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Publication Date

1984-03-01



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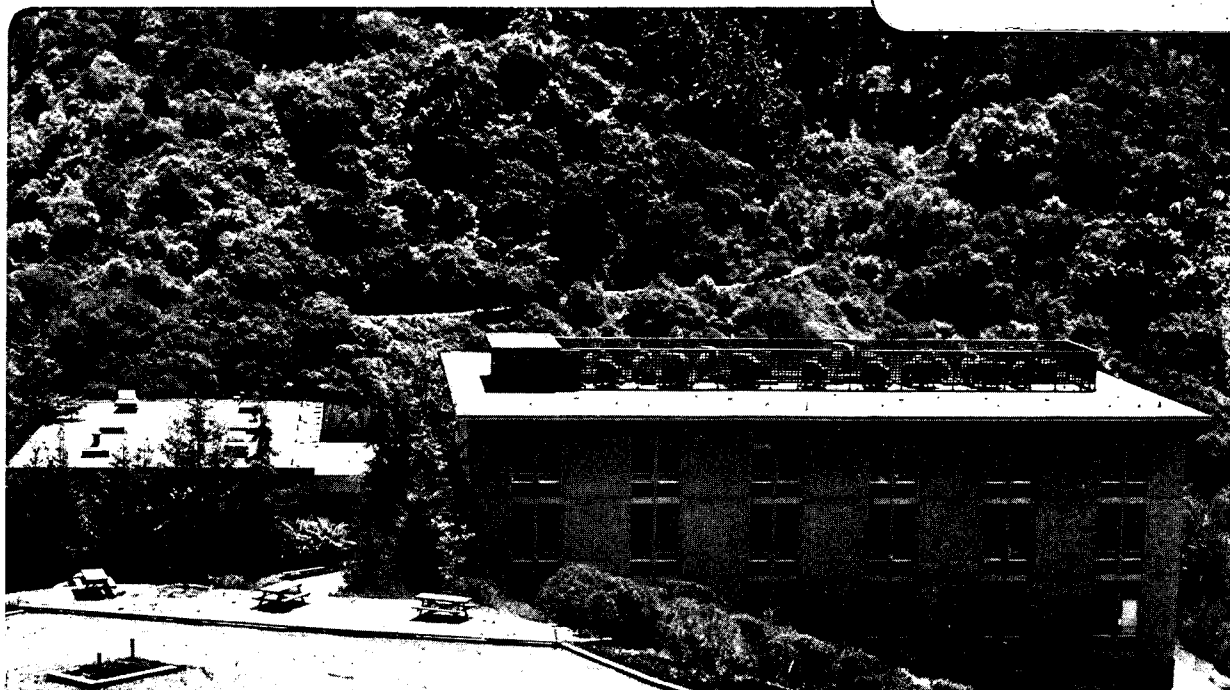
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March 1984

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**Phosphine Complexes of the f-Block Metals;
Ligand Substitution Reactions On Trivalent Uranium Complexes**

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Abstract

The trivalent uranium metallocenes, $(\text{MeC}_5\text{H}_4)_3\text{UL}$ where L is tetrahydrofuran, pyridine, quinuclidine, or trimethylphosphine, have been prepared and characterized, the latter by X-ray crystallography. The compound crystallizes in a monoclinic space group, Cn (No. 9) with $a = 13.949(5)$, $b = 9.280(4)$, $c = 16.194(6)$ Å, $\beta = 104.09(4)^\circ$, $V = 2033.2(\text{Å})^3$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 76.4 \text{ cm}^{-1}$. The structure was solved with Patterson and Fourier techniques and refined with 1532 data [$F^2 > 3\sigma(F^2)$] to R of 0.024. Equilibrium constant measurements show that the relative basicity towards $(\text{MeC}_5\text{H}_4)_3\text{U}$ lies in the order $\text{PMe}_3 > \text{py} > \text{quinuclidine} \sim \text{thf}$. The ligand displacement equilibria depends upon the substituent on the cyclopentadienyl ring, since for displacement of py by PMe_3 , K is 190 when $(\text{MeC}_5\text{H}_4)_3\text{U}$ is the reference acid and 80 when $(\text{C}_5\text{H}_5)_3\text{U}$ is the reference acid.

