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(M.S. Thesis)

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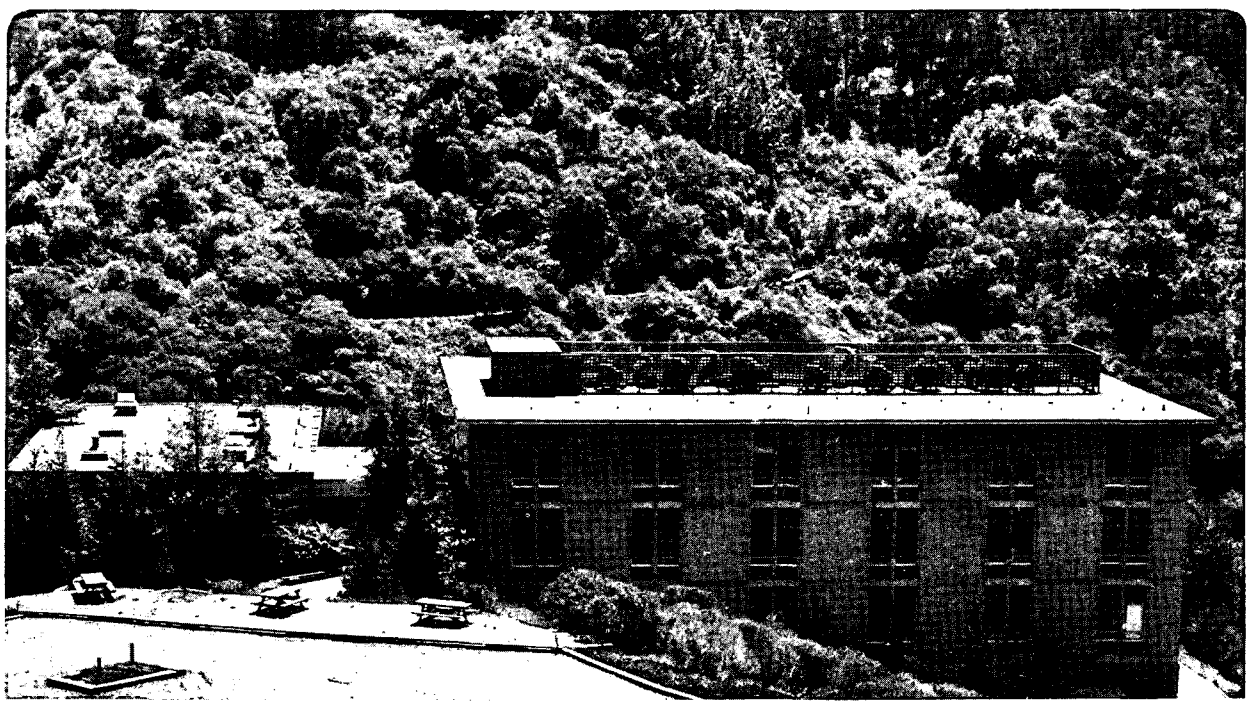

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Basicity of coordinating ligands in trivalent uranium and cerium metallocene complexes

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M.S. Thesis

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Introduction. Although much is known about the affinity of various Lewis bases for transition metal centers, the chemical literature contains only scant information about the relative affinities of Lewis bases for lanthanide and actinide metal centers.[1] Compounds of the lanthanide and actinide metals are, in contrast to those of the d-block metals, characterized by high coordination numbers and bonding which is generally thought of as ionic in nature. These differences between the f-metal compounds and compounds of the d-metals have been attributed[2] to the much larger size of the lanthanide and actinide ions (trivalent radii of f-metal ions = 0.85 - 1.08 Å) compared with transition metal ions (e.g., Cr^{+3} radius = 0.69 Å, Fe^{+3} radius = 0.64 Å) and to the inability of the f orbitals to form hybrid orbitals, which could lead to covalent bonding, with ligand orbitals. In terms of ligand affinities for f-metal centers, traditional HSAB theory[3] characterizes trivalent and tetravalent f-metal cations as "hard" acids, preferring to be coordinated to "hard" Lewis bases (e.g., nitrogen or oxygen donor ligands) rather than "soft" (e.g., phosphorus or sulfur donor ligands) Lewis bases.

