTEP drawings (15 pages); listings of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(17) (a) Bleeke, J. R.; Burch, R. R.; Coulman, C. L.; Schardt, B. C. *Inorg. Chem.* **1981**, *20*, 1316–1318. (b) Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418–5422. (c) Burch, R. R.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 188–197. (d) Sonoda, A.; Bailey, P. M.; Maitles, P. M. *J. Chem. Soc., Dalton, Trans.* **1979**, 346–350. (e) Behrens, U.; Weiss, E. *J. Organomet. Chem.* **1975**, *96*, 399–433, 435–450. (f) Chappel, S. D.; Cole-Hamilton, D. J.; Galas, A. M. R.; Hursthouse, M. B.; Walker, N. P. C. *Polyhedron* **1985**, *4*, 121–125.

(18) (a) Kanellakopulos, B. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; D. Reidel: Dordrecht, Holland, 1979; p 1. (b) Bursten, B. E.; Casarin, M.; DiBella, S.; Fang, A.; Fragala, I. *Inorg. Chem.* **1985**, *24*, 2169–2174.

(19) (a) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146–152, 153–158. (b) Hope, H.; Victor, D. *Ibid.* **1969**, *B25*, 1849–1853. (c) Wetherington, J. B.; Holmes, K. D.; Moncrief, J. W. *Ibid.* **1974**, *B30*, 246–249. (d) LePage, Y.; Gabe, E. J.; Wang, Y.; Barclay, L. R. C.; Holm, H. L. *Ibid.* **1980**, *B36*, 2846–2848. (e) LePage, Y.; Gabe, E. J.; Barclay, L. R. C.; Dust, J. M. *Ibid.* **1981**, *B37*, 926–978. (f) Gabe, E. J.; Wang, Y.; Barclay, L. R. C.; Dust, J. M. *Ibid.* **1981**, *B37*, 978–979. (g) Fukuyo, M.; Hirotsu, K.; Higuchi, T. *Ibid.* **1982**, *B38*, 640–643. (h) Merlino, S.; Sartori, F. *Ibid.* **1982**, *B38*, 1476–1480.

(20) (a) Dietrich, H.; Mahdi, W.; Knorr, R. *J. Am. Chem. Soc.* **1986**, *108*, 2462–2464. (b) Bartlett, R. A.; Dias, H. V. R.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Ibid.* **1986**, *108*, 6921–6926.

(21) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091–1094.

(22) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2, pp 71–102.