vs SCE, $E_a - E_c$ = 110 mV, primary reference internal Fc/Fc^+, $E_a - E_c$ = 105 mV). In the complex (dppf)$PdCl_2$, a single reversible oxidation process is also observed (+0.88 V vs SCE, $E_a - E_c$ = 70 mV, primary reference internal Fc/Fc^+, $E_a - E_c$ = 70 mV), which is shifted to a more positive potential with respect to the free ligand. This result is consistent with that reported for (dppf)$PtCl_2$, in which a reversible redox process is similarly observed (≈ +0.90 V vs SCE).[24] A reversible oxidation has also been observed for (dppf)$Re(CO)_3Cl$.[25] In contrast, **1** exhibits a single irreversible anodic wave in its cyclic voltammogram with E_a = +1.0 V vs SCE. The characteristics of this wave are unchanged upon varying the sweep rate (20–200 mV s^{-1}) and temperature (−25 to +25 °C). On the return sweep for **1**, a very broad reduction wave is observed at −0.02 V vs SCE. We have not isolated the product of the irreversible oxidation.

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Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, thermal parameters, and H atom coordinates (4 pages); a listing of structure factors (29 pages). Ordering information is given on any current masthead page.

Chemistry of Trivalent Cerium and Uranium Metallocenes: Reactions with Alcohols and Thiols

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The trivalent cerium metallocene $(Me_3CC_5H_4)_3Ce$ reacts with alcohols, HOR (R = $CHMe_2$ or Ph), or thiols, HSR (R = $CHMe_2$, or Ph), to give the dimers $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}ER)_2$ as shown by X-ray crystallography for the isopropoxide and isopropylthiolate derivatives. Crystals of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}OCHMe_2)_2$ are monoclinic, $P2_1/c$ with a = 11.962 (4) Å, b = 14.489 (5) Å, c = 12.384 (5) Å, β = 103.31 (3)°, and V = 2089 Å^3; the structure was refined by full-matrix least-squares methods to a conventional R factor of 0.028, 2874 data, $F^2 > 2\sigma(F^2)$. The Ce_2O_2 unit is planar, the geometry about the cerium atom is pseudotetrahedral, and the geometry is planar about the oxygen atom. Crystals of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$ are also monoclinic, $P2_1/n$ with a = 14.255 (9) Å, b = 13.585 (9) Å, c = 11.265 (7) Å, β = 96.02 (5)°, V = 2170 Å^3; the structure was refined by full-matrix least-squares methods to a conventional R factor of 0.028, 2899 data, $F^2 > 2\sigma(F^2)$. The Ce_2S_2 unit is planar, and the geometry about cerium is pseudotetrahedral though the geometry is pyramidal at sulfur so that the isopropyl groups are anti relative to the Ce_2S_2 ring. Methanol or water give an insoluble solid, presumably $Ce(OMe)_3$ or $Ce(OH)_3$, whereas $HECMe_3$ (E = O or S) do not react with $(Me_3CC_5H_4)_3Ce$, but the thiol does react with the sterically less bulky metallocene $(MeC_5H_4)_3Ce(THF)$ (THF = tetrahydrofuran) to give $(MeC_5H_4)_4Ce_2(\mu\text{-}SCMe_3)_2$. The p$K_a$'s ($H_2O$) of the organic acids generally predict the thermodynamic outcome of the proton-exchange reactions, though the latter set of experiments show that kinetic (i.e., steric) factors play a role. The uranium metallocene $(Me_3CC_5H_4)_3U$ reacts with HSPh at low temperature to give isolable $(Me_3CC_5H_4)_4U_2(\mu\text{-}SPh)_2$, which rearranges in solution to the monomeric, tetravalent species $(Me_3CC_5H_4)_3USPh$ and unidentified material. The dimer intermediate cannot be detected with the sterically smaller metallocene $(MeC_5H_4)_3U(THF)$, as only $(MeC_5H_4)_3UER$ (ER = OMe, $OCHMe_2$, OPh, and $SCHMe_2$) are isolated.

Binary alkoxide derivatives of the 4f transition metals (lanthanides) traditionally have been prepared by the exchange reaction of a metal halide with either an alkali-metal derivative of an alcohol or an alcohol in ammonia or by reaction of the metal with an alcohol.[1] These synthetic methods are not without difficulties due to halide or oxide contamination as well as formation of anionic compounds.[2] Cyclopentadienylmetal alkoxides have been prepared by metathetical exchange reactions, though difficulties with oxide or halide contamination often makes isolation of pure compounds difficult.[3] A clean synthesis of cyclopentadienyl derivatives such as $(Me_5C_5)_2Lu(OCMe_3)(THF)$ from $(Me_5C_5)_2LuMe_2Li(THF)_2$ and *tert*-butyl alcohol[4a,b] and $(Me_5C_5)_2Yb(OR)$ from $(Me_5C_5)_2Yb$ and diorgano peroxides[4c] are useful when the appropriate starting materials are available. Binary thiolates of the lanthanide elements have not been described,[5] though several cyclopentadienyl derivatives such as $(Me_5C_5)_2Yb(SR)(NH_3)$, prepared from $(Me_5C_5)_2Yb(NH_3)_2$ and R_2S_2, and $(Me_5C_5)_2Lu(SCMe_3)_2Li(THF)_2$, prepared from the thiol and $(Me_5C_5)_2LuMe_2Li(THF)_2$, have been isolated.[4a,b]