Recent work by Brennan[4] and Stults[5], however, has shown that, contrary to what HSAB theory would predict, trimethylphosphine has a much greater affinity than does pyridine for the metal center in $(MeC_5H_4)_3U$ and in $(MeC_5H_4)_3Ce$. In this work, a series

of complexes of the type $Cp_3M{\cdot}L$ (where Cp = MeC_5H_4 or $Me_3SiC_5H_4$) were prepared and the equilibrium, defined by equation 1, was measured.

$$Cp_3M{\cdot}L + L' \rightleftharpoons Cp_3M{\cdot}L' + L \qquad (1)$$

This work established the ligand displacement series PMe_3 >> pyridine (py) > quinuclidine (quin) ≈ tetrahydrofuran (thf) ≈ tetrahydrothiophene (tht) for both the uranium and cerium systems (with Cp = MeC_5H_4). Another finding of this work was that uranium has a greater affinity than does cerium for π-acceptor ligands (e.g., phosphines, phosphites, and isocyanides), a finding which is consistent with U-L π-backbonding in these complexes. This result is somewhat surprising, since the bonding in f-metal organometallic compounds has been generally thought of as ionic in nature.

To further investigate the significance of π-bonding in the uranium coordination complexes, we have extended the uranium and cerium ligand displacement series to include several sterically undemanding ligands with large dipole moments. In this work, we have found that PMe_3, the strongest ligand in the displacement series of Brennan and Stults, is quantitatively displaced by trimethylphosphine oxide in both the uranium and cerium systems. In the cerium system, trimethylphosphine sulfide and dimethyl sulfoxide were also found to quantitatively displace PMe_3. Trimethylphosphine oxide was found to be by

far the strongest ligand in both systems, quantitatively displacing all ligands studied in both systems, with one exception: in the $(Me_3SiC_5H_4)_3U$ system, *t*- butyl isocyanide is displaced, but not completely displaced, by $OPMe_3$.

Results and Discussion. The studies of Brennan and Stults showed not only that the "soft" base PMe_3 has a greater affinity for the uranium and cerium metal centers than such "hard" bases as pyridine and thf, but also indicated that phosphines, phosphites and isocyanides, ligands capable of acting as π-acceptors, have a markedly greater affinity for uranium than for cerium. We prepared a number of $Cp_3M{\cdot}L$ (Cp = MeC_5H_4 or $Me_3SiC_5H_4$) complexes, where L = a sterically undemanding ligand with a large dipole moment, in order to further investigate the effect of π-backbonding on the relative affinities of ligands toward uranium and to extend the uranium and cerium ligand displacement series.

The preparation of these complexes is straightforward. The tris(methylcyclopentadienyl) uranium and cerium coordination complexes are prepared from the $(MeC_5H_4)_3M{\cdot}thf$ complexes by displacement of the thf ligand:

$$(MeC_5H_4)_3M{\cdot}thf + L \longrightarrow (MeC_5H_4)_3M{\cdot}L + thf \qquad (1)$$

The larger trimethylsilylcyclopentadienyl ring is used when the coordinating ligand is very sterically undemanding (e.g., cyanides and isocyanides) in order to prevent the formation of a 1:2 adduct (which has been observed in the tris(methylcyclopentadienyl) complexes with

propionitrile and ethyl isocyanide). The tris(trimethylsilylcyclopentadienyl)uranium and cerium coordination complexes are prepared by adding one equivalent of the desired coordinating ligand to a solution of the base-free $(Me_3SiC_5H_4)_3M$ compounds:

$$(Me_3SiC_5H_4)_3M + L \longrightarrow (Me_3SiC_5H_4)_3M{\cdot}L \qquad (2)$$

Relative ligand basicities toward the uranium or cerium metal centers are determined by measurement of the equilibrium defined by equation 3. The position of this equilibrium is measured by ^1H NMR spectroscopy; the relative concentration of each coordination complex in solution is obtained by calculating the arithmetic contribution of each species to the observed resonance as shown in equation 4, where δ_{obs} is the observed chemical shift of an RC_5H_4 ligand resonance, δ_a and δ_b are known (from the ^1H NMR of the respective complexes), and x is the mole fraction of species a.