Phosphine complexes of the actinide metals of the type $\text{MX}_4(\text{dmpe})_2$, where X is Cl, Br, OPh, or Me, M is Th or U, and dmpe is $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ have been prepared recently^{1a} as has the trivalent complex $\text{U}(\text{C}_5\text{Me}_5)_2\text{H}(\text{dmpe})$.^{1b} The characterization of these complexes^{1a,c} demonstrates that phosphine ligands can form isolable complexes with actinide metals, in contrast to previously held views, though it does not establish how good phosphines are as ligands. Solution equilibrium quotient measurements are needed to show the relative coordinative affinity of oxygen, nitrogen, and phosphorus ligands towards f-metals. In this paper, we describe such a quantitative study.

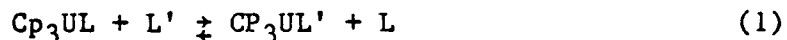
The coordinated phosphine in $\text{UCl}_4(\text{dmpe})_2$ is not displaced by $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2(\text{tmed})$ in refluxing toluene, though dmpe quantitatively displaces tmed from $\text{UCl}_4(\text{dmpe})_2$ at -50°C .^{1a} These qualitative studies clearly show that dmpe is a better ligand towards UCl_4 than tmed, but quantitative studies are difficult to do, since the equilibrium quotients are either very large or very small, and to interpret, since equilibria involving chelate ligands are complicated by entropy, ring-strain effects, etc.² In order to get around these difficulties we have prepared actinide complexes with a single, monodentate phosphine ligand in the inner coordination sphere of the actinide complex.

One strategy is to make complexes with the sterically bulky cyclopentadienyl ligand. The tetravalent compounds, Cp_3UCl or Cp_3UF , do not yield complexes with dmpe nor PMe_3 , probably due to steric effects.^{3a} The trivalent compound, Cp_3U , should be a better candidate since a number of complexes of the type Cp_3UL , where L is a monodentate oxygen or nitrogen ligand, are known.^{3b-d} The C_5H_5 complexes are sparingly soluble in hydrocarbon solvents and this property will complicate equilibrium quotient measurements in non-interacting solvents, though the MeC_5H_4 complexes, $(\text{MeC}_5\text{H}_4)_3\text{UL}$ where L is thf,

pyridine, quinuclidine or PMe_3^4 are soluble in aromatic hydrocarbons.

The crystal structure of the $(\text{MeC}_5\text{H}_4)_3\text{UPMe}_3$ complex was determined⁶ and an ORTEP view is shown in Figure I. The averaged U-C distance is 2.79 ± 0.05 Å, the averaged U-Cp(centroid) distance is 2.52 Å, and the U-P distance is 2.969(9) Å. The averaged Cp(centroid)-U-Cp(centroid) and Cp(centroid)-U-P angles are 112° and 106° , respectively.

The equilibrium quotients, defined by equation 1, where Cp, is either C_5H_5 or MeC_5H_4 , were



measured in toluene- d_8 at low temperature by ^1H NMR spectroscopy, are shown in Table I.⁷ The order of ligand basicity relative to $(\text{MeC}_5\text{H}_4)_3\text{U}$ is $\text{PMe}_3 >$ pyridine $>$ quinuclidine \sim thf, rather different from the gas phase proton-affinity of these ligands which lie in the order quinuclidine (229) $>$ PMe_3 (224) $>$ pyridine (218) $>$ thf (196).⁸ These data strongly suggest that intramolecular steric effects are the principal factor that affects the equilibria since, qualitatively, quinuclidine is larger than pyridine. However it is difficult to know how the cone angle of PMe_3 relates to that of pyridine and quinuclidine. This point is being studied by X-ray crystallographic studies. In addition, the nature of the substituent on the cyclopentadienyl ring plays a role since for a given set of reactions in which L and L' are constant the value of K changes by a factor of over two when MeC_5H_4 is replaced by C_5H_5 (Table I). Clearly the factors that effect the equilibrium quotients are complicated and a detailed study is in progress.

Acknowledgment

This work was supported by the director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract DE-AC03-76SF00098.

Supplementary Material

A listing of the positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

Table I. Equilibrium Constants for Equation 1.