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Table I. ^{1}H NMR Data for $(RC_5H_4)_4Ce_2(\mu\text{-}ER)_2$ and $(RC_5H_4)_3UER$[a]

compound	δ(CH(A))	δ(CH(B))	δ(R(X))	δ(ligand)
$(MeC_5H_4)_4Ce_2(\mu\text{-}SCMe_3)_2$	20.54 (≈80 Hz)	18.79 (≈90 Hz)	4.71 (26 Hz)	−22.22 (9 H, 20 Hz)
$(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$	21.85 (50 Hz)	20.51 (45 Hz)	−4.96 (17 Hz)	−12.37 (1 H), −17.49 (6 H, 20 Hz)
$(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SPh)_2$	25.73 (77 Hz)	19.23 (74 Hz)	−8.97 (18 Hz)	2.69 (2 H), 1.15 (1 H), −4.67 (2 H)
$(Me_3CC_5H_4)_4Ce_2(\mu\text{-}OCHMe_2)_2$				
30 °C	18.4 (≈110 Hz)	overlap A	0.98 (28 Hz)	−3.87 (1 H, 25 Hz), −19.90 (6 H, 67 Hz)
70 °C	16.90 (≈90 Hz)	overlap A	0.84 (20 Hz)	−3.25 (1 H, 17 Hz), −17.34 (6 H, 34 Hz)
$(Me_3CC_5H_4)_4Ce_2(\mu\text{-}OPh)_2$	21.52 (72 Hz)	14.98 (73 Hz)	−4.57 (16 Hz)	−3.41 (1 H), −5.03 (2 H, d, 7 Hz), −16.23 (2 H)
$(MeC_5H_4)_3UOMe$	−10.60 (6 H, 12 Hz)	−22.41 (6 H, 11 Hz)	−0.32 (9 H, 8 Hz)	45.13 (3 H, 12 Hz)
$(MeC_5H_4)_3UOCHMe_2$	−13.93 (6 H, 8 Hz)	−23.31 (6 H, 8 Hz)	−1.54 (9 H, 3 Hz)	55.5 (1 H, 20 Hz), 15.7 (6 H, 8 Hz)
$(MeC_5H_4)_3UOPh$	−4.75 (6 H, 7 Hz)	−11.97 (6 H, 7 Hz)	−3.11 (9 H, 3 Hz)	4.72 (2 H, t, 8 Hz), 3.96 (2 H, t, 8 Hz), −10.48 (1 H)
$(MeC_5H_4)_3USCHMe_2$	−1.24 (6 H, 7 Hz)	−8.77 (6 H, 7 Hz)	−1.58 (9 H, 3 Hz)	−19.7 (6 H, d, 7 Hz), −44.7 (1 H, m, 7 Hz)
$(MeC_5H_4)_3UOC_6F_5$	3.55 (6 H, 10 Hz)	−9.92 (6 H, 9 Hz)	−5.14 (9 H, 3 Hz)	
$(Me_3CC_5H_4)_3USPh$	3.64 (6 H, 7 Hz)	−12.16 (6 H, 7 Hz)	−2.43 (27 H, 4 Hz)	−1.38 (2 H), −8.43 (1 H), −21.2 (2 H, t, 8 Hz)

[a] The observed spectra show that A = A′, B = B′, and X = X′ in the $AA'BB'X_3$ or $AA'BB'X_9$ spin systems of these complexes. All spectra were recorded in C_6D_6 and referenced relative to tetramethylsilane, $\delta = 0$, at 30 °C with positive values being to high frequency. The A protons are arbitrarily assigned to those farthest downfield. Relative intensities and line widths at half peak height are given in parentheses.

In addition, $[(Me_3Si)_2N]_4Eu_2(\mu\text{-}SCMe_3)_2$ has been isolated from $Eu[N(SiMe_3)_2]_3$ and the thiol,[6a] and cerium silylamides have been used to prepare several cerium phenoxides.[6b] Recently, $(Me_5C_5)_2Ce_2(OCMe_3)_2(\mu\text{-}OCMe_3)_2$ has been prepared from $(Me_5C_5)_2CeCH(SiMe_3)_2$ and Me_3COH.[6c]

It is apparent that there is no generally applicable synthetic route to cyclopentadienyllanthanide alkoxides or thiolates. Since the pK_a of many alcohols and thiols in water[7a] is less than that of cyclopentadiene (pK_a in water is 16[7c] and in dimethyl sulfoxide, DMSO, is 18[7b]), the reaction of binary metallocenes of the lanthanide metals should provide a general synthetic route to this class of compound. Indeed, this type of reaction has been used to prepare cyclopentadienyl halides, alkynyls, and acetylacetonate derivatives from the metallocenes and ammonium halides, acetylenes, and acetylacetone, respectively, though no alkoxides nor thiolates have been prepared by this route.[8] It is difficult to use solution equilibrium acidity scales with absolute confidence since these scales depend upon the extent of hydrogen bonding and ion pairing in solvents such as water[7a] or DMSO,[7b] particularly since the reactions of interest in this paper are done in hydrocarbon solvents. The acidity scale in water predicts the course of the reactions in the experiments described in this paper more satisfactorily than those in DMSO. This is illustrated by the observations that the pK_a of MeOH in water is 15.5 and in DMSO it is 29 and methanol does indeed react with the metallocenes discussed in this paper. The main reason for the large difference in acidity in these two solvents is that hydrogen-bonding interactions in water between small, highly charged anions such as methoxide does not change much with change in size of the anion though the negative charge–dipole interaction substantially changes in solvents with high dielectric constants such as DMSO. Since the cyclopentadienide anion is charge delocalized, the difference in solvation energies between it and, say, methoxide anion will vary enormously in solvents with high dielectric constants, such as DMSO, whereas the hydrogen-bonding interactions in this pair of anions will not vary as much. This qualitative rationalization is consistent with the experimental results described in this paper and helps to understand the reasons for the greater utility of the acidity scale in water rather than that in DMSO. As will be described, steric effects also play a role in the proton-exchange reactions.