$$Cp_3M{\cdot}L + L' \rightleftharpoons Cp_3M{\cdot}L' + L \qquad (3)$$

$$\delta_{obs} = (x)\,\delta_a + (1\text{-}x)\,\delta_b \qquad (4)$$

$$K_{eq} = [\,Cp_3M{\cdot}L'\,]\,[\,L\,]\ /\ [\,Cp_3M{\cdot}L\,]\,[\,L'\,] \qquad (5)$$

After determining the relative concentration of each species in solution, the

equilibrium constant K_{eq} for equation 3 (shown in equation 5) may be determined. A detailed description of the experimental procedure for these equilibrium measurements is given by Brennan.[4]

The equilibrium measurements made in this study showed that $OPMe_3$ clearly has the greatest affinity for the uranium and cerium metal centers of all the Lewis bases studied, including those studied by Stults and Brennan. In both the uranium and cerium systems, $OPMe_3$ quantitatively displaces all ligands studied, with the exception of $CNCMe_3$ in the uranium system. The term "quantitative displacement" as used here means that when one equivalent of the L' ligand is added to a solution of $(RC_5H_4)_3M{\cdot}L$, no $(RC_5H_4)_3M{\cdot}L$ is observed to be present; i.e., the ^1H NMR spectrum shows resonances only for free, uncoordinated L and for $(RC_5H_4)_3M{\cdot}L'$.

Tables 1 and 2 provide a summary of the equilibria studied. It should be noted that uranium-dimethyl sulfoxide and uranium-phosphine sulfide complexes could not be prepared because addition of these ligands to a solution of $(MeC_5H_4)_3U{\cdot}thf$ caused oxidation of uranium to the tetravalent state. In the case of phosphine sulfide, addition of ligand to $(MeC_5H_4)_3U{\cdot}thf$ yielded $[(MeC_5H_4)_3U]_2S$ (see Experimental section for details).

Table 1: $(RC_5H_4)_3U{\cdot}L + L' \rightleftharpoons (RC_5H_4)_3U{\cdot}L' + L$

R	L	L'	result
Me	PMe_3	$OPMe_3$	quantitative displacement at 30°C
Me	$OP(OCH_2)_3CEt$	$OPMe_3$	quantitative displacement at 30°C
Me_3Si	$OP(OCH_2)_3CEt$	$OPMe_3$	quantitative displacement at 30°C
Me_3Si	$CNCMe_3$	$OPMe_3$	$K_{eq} = 1.25 \times 10^3$ at -50°C

Table 2: $(RC_5H_4)_3Ce{\cdot}L + L' \rightleftharpoons (RC_5H_4)_3Ce{\cdot}L + L$

R	L	L'	result
Me	PMe_3	$OPMe_3$	quantitative displacement at 30°C
Me	$SPMe_3$	$OPMe_3$	quantitative displacement at 30°C
Me	$OSMe_2$	$OPMe_3$	quantitative displacement at 30°C
Me	$OP(OCH_2)_3CEt$	$OPMe_3$	quantitative displacement at 30°C
Me	PMe_3	$OSMe_2$	quantitative displacement at 30°C
Me	$SPMe_3$	$OSMe_2$	quantitative displacement at 30°C
$SiMe_3$	$OP(OCH_2)_3CEt$	$OPMe_3$	quantitative displacement at 30°C
$SiMe_3$	$CNCMe_3$	$OPMe_3$	quantitative displacement at 30°C

The results of these experiments show that PMe_3, the strongest base in the $(MeC_5H_4)_3M$ ligand displacement series of Stults and Brennan, has a much smaller affinity for the cerium and uranium metal centers than the ligands studied here. These results, like those of Brennan and Stults' experiments, are largely consistent with the gas-phase basicities of the ligands.[6,7] Steric requirements of the ligands and of $(RC_5H_4)_3M$ must also be taken into account when analyzing the relative ordering of the ligands in the displacement series; the ligands of this study are all sterically undemanding, which is not the case for many of the ligands studied by Brennan and Stults.