L	L'	Cp	K (°C)
py	PMe ₃	MeC ₅ H ₄	190 (-51)
quinuclidine	py	MeC ₅ H ₄	130 (-51)
quinuclidine	thf	MeC ₅ H ₄	2.4 (-50)
py	PMe ₃	C ₅ H ₅	80 (-51)

References

1. (a) Edwards, P. G.; Andersen, R. A.; Zalkin, A. J. Am. Chem. Soc. 1981, 103, 7792-7794. (b) Duttera, M. R.; Fagan, P. S.; Marks, T. J.; Day, V. W. Ibid. 1982, 104, 865-867. (c) Tilley, T. D.; Andersen, R. A.; Zalkin, A. Inorg. Chem. 1983, 22, 856-859. (d) Edwards, P. G.; Unpublished results.
2. Wilkins, R. G. Acc. Chem. Res. 1970, 3, 408-412.
3. (a) Bombieri, G.; Benetollo, F.; Klähne, E.; Fischer, R. D. J. Chem. Soc. Dalton Trans. 1983, 1115-1121. (b) Kanellakopulos, B.; Fischer, E. O.; Dornberger, E.; Baumgärtner, F. J. Organomet. Chem. 1970, 24, 507-514. (c) Kanellakopulos, B. in "Organometallics of the f-Elements" Marks, T. J.; Fischer, R. D. ed. D. Reidel, Boston, 1979, p. 1-35. (d) Wasserman, H. J.; Zozulin, A. J.; Moody, D. C.; Ryan, R. R.; Salazar, K. V. J. Organomet. Chem. 1983, 254, 305-311.
4. (a) The thf complex was prepared from UCl_3^5 and $NaMeC_5H_4$ in thf followed by crystallization from hexane:thf (50:1) as dark (black) needles in 33% yield, mp 136-140°C. Anal. Calcd for $C_{22}H_{29}OU$: C, 48.3; H, 5.33. Found: C, 47.9; H, 5.31. 1H NMR (C_6H_6 , $\delta = 7.15$, 27.5°C): δ -11.62 (s, 6H), -13.99 (s, 4H), -14.39 (s, 6H), -15.61 (s, 9H), -31.06 (s, 4H). The second and fifth resonances undergo exchange with added thf. (b) The pyridine complex was prepared by addition of pyridine to a toluene solution of the thf complex, followed by crystallization from toluene (-20°C) as black needles in 62% yield, mp 126-129°C. Anal. Calcd for