In this paper we describe the synthesis of several $(RC_5H_4)_4Ce_2(\mu\text{-}ER)_2$ derivatives, prepared from reaction of $(RC_5H_4)_3Ce$ and alcohols and thiols, and the extension of this synthetic method to the trivalent uranium metallocenes, which gives the tetravalent compounds $(RC_5H_4)_3UER$ as the final product.

Synthetic Studies

Addition of 1 mol equiv of isopropyl alcohol [p$K_a(H_2O)$ = 17.1] to $(Me_3CC_5H_4)_3Ce$ in hexane results in a series of color changes that go from purple to brown to green to yellow followed by precipitation of a yellow solid. Yellow crystals of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}OCHMe_2)_2$ may be isolated in good yield by crystallization of the yellow solid from toluene. Experimental details for the synthesis and characterization of this compound and all of the compounds described in this manuscript are in the Experimental Section, and ^{1}H NMR spectroscopic data are shown in Table I. The isopropoxide compound gives a dimeric molecular ion in the mass spectrum, and a single-crystal X-ray diffraction study shows that the compound is a

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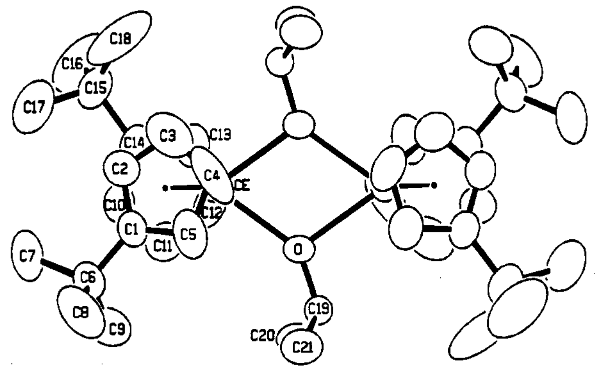

Figure 1. ORTEP diagram of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}OCHMe_2)_2$, 50% probability ellipsoids; C(19) is disordered and refined as two isotropic half-atoms, only one conformation of which is shown. Ce–C (av) = 2.83 ± 0.04 Å; Ce–Cp (cent) = 2.58 Å; Ce–O = 2.373 (3) Å, 2.369 (3) Å; Ce···Ce = 3.844 (2) Å; Ce–O–Ce = 108.3 (1)°; O–Ce–O = 71.7 (1)°; Ce–O–C(19) = 143.3 (5)°, 108.2 (5)°; Cp (cent)–Ce–Cp (cent) = 128.5°.

dimer in solid state with bridging isopropoxide groups, Figure 1. Phenol [$pK_a(H_2O)$ = 10.0] behaves similarly, giving yellow $(Me_3CC_5H_4)_2CeOPh$, which presumably is dimeric, though we have been unable to observe a molecular ion in the mass spectrum and we have been unable to obtain crystals suitable for a X-ray diffraction study. Addition of MeOH [$pK_a(H_2O)$ = 15.5] or H_2O to $(Me_3CC_5H_4)_3Ce$ gives a white precipitate, presumably $Ce(OMe)_3$ or $Ce(OH)_3$ as, perhaps, its hydrated oxide and the starting material $(Me_3CC_5H_4)_3Ce$ as the only product isolated in low (30–50%) yield (eq 1). Further,

$$(RC_5H_4)_3Ce + ROH \rightarrow \tfrac{2}{3}(RC_5H_4)_3Ce + \tfrac{1}{3}Ce(OR)_3 + RC_5H_5 \qquad (1)$$

Me_2CHOH, MeOH, or H_2O behave similarly with $(MeC_5H_4)_3Ce(THF)$, viz., a white precipitate and $(MeC_5H_4)_3Ce(THF)$ are formed. From the color changes, it is apparent that $(MeC_5H_4)_3Ce(THF)$ reacts faster with a given alcohol than does $(Me_3CC_5H_4)_3Ce$ and the former also undergoes ligand redistribution reactions faster than does the latter. *tert*-Butyl alcohol [$pK_a(H_2O)$ = 19.2] does not react with $(Me_3CC_5H_4)_3Ce$ under reflux in toluene for 5 days.

Thiols also react with the cerium metallocenes by proton transfer. Addition of 1 mol equiv of Me_2CHSH [$pK_a(H_2O)$ = 10.9] to $(Me_3CC_5H_4)_3Ce$ in hexane slowly gives a magenta solution from which magenta crystals of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$ may be isolated by crystallization from pentane. A dimeric molecular ion is observed in the mass spectrum, and an X-ray study shows that the thiolate is dimeric in solid state with bridging thiolate groups (Figure 2). Thiophenol [$pK_a(H_2O)$ = 6.6] behaves similarly, giving pink $(Me_3CC_5H_4)_2CeSPh$, which is presumably dimeric though the mass spectrum gives, as the highest mass peak, an ion due to $[M - (Ph)_2]^+$. Curiously, Me_3CSH [$pK_a(H_2O)$ = 11.2] does not react with $(Me_3CC_5H_4)_3Ce$ though it does react with $(MeC_5H_4)_3Ce(THF)$ to give $(MeC_5H_4)_2CeSCMe_3$, which we assume is a dimer with bridging thiolate groups.