It should also be noted from the Tables that the only case of less-than-complete displacement by $OPMe_3$ in this entire series of experiments occurs in the $(Me_3SiC_5H_4)_3U$ system when the competing ligand is the sterically undemanding π-acceptor $CNCMe_3$. In the analogous cerium system, $CNCMe_3$ is quantitatively displaced by $OPMe_3$. These observations are consistent with the postulate that the stability of uranium complexes involving π-acceptor ligands is increased by U-L π-bonding.

Earlier evidence for this postulate was presented by Andersen,[8] who showed that the M-L bond lengths in the quinuclidine adducts of $(MeC_5H_4)_3U$ and $(MeC_5H_4)_3Ce$ are comparable, while the U-L bond length in the analogous phosphite adduct is substantially shorter than the Ce-L bond length in its counterpart. Further evidence is provided by Brennan's observation[4] that carbon monoxide coordinates to $(Me_3SiC_5H_4)_3U$ in solution,

with a change in color from green to purple upon addition of CO and a greatly lowered CO stretching frequency in the infrared spectrum, and Stults' observation[5] that there is no evidence of any reaction when CO is added to solutions of $(Me_3SiC_5H_4)_3Ce$ or $(Me_3SiC_5H_4)_3Nd$. Evidence[4] that isocyanide is acting as a π-acceptor ligand in $(Me_3SiC_5H_4)_3U{\cdot}CNR$ comes from the infrared stretching frequencies of the uranium and cerium isocyanide adducts (ν_{CN} = 2160 cm^{-1} in $(Me_3SiC_5H_4)_3U{\cdot}CNEt$, 2200 cm^{-1} in the Ce analogue, and 2151 cm^{-1} in free CNEt) and the complete displacement of cerium by uranium when base-free uranium compound is added to a solution of $(Me_3SiC_5H_4)_3Ce{\cdot}CNEt$, showing that the U-CNR bond is stronger than the Ce-CNR bond:

$$(Me_3SiC_5H_4)_3U + (Me_3SiC_5H_4)_3Ce{\cdot}CNEt \longrightarrow (Me_3SiC_5H_4)_3U{\cdot}CNEt + (Me_3SiC_5H_4)_3Ce \qquad (6)$$

Since the U-CNR bond is stronger than the Ce-CNR bond, the lowered isocyanide stretching frequency in the uranium complex may be attributed to π-backbonding (rather than to a weaker metal-ligand interaction).

The ability of $CNCMe_3$ to compete for the uranium coordination site in the presence of $OPMe_3$, along with the inability of $CNCMe_3$ to compete in the analogous cerium case and the inability of any other ligand studied to compete for either metal coordination site in

the presence of phosphine oxide, is consistent with the above evidence and with the postulate that the uranium-isocyanide bond, is strengthened by π-backbonding. The fact that $OPMe_3$ has a much stronger affinity for uranium than $CNCMe_3$ (and a much, much stronger affinity for uranium than any other ligand studied other than isocyanide) is also informative in that it helps to quantify the effect of π-backbonding on the uranium ligand displacement series, at least to the extent that it puts an upper limit on that effect.

The cumulative uranium and cerium ligand displacement series, then, roughly parallel the gas phase basicities of the coordinating ligands. The results of this study and the other evidence discussed above are consistent with the postulate that U-L π-backbonding increases the strength of U-L bonds in these coordination complexes, and this effect should be taken into account when examining or predicting relative ligand affinities for uranium. Furthermore, in both the uranium and cerium series, the steric requirements of the coordinating ligand and of the $(RC_5H_4)_3M$ system are of importance in determining relative ligand affinities.