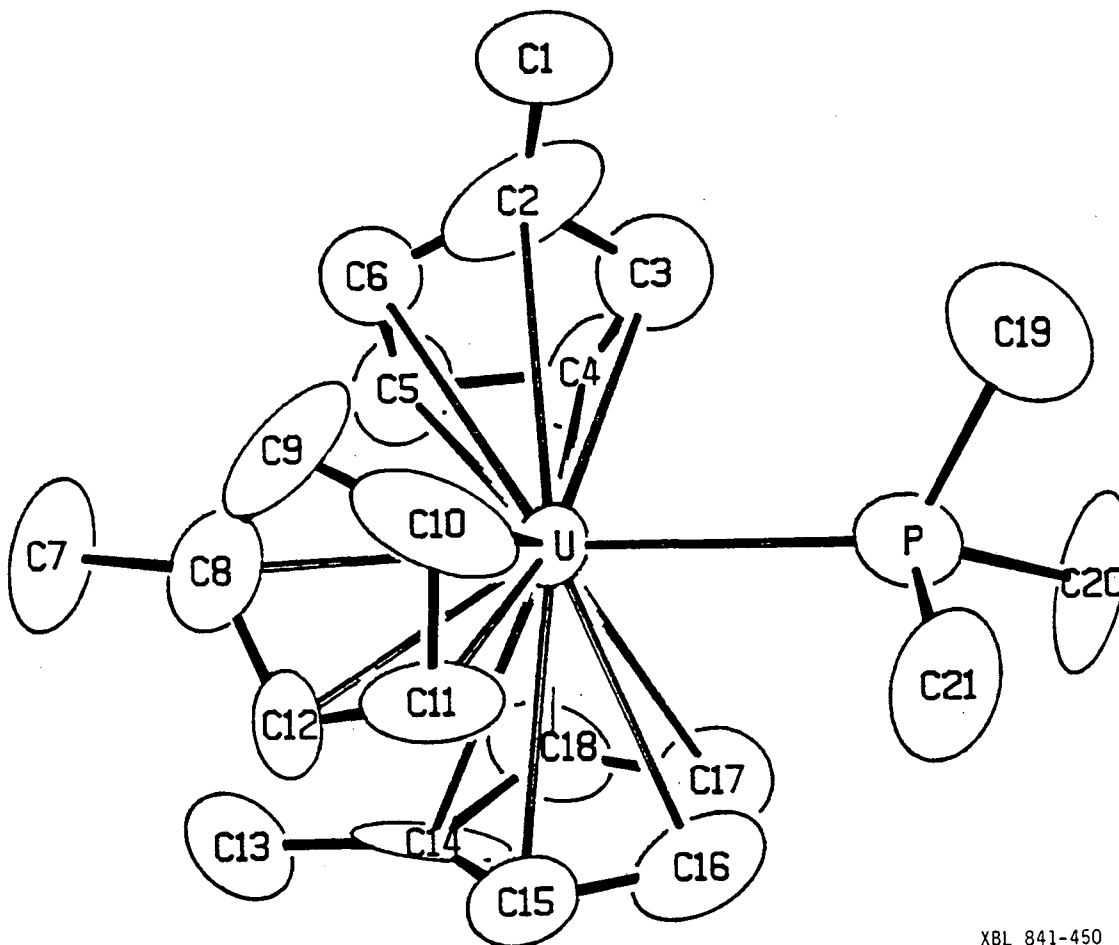
$C_{26}H_{23}NU$: C, 49.8; H, 4.73; N, 2.53. Found: C, 49.7; H, 4.55; N, 2.32. 1H NMR (C_6D_6 , $27^\circ C$): δ 8.47 (t, p-CH, $J = 7.7$ Hz, 1H), -5.21 (s, 2H), -10.10 (s, 6H), -14.25 (s, 9H), -17.06 (s, 6H), -19.08 (s, 2H). Addition of excess pyridine causes the first, second, and last resonances to undergo exchange. (c) The quinuclidine complex was prepared by addition of quinuclidine, 2-azabicyclo[2.2.2]octane, to a toluene solution of the thf complex followed by crystallization from hexane: toluene (5:1, $-20^\circ C$) as red needles in 23% yield, mp $159-162^\circ C$. Anal. Calcd for $C_{25}H_{34}NU$: C, 51.2; H, 5.84; N, 2.39. Found: C, 50.6; H, 5.73; N, 2.29. 1H NMR (C_6D_6 , $28^\circ C$): -10.14 (s, 6H), -10.78 (s, 1H), -11.09 (s, 6H), -14.27 (s, 9H), -14.64 (s, 6H), -28.64 (s, 6H). Addition of an excess of the amine causes the second, third, and last resonances to undergo exchange. (d) The PMe_3 complex was prepared by addition of PMe_3 to a pentane solution of the thf complex followed by crystallization as red needles from pentane ($-20^\circ C$), 80% yield, mp $228-232$ (dec) $^\circ C$. Anal. Calcd for $C_{21}H_{30}PU$: C, 45.7; H, 5.48; P, 5.62. Found: C, 45.5; H, 5.52; P, 4.66. 1H NMR (C_6D_6 , $31^\circ C$): -12.68 (s, 6H), -13.55 (s, 6H), -21.18 (s, 9H), -21.68 (s, 9H). The last resonance exchanges with added free phosphine.

5. Andersen, R. A. Inorg. Chem. 1979, 18, 1507-1509.
6. Crystal Data: $C_{21}H_{30}PU$, Fw = 551.47; Space Group, Cn (No. 9), monoclinic; $a = 13.949(5)$ Å, $b = 9.280(4)$ Å, $c = 16.194(6)$ Å, $\beta = 104.09(4)^\circ$; $v = 2033.2$ (Å) 3 ; ρ calc = 1.80 g cm^{-3} ; $Z = 4$; $\mu(Mo-K_\alpha) = 76.4$ cm^{-1} ; $\lambda = 0.70930$ Å. The structure was solved by Patterson and Fourier Methods and refined with 1532 data [$F^2 > 3\sigma(F^2)$] measured on a Picker

FACS-1 automated diffractometer, $R = 0.024$. The R for all data (1816) was 0.034.

7. A sample of $(\text{MeC}_5\text{H}_4)_3\text{UL}$ and L' of known concentration in toluene- d_8 (ca. 10^{-3}M) was cooled slowly (over ca. 1h) to -50°C and allowed to equilibrate at that temperature for 30 min, then the concentration of each species in solution was determined by integration.

- (8) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. J.; Beauchamp, J. L.; Taft, R. W. J. Am. Chem. Soc. 1977, 99, 5417-5429.



XBL 841-450

Figure I. ORTEP Diagram of $(\text{MeC}_5\text{H}_4)_3\text{UPMe}_3$

Supplementary Material For

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Trivalent Uranium Complexes

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Chemistry Department and Material and Molecular Research Division of Lawrence
Berkeley Laboratory, University of California, Berkeley, California 94720

Positional Parameters for $(\text{MeC}_5\text{H}_4)_3\text{UPMe}_2$

List of Atomic Input Positions.