The observation that neither Me_3COH nor Me_3CSH react with $(Me_3CC_5H_4)_3Ce$, though the thiol reacts with the sterically less congested metallocene $(MeC_5H_4)_3Ce(THF)$, seems to suggest that equilibrium acidities are not always a reliable measure of the extent of reaction and that kinetic factors play a role. This statement is deliberately vague since we do not know the pK_a of either $Me_3CC_5H_5$ or MeC_5H_5 though both will be poorer acids than C_5H_6, nor do we know the mechanism of the proton-transfer reaction. Relative to mechanism, it has been shown that Cp_2Ni reacts with RSH in an associative, rate-determining step followed by a fast proton-transfer step.[9] If we assume a similar mechanism in the cerium compounds, then steric effects in the transition state of an associative substitution mechanism will be important and the lack of reaction of Me_3CSH can be understood as a kinetic effect.

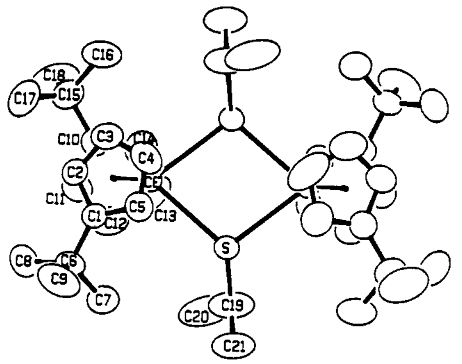

Figure 2. ORTEP diagram of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$, 50% probability ellipsoids. Ce–C (av) = 2.78 ± 0.02 Å; Ce–Cp (cent) = 2.52 Å; Ce–S = 2.870 (2), 2.894 (2) Å; Ce···Ce = 4.449 (2) Å; Ce–S–Ce = 101.06 (6)°; S–Ce–S = 78.94 (6)°; Ce–S–C(19)°, 128.5 (3)°, 118.2 (4)°; Cp (cent)–Ce–Cp (cent) = 131°.

In solution the thiolate dimers undergo chemical exchange. This was shown by mixing the phenylthiolate and isopropylthiolate at room temperature in a 1:1 molar ratio in $PhMe\text{-}d_8$ in an NMR tube at 30 °C. The resulting spectrum consists of resonances due to the individual thiolates, most easily monitored by the Me_3C resonance on each species in equal ratios at δ −5.06 for $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$ and δ −8.73 for $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SPh)_2$ and a new Me_3C resonance at δ −7.21, the intensity of which is twice that of each of the other Me_3C resonances. The other features in the spectrum may be assigned by assuming that it is a 1:1:2 mixture of the components shown in eq 2. The area ratio of the

$$(RC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2 + (RC_5H_4)_4Ce_2(\mu\text{-}SPh)_2 \rightleftharpoons 2(RC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)(\mu\text{-}SPh) \qquad (2)$$

resonances due to the three species does not change with temperature, and the resonances do not coalesce though the chemical shifts do change as expected for a paramagnetic compound. The ^1H NMR experiment shows that the thiolates do exchange bridging ligands in solution and that once chemical equilibrium is reached, the rate of intermolecular chemical exchange is slow on the NMR time scale. The ^1H NMR data do not allow us to distinguish between a mechanism that involves dissociation of the dimers into two monomers then recombination or partial bridge opening followed by exchange then recombination.

The trivalent uranium metallocene $(MeC_5H_4)_3U(THF)$ behaves differently than the cerium metallocenes with alcohols and thiols. In the uranium case, the net result is oxidation of uranium as shown in eq 3, where ER is

$$(MeC_5H_4)_3U(THF) + HER \rightarrow (MeC_5H_4)_3UER + \ldots \qquad (3)$$

OMe, $OCHMe_2$, OPh, or $SCHMe_2$. The red $(Me_3CC_5H_4)_3USPh$ derivative was prepared similarly. Experimental details are in the Experimental Section, and ^1H NMR data are in Table I. Derivatives of the type Cp_3UER, where E is oxygen or sulfur, have been prepared previously by metathetical exchange reactions, so this class of compound is not new though the synthetic reaction in eq 3 is new.[10] The different type of reaction shown by

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cerium and uranium metallocenes toward alcohols and thiols most likely reflects the case of oxidizing uranium: the U(IV)/U(III) couple is −0.63 V in aqueous acid whereas the Ce(IV)/Ce(III) couple is +1.74 V.[11] Oxidation of trivalent uranium metallocenes to tetravalent compounds has been observed previously; this electron-transfer reaction is emerging as a general pattern whenever the resulting tetravalent metallocene is kinetically accessible.[12]

It is noteworthy that the isolated yield of the tetravalent uranium compounds never exceeds ca. 35%. Perhaps the low yields are due to some type of ligand substitution, redistribution reactions shown in eqs 4–6. Equation 4 is

$$(RC_5H_4)_3U + HER \rightarrow (RC_5H_4)_2UER + RC_5H_5 \quad (4)$$

$$(RC_5H_4)_2UER + (RC_5H_4)_3U \rightarrow (RC_5H_4)_3UER + \text{“}(RC_5H_4)_2U\text{”} \quad (5)$$

$$2(RC_5H_4)_2UER \rightarrow (RC_5H_4)_3UER + \text{“}(RC_5H_4)_2U\text{”} \quad (6)$$

a proton-transfer reaction analogous to that found in the cerium metallocenes described above, and eqs 5 and 6 show two types of valence disproportionation reactions, which would account for the low yield of product; the fate of “$(RC_5H_4)_2U$” is unknown. An additional reaction, shown in eq 7, is not likely since we do not detect hydrogen evolution in the synthetic reaction and the yield of this hypothetical reaction would be higher than that found in the actual reaction.