Experimental

General. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Diethyl ether, tetrahydrofuran, hexane and toluene were distilled from sodium/benzophenone under nitrogen immediately prior to use. Trimethylphosphine oxide and $O{=}P(OCH_2)_3CEt$ were sublimed prior to use. Dimethyl sulfoxide was dried over calcium hydride and distilled prior to use. Trimethylphosphine sulfide was prepared according to the method of Harwood and Pollart[9] and then sublimed prior to use. t-Butyl isocyanide was dried over sodium and distilled prior to use. $(MeC_5H_4)_3U{\cdot}thf$ and $(Me_3SiC_5H_4)_3U$ were prepared as described by Brennan,[4] and $(MeC_5H_4)_3Ce{\cdot}thf$ and $(Me_3SiC_5H_4)_3Ce$ were prepared as described by Stults.[5] All compounds were handled using standard Schlenk techniques under a nitrogen atmosphere or in an inert atmosphere dry box under argon.

Melting points were taken in sealed capillaries under nitrogen and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer as Nujol mulls between CsI plates. ^1H (90 MHz) NMR spectra were recorded on a JEOL FX-90Q spectrometer in perdeuterated benzene or toluene dried and distilled over Na under nitrogen. Solvent was used as an internal reference; in C_6D_6, $\delta = 7.15$, and in C_7D_8, the methyl signal was used, $\delta = 2.09$. Mass spectra were obtained with an Atlas MS-12 spectrometer.

Elemental analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California, Berkeley.

$(MeC_5H_4)_3U{\cdot}OPMe_3$

Trimethylphosphine oxide (0.11 g, 1.2 mmol) was dissolved in toluene (25 mL) at 40°C and added to a solution of $(MeC_5H_4)_3U{\cdot}thf$ (0.60 g, 1.1 mmol) in toluene (30 mL). The solution was stirred for 1 hr. The solvent was then removed under reduced pressure and the red-brown precipitate was heated in a warm-water bath under reduced pressure for 1 hr. The precipitate was extracted into toluene (30 mL), filtered, concentrated (to about 25 mL) and cooled to -20°C. Reddish-brown needles (0.41 g, 66%), mp 224-226°C, were collected and dried under reduced pressure. ^1H NMR (C_6D_6, 27°C): δ = -9.93 (6H, $\nu_{1/2}$ = 15.6 Hz), -10.92 (d, J_{H-P} = 11.7 Hz, 12H), -11.82 (9H, $\nu_{1/2}$ = 5.9 Hz), -18.96 (6H, $\nu_{1/2}$ = 14.6 Hz). The doublet shifts toward the diamagnetic region of the spectrum upon addition of $OPMe_3$; this is the only resonance which shifts. Variable temperature NMR spectroscopy shows that the compound obeys the Curie law. (C_7D_8, -30°C): δ = -12.80 (6H), -13.20 (12H), -14.82 (9H), -24.71 (6H). Note that the integration of the spectra indicate that the coordination complex is not 1:1. IR: 1309m, 1291s, 1130s, 1041w, 1028w, 941m, 860w, 845w, 810m, 741s, 731s, 610m, 359m, 322w cm^{-1}. The elemental

analyses for this compound were always unsatisfactory.

$(MeC_5H_4)_3Ce{\cdot}OPMe_3$

Trimethylphosphine oxide (0.13 g, 1.4 mmol) was dissolved in toluene (25 mL) at 40°C and added to a solution of $(MeC_5H_4)_3Ce{\cdot}thf$ (0.63 g, 1.4 mmol) in toluene (30 mL). A pale yellow precipitate began to form a few minutes after addition of the phosphine oxide. The solution was stirred for 1 hr. The solvent was then removed under reduced pressure and the pale yellow precipitate was heated in a warm-water bath under reduced pressure for 1 hr. The precipitate was extracted into hot (100°C) toluene (40 mL), filtered and cooled to -20°C, yielding pale yellow needles (0.50 g, 76%), mp 265-268°C. ^1H NMR (C_6D_6, 27°C): δ = 7.55 (6H), 6.95 (6H), -0.34 (9H, $\nu_{1/2}$ = 6.8 Hz), -3.37 (d, J_{H-P} = 11.7 Hz, 9H). The doublet shifts toward the diamagnetic region of the spectrum upon addition of $OPMe_3$. Variable temperature NMR spectroscopy shows that the compound obeys the Curie law. (C_7D_8, -68°C): δ = 8.36 (6H), 6.18 (6H), -1.74 (9H, $\nu_{1/2}$ = 18.6 Hz), -3.92 (9H, $\nu_{1/2}$ = 28.1 Hz). IR: 2024w, 1411m, 1307m, 1291s, 1232w, 1133s, 1059w, 1041m, 1029m, 972w, 941m, 860w, 848w, 812m, 742s, 733s, 682w, 619m, 359m, 321w, 232m cm^{-1}. <u>Anal.</u> Calcd. for $C_{21}H_{30}OPCe$: C 53.7, H 6.44, P 6.60. Found: C 53.3, H 6.45, P 5.57.