ATOM	X	Y	Z
U	.250000	.088294	.250000
P	.282521	-.073905	.412515
C(1)	.390568	.400090	.373114
C(2)	.390716	.303588	.300369
C(3)	.445261	.174593	.303087
C(4)	.443728	.125885	.223644
C(5)	.383907	.216960	.161444
C(6)	.357907	.323786	.210616
C(7)	.118828	.347837	.072499
C(8)	.109698	.269863	.154505
C(9)	.120232	.325923	.237280
C(10)	.097345	.216899	.294768
C(11)	.056999	.099679	.239782
C(12)	.058653	.142542	.156275
C(13)	.162216	.032053	.014838
C(14)	.201792	-.063331	.089358
C(15)	.146537	-.124797	.143985
C(16)	.212556	-.200586	.207390
C(17)	.307484	-.180687	.195591
C(18)	.301684	-.086547	.128422
C(19)	.340711	.010731	.524278
C(20)	.375088	-.221798	.429701
C(21)	.172007	-.155224	.435940
H(1)	.477262	.125029	.355858
H(2)	.479859	.040986	.211004
H(3)	.364547	.205418	.099657
H(4)	.320085	.409402	.185470
H(5)	.139818	.425013	.253908
H(6)	.106309	.223168	.356628
H(7)	.033381	.007740	.256626
H(8)	.025370	.088996	.105153
H(9)	.075065	-.115595	.137692
H(10)	.195215	-.257406	.252731
H(11)	.367904	-.225826	.229262
H(12)	.357903	-.044121	.110839

Thermal Parameters for $(\text{MeC}_5\text{H}_4)_3\text{UPMe}_3$

Thermal Parameters in Units of Angstroms Squared.

A	2.504600	2.802900	3.563900	.204900	.683900	.538800
P	4.737100	5.335400	5.145400	-.369000	.557100	-.724600
C(1)	6.065300	5.428200	7.937300	-.678400	1.580600	-2.546600
C(2)	4.459200	5.094100	16.181400	-1.758600	6.591800	-.350200
C(3)	5.569600	0.	0.	0.	0.	0.
C(4)	4.202100	3.567700	6.129300	.200600	2.536100	2.575700
C(5)	4.337500	5.592600	6.428800	-.205900	1.944600	1.723800
C(6)	4.130400	5.422200	6.392900	-1.906400	.118100	.899800
C(7)	10.203000	7.190000	7.227500	1.234800	2.110000	4.230400
C(8)	4.643000	4.910200	10.858300	2.015200	-.704100	1.675700
C(9)	5.727300	2.508600	13.851600	2.216200	5.583000	2.144800
C(10)	3.791200	11.747700	7.173600	-.157100	1.772600	-5.923100
C(11)	2.979700	4.611800	8.437700	-.931400	2.894100	-3.479800
C(12)	2.761900	4.860700	6.286800	.026700	-.685700	1.927100
C(13)	8.485500	8.768300	4.515600	-3.175700	-1.080600	1.190700
C(14)	9.140000	7.840400	4.233200	-6.136400	1.131200	-4.200700
C(15)	5.426200	4.225100	6.198100	-1.258200	1.377800	-.225600
C(16)	7.549100	4.048400	9.257400	-.341500	3.656500	-1.202700
C(17)	8.114600	4.404400	7.190500	1.999200	-.097200	-2.011200
C(18)	5.827200	6.836700	4.484300	.263600	.997100	-2.685700
C(19)	10.008700	11.186800	5.713200	.622700	2.063000	-2.382100
C(20)	12.927300	6.870800	9.890400	6.765200	3.557100	5.061800
C(21)	6.379000	9.404400	11.689700	-.931300	2.239700	5.308100
H(1)	10.000000	0.	0.	0.	0.	0.
H(2)	10.000000	0.	0.	0.	0.	0.
H(3)	10.000000	0.	0.	0.	0.	0.
H(4)	10.000000	0.	0.	0.	0.	0.
H(5)	10.000000	0.	0.	0.	0.	0.
H(6)	10.000000	0.	0.	0.	0.	0.
H(7)	10.000000	0.	0.	0.	0.	0.
H(8)	10.000000	0.	0.	0.	0.	0.
H(9)	10.000000	0.	0.	0.	0.	0.
H(10)	10.000000	0.	0.	0.	0.	0.
H(11)	10.000000	0.	0.	0.	0.	0.
H(12)	10.000000	0.	0.	0.	0.	0.

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