$$(RC_5H_4)_3U + HER \rightarrow (RC_5H_4)_3UER + \tfrac{1}{2}H_2 \quad (7)$$

To test these two sets of reactions, viz., the valence disproportionation reactions shown in eqs 4–6 or the oxidation by hydrogen reduction reaction in eq 7, we have done the following experiment. Addition of 1 mol equiv of benzenethiol to $(Me_3CC_5H_4)_3U$ in hexane at −25 °C results in a color change from green to red and precipitation of a green solid from the red mother liquor. The green solid was dissolved in toluene at −30 °C and crystallized as dark green crystals from that solvent in an isolated yield of 24%. The green crystals were shown to be dimeric $(Me_3CC_5H_4)_4U_2(\mu\text{-}SPh)_2$ by elemental analysis and mass spectroscopy. It is noteworthy that the other uranium compounds reported herein all give monomeric molecular ions. The infrared spectrum of the dimeric uranium compound is virtually superimposable upon that of the cerium analogue, suggesting that the compounds have a similar structure. Dissolution of the green crystals in C_6D_6 followed by observation of the ^1H NMR spectrum shows two sets of $Me_3CC_5H_4$ resonances in a 9:2:2 ratio at δ −17.6, 6.28, −7.58 and δ 2.43, 3.64,−12.2. The former set of resonances was substantially broader, by ca. an order of magnitude, than the latter, and the intensity of the former set diminished at the expense of the latter set of resonances with time, concomitant with a color change from green to red. The latter set of resonances is due to $(Me_3CC_5H_4)_3USPh$; the narrow line widths are consistent with tetravalent uranium.[12a] We interpret the NMR experiment in the following way: the initially formed green compound $(Me_3CC_5H_4)_2USPh$, which is a dimer, prepared by proton transfer according to eq 4, undergoes a ligand and valence redistribution reaction, either as illustrated in eq 5 or 6 to give the red isolated product, $(Me_3CC_5H_4)_3USPh$, and a subvalent uranium species that decomposes. Hence, the difference in behavior shown by trivalent uranium and cerium metallocenes with protic acids whose pK_a's are similar to or less than that of C_5H_6 is due to the M(IV)/M(III) redox couple being more favorable for uranium than cerium in these metallocenes.

Table II. Positional Parameters with Estimated Standard Deviations for $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$

atom	*x*	*y*	*z*
Ce	0.36143 (2)	0.02427 (2)	0.06954 (2)
S	0.47679 (10)	0.10219 (11)	−0.10508 (15)
C1	0.1902 (4)	0.0068 (4)	−0.0762 (5)
C2	0.1763 (4)	−0.0424 (4)	0.0311 (5)
C3	0.2325 (5)	−0.1288 (5)	0.0402 (6)
C4	0.2808 (5)	−0.1327 (5)	−0.0600 (6)
C5	0.2553 (4)	−0.0499 (5)	−0.1328 (5)
C6	0.1370 (4)	0.0966 (4)	−0.1275 (6)
C7	0.2064 (5)	0.1752 (6)	−0.1656 (8)
C8	0.0780 (5)	0.1450 (6)	−0.0358 (7)
C9	0.0685 (6)	0.0619 (7)	−0.2368 (7)
C10	0.3347 (4)	0.0772 (4)	0.3084 (5)
C11	0.2828 (5)	0.1468 (5)	0.2320 (5)
C12	0.3433 (7)	0.2048 (5)	0.1753 (7)
C13	0.4356 (7)	0.1719 (7)	0.2164 (7)
C14	0.4308 (5)	0.0943 (6)	0.2949 (6)
C15	0.2961 (6)	0.0080 (5)	0.3997 (6)
C16	0.3502 (7)	−0.0934 (6)	0.4000 (8)
C17	0.1903 (7)	−0.0108 (8)	0.3722 (10)
C18	0.3200 (10)	0.0601 (9)	0.5251 (7)
C19	0.4952 (8)	0.2314 (6)	−0.1453 (8)
C20	0.4834 (10)	0.3030 (7)	−0.0598 (10)
C21	0.4591 (7)	0.2513 (6)	−0.2730 (7)

Table III. Positional Parameters with Estimated Standard Deviations for $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}OCHMe_2)_2$

atom	*x*	*y*	*z*
Ce	0.13015 (2)	0.02736 (1)	0.11893 (2)
O	−0.07319 (29)	0.01614 (23)	0.07023 (27)
C1	0.2144 (4)	−0.0744 (4)	0.3244 (4)
C2	0.3015 (5)	−0.0764 (5)	0.2674 (5)
C3	0.2686 (8)	−0.1272 (6)	0.1708 (6)
C4	0.1578 (10)	−0.1597 (4)	0.1659 (5)
C5	0.1221 (6)	−0.1250 (4)	0.2595 (5)
C6	0.2208 (5)	−0.0383 (4)	0.4399 (4)
C7	0.3425 (7)	−0.0017 (6)	0.4901 (6)
C8	0.2022 (9)	−0.1212 (6)	0.5152 (5)
C9	0.1330 (7)	0.0397 (5)	0.4405 (6)
C10	0.2505 (5)	0.1819 (4)	0.2328 (5)
C11	0.1332 (5)	0.2058 (4)	0.2033 (6)
C12	0.1042 (5)	0.2176 (4)	0.0874 (6)
C13	0.2015 (5)	0.1998 (4)	0.0463 (5)
C14	0.2942 (4)	0.1793 (3)	0.1368 (4)
C15	0.4212 (5)	0.1720 (5)	0.1347 (5)
C16	0.4620 (8)	0.2627 (7)	0.0960 (10)
C17	0.4947 (7)	0.1584 (11)	0.2518 (8)
C18	0.4428 (8)	0.0939 (10)	0.0633 (15)
C19	−0.1733 (9)	0.0316 (7)	0.1099 (8)
C19[a]	−0.1241 (12)	0.0405 (9)	0.1563 (11)
C20	−0.1804 (5)	0.1337 (4)	0.1448 (5)
C21	−0.1858 (6)	−0.0362 (5)	0.1995 (5)