$(MeC_5H_4)_3Ce{\cdot}OSMe_2$

$(MeC_5H_4)_3Ce{\cdot}thf$ (0.48 g, 1.1 mmol) was dissolved in toluene (25 mL) and dimethyl sulfoxide (0.30 mL, 2.7 mmol) was added by syringe. The solution was stirred for 10 min. The solvent was then removed under reduced pressure and the yellow precipitate was heated in a warm-water bath under reduced pressure for 90 min. to ensure the removal of excess DMSO. The precipitate was then extracted into warm (55°C) toluene (30 mL), filtered and cooled to -20°C. Yellow crystals (0.32 g, 64%), mp 235-237°C, were collected and dried under reduced pressure. ^1H NMR (C_6D_6, 32°C): δ = 8.37 (6H, $\nu_{1/2}$ = 18.4 Hz), 7.85 (6H, $\nu_{1/2}$ = 18.9 Hz), -0.65 (9H, $\nu_{1/2}$ = 5.8 Hz), -3.85 (6H, $\nu_{1/2}$ = 5.9 Hz). The last resonance listed shifts toward the diamagnetic region of the spectrum upon addition of DMSO. Variable temperature NMR spectroscopy shows that the compound obeys the Curie law. (C_7D_8, -71°C): δ = 8.61 (6H), 8.35 (6H), -2.36 (9H, $\nu_{1/2}$ = 11.8 Hz), -4.96 (6H, $\nu_{1/2}$ = 11.7 Hz). IR: 1362s, 1321m, 1235w, 1169m, 1152w, 1044m, 1038s, 1008s, 959m, 929w, 850w, 818s, 749s, 738s, 618m, 400w, 336w, 322w cm^{-1}. Anal. Calcd. for $C_{20}H_{27}OSCe$: C 52.7, H 5.97, S 7.04. Found: C 53.2, H 6.03, S 6.97.

$[(MeC_5H_4)_3U]_2S$ (from $(MeC_5H_4)_3U{\cdot}thf$ and $SPMe_3$)

$(MeC_5H_4)_3U{\cdot}thf$ (0.24 g, 0.44 mmol) dissolved in toluene (10 mL) was added to $SPMe_3$ (0.06 g, 0.55 mmol) in toluene (5 mL). The resulting red-orange solution was stirred for 5 min., and the solvent was then removed under reduced pressure. The precipitate was extracted into toluene (20 mL), filtered, concentrated, and cooled to -20°C, yielding red crystals (0.10 g, 46% based on $(MeC_5H_4)_3U{\cdot}thf$) of $[(MeC_5H_4)_3U]_2S$ as characterized by melting point and ^1H NMR spectroscopy.[4]

$(MeC_5H_4)_3Ce{\cdot}SPMe_3$

Trimethylphosphine sulfide (0.14 g, 1.3 mmol) was dissolved in toluene (15 mL) at 55°C and added to a solution of $(MeC_5H_4)_3Ce{\cdot}thf$ (0.55 g, 1.2 mmol) in toluene (10 mL). The resulting solution was stirred for 2 min., and the solvent was then removed under reduced pressure. The precipitate was extracted into hot (100°C) toluene (15 mL), filtered and cooled to -20°C, yielding yellow-green crystals (0.41 g, 70%), mp 172-173°C. ^1H NMR (C_6D_6, 30.5°C): δ = 11.00 (6H, $\nu_{1/2}$ = 30.3 Hz), 10.00 (6H, $\nu_{1/2}$ = 28.3 Hz), -1.54 (9H, $\nu_{1/2}$ = 10.7 Hz), -4.50 (9H, $\nu_{1/2}$ = 17.5 Hz). The last resonance listed shifts toward the diamagnetic region of the spectrum upon addition of $SPMe_3$. IR: 1305w, 1283w, 1232m, 1165m, 1150w, 1032s, 951s, 938s, 845m, 821s, 768s, 755s, 740s, 720s, 700m, 611m, 550m, 325m, 212s cm^{-1}. <u>Anal.</u> Calcd. for $C_{21}H_{30}PSCe$: C 51.9, H 6.23, S 6.60.

Found: C 52.2, H 6.15, S 6.38.

$(Me_3SiC_5H_4)_3U{\cdot}OPMe_3$

Trimethylphosphine oxide (0.18 g, 2.0 mmol) was dissolved in toluene (10 mL) and the solution was added to a Schlenk tube containing $(Me_3SiC_5H_4)_3U$ (0.60 g, 0.92 mmol). The solution turned reddish-brown and was stirred for 15 min. The solvent was removed under reduced pressure and the precipitate was heated in a warm-water bath for 30 min. to remove excess $OPMe_3$. The precipitate was then extracted into a mixture of hexane (20 mL) and ether (10 mL), filtered, concentrated to 25 mL, and cooled to -20°C, producing large black crystals (0.44 g, 64%), mp 127-129°C. ^1H NMR (C_6D_6, 30°C): δ = -3.41 (27H, $\nu_{1/2}$ = 4.1 Hz), -7.01 (6H, $\nu_{1/2}$ = 13.7 Hz), -10.0 (9H, $\nu_{1/2} \approx$ 100 Hz), -15.69 (6H, $\nu_{1/2}$ = 14.6 Hz). The peak at -10.0 shifts toward the diamagnetic region of the spectrum upon addition of $OPMe_3$. Variable temperature NMR spectroscopy shows that the compound obeys the Curie law. (C_7D_8, -75°C): δ = -5.66 (27H, $\nu_{1/2}$ = 8.8 Hz), -14.00 (6H, $\nu_{1/2}$ = 34.1 Hz), -15.14 (9H, d, $J_{H\text{-}P}$ = 11.7 Hz), -26.31 (6H, $\nu_{1/2}$ = 42.8 Hz). IR: 1308m, 1295m, 1239m, 1176m, 1125s, 1060w, 1033m, 942s, 900s, 825s, 761s, 745s, 720s, 680m, 631m, 620m, 416m, 359m, 309m cm^{-1}. <u>Anal.</u> Calcd. for $C_{27}H_{48}OPSi_3U$: C 43.0, H 6.42, P 4.11. Found: C 41.7, H 6.46, P 3.32.

$(Me_3SiC_5H_4)_3U{\cdot}CNCMe_3$

$(Me_3SiC_5H_4)_3U$ (0.55 g, 0.84 mmol) was dissolved in Et_2O (15 mL). $CNCMe_3$ (0.25 mL, 2.2 mmol) was added and the solution was stirred for 15 min. The solvent was removed under reduced pressure. The precipitate was extracted into warm (45°C) hexane (25 mL), filtered and cooled to -20°C, yielding fluffy red-brown crystals (0.47 g, 75%), mp 103-104°C. ^1H NMR (C_6D_6, 30°C): δ = -2.29 (6H, $\nu_{1/2}$ = 21.5 Hz), -6.20 (27H, $\nu_{1/2}$ = 5.9 Hz), -10.41 (9H, $\nu_{1/2}$ = 8.8 Hz), -17.16 (6H, $\nu_{1/2}$ = 17.5 Hz). The third resonance listed shifts toward the diamagnetic region of the spectrum upon addition of $CNCMe_3$. Variable temperature NMR spectroscopy shows that the compound obeys the Curie law. (C_7D_8, -75.5°C): δ = -6.67 (6H, $\nu_{1/2}$ = 49.8 Hz), -10.01 (27H, $\nu_{1/2}$ = 26.3 Hz), -17.03 (9H, $\nu_{1/2}$ = 52.7 Hz), -28.33 (6H, $\nu_{1/2}$ = 48.8 Hz). IR: 2141m, 1307w, 1290w, 1271m, 1060w, 1038s, 900s, 830s, 782m, 761s, 746s, 685m, 630m, 619m, 520w, 420m, 314m cm^{-1}. <u>Anal.</u> Calcd. for $C_{29}H_{48}NSi_3U$: C 46.8, H 6.50, N 1.88. Found: C 46.9, H 6.84, N 1.92.