[a] Half-atom of a disordered position.

Structural Studies

An ORTEP diagram of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}OCHMe_2)_2$ is shown in Figure 1 and of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$ in Figure 2. Positional parameters are in Tables II and III, and crystal data are in Table IV. Both compounds are

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Table IV. Crystallographic Summary and Data Processing

	$(Me_3CC_5H_4)$-$Ce_2(\mu$-$SCHMe_2)_2$	$(Me_3CC_5H_4)_4$-$Ce_2(\mu$-$OCHMe_2)_2$
a, Å[a]	14.255 (9)	11.962 (4)
b, Å	13.585 (9)	14.489 (5)
c, Å	11.265 (7)	12.384 (5)
β, deg	96.02 (5)	103.31 (3)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
vol, Å^3	2169.5	2088.7
d(calcd), g/cm^3	1.401	1.789
Z	2	2
temp, °C	23	22
empirical formula	$C_{42}H_{66}S_2Ce_2$	$C_{42}H_{66}O_2Ce_2$
f(000)	932	900
fw	915.36	883.23
color	purple	yellow
abs coeff, cm^{-1}	22.23	22.16
hkl limits	h,−16,16; k,0, 16; l−13,13	h,−14,14; k,0,17; l,−14,14
no. of scan data	7665	7397
no. of unique reflns	3847	3707
R_{int}[b]	0.019	0.021
no. of nonzero weighted data	2899 $[F^2 > 2\sigma(F^2)]$	2874 $[F^2 > 2\sigma(F^2)]$
p[c]	0.060	0.050
extinction k[d]	1.63×10^{-7}	1.99×10^{-7}
max extinction corr, %	12.6	12.9
no. of parameters	208	207
R(nonzero wtd dat)[e]	0.028	0.028
R_w[f]	0.046	0.042
R (all data)	0.045	0.044
goodness of fit[g]	1.23	1.30
max shift/esd in least squares	0.02	0.003
max/min in diff man, e/Å^3	0.63, −0.40	0.69, −0.44

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 31 reflections ($20 < 2\theta < 34$) for the S-containing compound and 33 reflections ($20 < 2\theta < 35$) for the O-containing compound. [b] R_{int} = agreement factor between equivalent or multiply measured reflections $= \sum_i\sum_j[I(hkl)_j - \langle I(hkl)_i]/\sum(I(hkl)_i\rangle]$. [c] In the least-squares analysis the assigned weights to the data, $w = 1.0/[\sigma F]^2$, 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 weighted residuals of the strong reflections to be comparable to the weak ones. [d] Simple extinction correction has the form $(F_{obs})_{corr} = (1 + kI)F_{obs}$, where I is the uncorrected intensity and F_{obs} is the observed scattering amplitude. [e] $R = \sum[|F_{obs} - |F_{calc}|]/\sum(F_{obs})$. [f] $R_w = \{\sum[w^*|F_{obs}| - |F_{calc}|]^2/\sum(w_xF_{obs}{}^2)\}^{1/2}$. [g] σ_1 = error in observation of unit weight $= \{\sum(w_x[|F_{obs}| - |F_{calc}|]^2)/(no - n_v)\}$, where o_0 is the number of observations and n_v is the number of variables.

centrosymmetric; the Ce_2O_2 and Ce_2S_2 units are planar, and the geometry at cerium in both compounds may be described as pseudotetrahedral. The geometry at oxygen in the isopropoxide is planar since the angles sum to 359.8°; since the two independent Ce–O–C(19) angles are not equal, the geometry at oxygen is not trigonal planar. Planar geometry at oxygen is inevitably observed in bridging alkoxide compounds.[13] On the other hand, the geometry at sulfur in the isopropylthiolate is pyramidal, since the angles about sulfur sum to 348°, and the isopropyl groups are in an anti configuration relative to the Ce_2S_2 ring. This is also the usual geometry found in compounds in which the thiolate group bridges two metal centers.[4a,5]

The two independent Ce–O distances in the isopropoxide are equal, the averaged distance being 2.371 ± 0.001 Å. The two Ce–S distances in the isopropylthiolate are, however, not equal; the individual distances are 2.870 (2) and 2.894 (2) Å, with the average being 2.882 ± 0.006 Å. It is difficult to find examples in the literature of two equivalent molecules that differ only in the identity of the bridging atom. In the gas-phase structures of $Me_4Al_2(\mu$-$OCMe_3)_2$[14a] and $Me_4Al_2(\mu$-$SMe)_2$,[14b] the Al–S distance is 0.51 Å longer than the Al–O distance; exactly the difference found in the cerium molecules described in this paper. The longer Ce–S distance, relative to Ce–O, is responsible for the slight distortions of the coordination geometry that is apparent upon detailed comparison of the two compounds; see Figures 1 and 2.