$(Me_3SiC_5H_4)_3U{\cdot}OP(OCH_2)_3CEt$

The phosphite oxide $OP(OCH_2)_3CEt$ (0.15 g, 0.79 mmol) and $(Me_3SiC_5H_4)_3U$ (0.48 g, 0.74 mmol) were placed in a Schlenk tube. Toluene (20 mL) was added and the

mixture stirred for 30 min. The toluene was removed under vacuum and the precipitate heated under vacuum at 100°C for 90 min. to remove excess ligand. The precipitate was then extracted into hot (55°C) hexane (15 mL), filtered and cooled to -20°C, yielding black crystals (0.33 g, 53%), mp 203-205°C. ^1H NMR (C_6D_6, 30°C): δ = -2.80 (6H), -2.89 (6H), -3.21 (5H), -4.60 (27H, $\nu_{1/2}$ = 4.8 Hz), -16.12 (6H, $\nu_{1/2}$ = 15.8 Hz). The first and third resonances listed shift toward the diamagnetic region of the spectrum upon addition of free ligand. IR: 1307w, 1270m, 1242m, 1172m, 1151m, 1037m, 970m, 957w, 944m, 901m, 881m, 828s, 760s, 731s, 720s, 680m, 621s, 460m, 411m, 321m, 307m, 235w cm^{-1}. Anal. Calcd. for $C_{30}H_{50}O_4PSi_3U$: C 42.9, H 6.00, P 3.69. Found: C 42.9, H 6.03, P 3.01.

$(Me_3SiC_5H_4)_3Ce{\cdot}OP(OCH_2)_3CEt$

The phosphite oxide $OP(OCH_2)_3CEt$ (0.15 g, 0.79 mmol) was dissolved in hot (100°C) toluene (26 mL) and cannulated into a Schlenk tube containing $(Me_3SiC_5H_4)_3Ce$ (0.31 g, 0.56 mmol). The solution immediately turned yellow and was stirred for 1 hr. The solvent was removed under reduced pressure, and the precipitate was extracted into hot (100°C) toluene (25 mL), filtered and cooled to -20°C. Pale yellow crystals (0.29 g, 70%), mp 190-192°C, were collected and dried under reduced pressure. ^1H NMR (C_6D_6, 30°C): δ = 10.55 (6H, $\nu_{1/2}$ = 16.6 Hz), 7.80 (6H, $\nu_{1/2}$ = 19.6 Hz), 0.86 (6H, $\nu_{1/2}$ = 10.7 Hz),

-1.21 (5H), -1.50 (27H, $\nu_{1/2}$ = 4.9 Hz). The third and fourth resonances listed shift toward the diamagnetic region of the spectrum upon addition of free ligand. IR: 1307w, 1278s, 1242m, 1178m, 1153m, 1038m, 979m, 971m, 959w, 947m, 901m, 881m, 828s, 765s, 750m, 724m, 683w, 637w, 625m, 463m, 414m, 320m, 308m, 244m cm^{-1}. Anal. Calcd. for $C_{30}H_{50}O_4PSi_3Ce$: C 49.4, H 6.90, P 4.24. Found: C 50.7, H 7.19, P 3.75.

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