Experimental Section

All of the compounds were handled as previously described by using techniques and instruments previously described.[15]

$(Me_3CC_5H_4)_4Ce_2(\mu$-$OCHMe_2)_2$. To $(Me_3CC_5H_4)_3Ce$[16] (1.48 g, 2.96 mmol) dissolved in hexane (30 mL) was added, via syringe, isopropyl alcohol (0.23 mL, 3.0 mmol). The solution color gradually turned from purple to brown to green and finally to yellow, and a yellow precipitate was observed. The suspension was stirred for 6 h, and then the solvent was removed under reduced pressure. The yellow solid was dissolved in toluene (50 mL) and filtered, and the filtrate was concentrated to ca. 30 mL. Cooling the extract to −20 °C for 3 h, followed by cooling to −80 °C, yielded yellow microcrystals (0.83 g, 64%), mp 240–241 °C. Anal. Calcd for $C_{42}H_{66}Ce_2O_2$: C, 57.1; H, 7.53. Found: C, 56.9; H, 7.64. IR 1270s (br), 1155 (m, 1110 m, 1070 w, 1048 w, 1033 w, 950 m, 850 w, 822 m, 810 w, 755 s, 735 m, 673 m, 530 w, 440 w, 335 m (br), 258 w cm^{-1}. The EI mass spectrum showed a molecular ion at m/e = 882 amu. The molecular ion isotropic cluster was simulated: m/e (calcd %, obsvd %) 882 (100, 100), 883 (46.9, 22.3), 844 (36.2, 10.3), 885 (13.6, 28.0).

$(Me_3CC_5H_4)_4Ce_2(\mu$-$OPh)_2$. To $(Me_3CC_5H_4)_3Ce$ (0.70 g, 1.4 mmol) dissolved in hexane (30 mL) was added phenol (0.13 g, 1.4 mmol) dissolved in hexane (10 mL). The purple solution turned yellow upon addition with formation of a yellow precipitate. The suspension was stirred for 4 h, and then the solvent was removed under reduced pressure. The yellow solid was extracted with toluene (45 mL) and filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the extract to −20 °C afforded yellow crystals (0.33 g, 50%), mp 258–260 °C. Anal. Calcd for $C_{48}H_{62}Ce_2O_2$: C, 60.6; H, 6.57. Found: C, 61.2; H, 6.59. IR 1588 s, 1575 m, 1273 m, 1222 s, 1160 m, 1150 w, 1065 m, 1048 m, 1035 m, 1015 m, 975 w, 915 w, 890 w, 835 m, 818 s, 810 m, 760 s, 735 m, 720 m, 692 m, 672 m, 567 m, 448 m, 350 m, 262 m cm^{-1}. The EI mass spectrum did not show a molecular ion at m/e = 950 amu; the observed parent ion was m/e = 503, which corresponds to $(Me_3CC_5H_4)_3Ce$.

$(Me_3CC_5H_4)_4Ce_2(\mu$-$SCHMe_2)_2$. Isopropyl thiol (0.31 g, 3.4 mmol) was added, via syringe, to $(Me_3CC_5H_4)_3Ce$ (1.70 g, 3.37 mmol) dissolved in hexane (30 mL). The purple solution was stirred for 18 h, during which time the color gradually turned to magenta. The solvent was removed under reduced pressure. The pink solid was dissolved in hexane (30 mL) and filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to −20 °C afforded magenta crystals (0.84 g, 55%), mp 139–142 °C. An additional 10–20% can be obtained by concentrating the mother liquor to ca. 7 mL and cooling to −20 °C. Anal. Calcd for $C_{42}H_{66}Ce_2S_2$: C, 55.1; H, 7.27; S, 7.00. Found: C, 55.3; H, 7.28; S, 6.95. IR 1272 m, 1248 w, 1200 w, 1152 s, 1045 m, 1038 m, 970 w, 910 w, 820 s, 753 s, 672 m, 605 m, 452 w, 353 w, 260 w cm^{-1}. The EI mass spectrum showed a molecular ion at m/e = 914 amu. The molecular ion isotopic cluster was simulated: m/e (calcd %, obsvd %) 914 (100, 100), 915 (48.4, 49.4), 916 (45.4, 44.6), 917 (18.1, 17.7), 918 (8.1, <1).

$(Me_3CC_5H_4)_4Ce_2(\mu$-$SPh)_2$. To $(Me_3CC_5H_4)_3Ce$ (0.91 g, 1.8 mmol) dissolved in hexane (30 mL) was added, via syringe,

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thiophenol (0.12 mL, 1.7 mmol). After ca. 1 min a pink precipitate began to form in the purple solution. The mixture was stirred for 12 h, and then the solvent was removed under reduced pressure. The pink residue was dissolved in toluene (30 mL) and filtered, and the filtrate was concentrated to ca. 25 mL. Cooling the extract to −20 °C afforded pink crystals that crumbled and collapsed to a powder when exposed to vacuum (0.61 g, 69%), mp 191–194 °C. Anal. Calcd for $C_{48}H_{62}Ce_2S_2$: C, 58.6; H, 6.34; S, 6.52. Found: C, 59.1; H, 6.47; S, 6.12. IR 1570 w, 1407 w, 1300 w, 1273 m, 1200 w, 1187 w, 1165 w, 1151 m, 1120 w, 1078 m, 1060 w, 1045 m, 1038 w, 1020 m, 970 w, 912 w, 822 m, 775 m, 768 s, 757 mw, 740 s, 720 mw, 690 s, 680 m, 483 w, 455 w, 425 w, 258 m cm^{-1}. The EI mass spectrum did not give a molecular ion at *m/e* = 983 amu; the observed parent ion corresponds to $(Me_3CC_5H_4)_4Ce_2S_2$, M^+ = 796 amu.

$(MeC_5H_4)_4Ce_2(\mu\text{-}SCMe_3)_2$. To $(MeC_5H_4)_3Ce(THF)$[15] (0.84 g, 3.4 mmol) dissolved in diethyl ether (40 mL) was added, via syringe, *tert*-butyl thiol (0.38 mL, 3.4 mmol). The solution gradually turned from yellow to brown then to purple. The solution was stirred for 12 h, and then the solvent was removed in vacuo. The purple solid was extracted with hexane (2 × 30 mL) and filtered, and the filtrate was concentrated to ca. 50 mL. Cooling the extract to −20 °C afforded purple crystals (0.31 g, 24%), mp 266–268 °C (dec). Anal. Calcd for $C_{32}H_{46}Ce_2S_2$: C, 49.6; H, 5.98. Found: C, 49.7; H, 5.81. IR 1300 w, 1232 w, 1205 w, 1168 w, 1142 s, 1060 w, 1040 w, 1028 m, 970 w, 928 m, 850 w, 820 s, 765 s, 618 m, 588 m, 390 m, 325 m, 250 s, 220 w cm^{-1}.

$(MeC_5H_4)_3UOMe$. Methanol (0.08 mL, 2.0 mmol) was added, via syringe, to $(MeC_5H_4)_3U(THF)$[12a] (1.15 g, 2.10 mmol) dissolved in diethyl ether (30 mL). The red solution slowly turned green after addition. The solution was stirred for 20 h, and then the solvent was removed under reduced pressure. The green solid was dissolved in hexane (40 mL) and filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to −20 °C afforded green microcrystals (0.32 g, 30%), mp 274–275 °C (turned brown at 120 °C). Anal. Calcd for $C_{19}H_{24}OU$: C, 45.1; H, 4.78. Found: C, 44.8; H, 4.78. IR 1260 w, 1248 w, 1168 w, 1150 w, 1070 w, 1045 w, 1030 w, 970 w, 930 m, 890 w, 820 s (br), 760 s, 608 m, 422 s, 330 s, 225 s cm^{-1}. The EI mass spectrum showed a molecular ion at *m/e* = 506 amu.

$(MeC_5H_4)_3UOCHMe_2$. This compound was prepared from $(MeC_5H_4)_3U(THF)$ and isopropyl alcohol in a manner similar to that used to prepare the methoxide, above, and crystallized as flaky green crystals in 37% yield from hexane (−20 °C), mp 196–200 °C. Anal. Calcd for $C_{21}H_{28}OU$: C, 47.2; H, 5.28. Found: C, 47.0; H, 5.11. IR 1330 m, 1240 w, 1160 m, 1130 s, 1065 w, 1045 m, 1035 m, 1030 m, 990 s, 930 w, 885 w, 842 s, 820 m, 760 s, 605 m, 550 s, 450 m, 421 m, 330 s, 228 s cm^{-1}. The EI mass spectrum showed a molecular ion at *m/e* = 534 amu.

$(MeC_5H_4)_3UOPh$. This compound was prepared in a manner similar to that used to prepare the methoxide, above, and crystallized as green crystals from hexane (−20 °C) in 34% yield, mp 127–128 °C. Anal. Calcd for $C_{24}H_{26}OU$: C, 50.7; H, 4.61. Found: C, 50.6; H, 4.53. IR 1580 s, 1300 w, 1258 s, 1158 m, 1150 w, 1065 w, 1049 w, 1029 w, 1018 w, 995 w, 973 w, 931 w, 884 w, 861 s, 845 w, 838 w, 812 w, 775 m, 762 s, 720 m, 690 m, 600 m, 520 w, 442 w, 337 w, 238 w cm^{-1}. The EI mass spectrum showed a molecular ion at *m/e* = 569 amu.

$(MeC_5H_4)_3USCHMe_2$. The thiolate was prepared from $(MeC_5H_4)_3U(THF)$ and isopropyl thiol in a manner similar to that used to prepare the methoxide, above, and crystallized as golden brown flakes from hexane (−20 °C) in 27% yield, mp 121–123 °C. Anal. Calcd for $C_{21}H_{28}SU$: C, 45.8; H, 5.13; S, 5.82. Found: C, 44.8; H, 5.13; S, 5.31. IR 1305 w, 1260 w, 1235 w, 1142 m, 1070 w, 1045 w, 1032 m, 972 w, 928 w, 890 w, 863 m, 851 m, 847 m, 795 m, 775 s, 720 s, 624 m, 605 m, 570 w, 440 mw, 363 mw, 341 m, 331 m, 242 m cm^{-1}. The EI mass spectrum showed a molecular ion at *m/e* = 550 amu.

$(Me_3CC_5H_4)_3USPh$. To $(Me_3CC_5H_4)_3U$ (1.07 g, 1.76 mmol) dissolved in hexane (30 mL) was added, via syringe, thiophenol (0.18 mL, 1.8 mmol). The green solution turned red, and a light red-brown precipitate formed. The solution was stirred for 5 h, and then the solvent was removed under reduced pressure. The red solid was extracted with hexane (30 mL) and filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to −20 °C afforded red crystals (0.28 g, 22%), mp 142–143 °C. Anal. Calcd for $C_{33}H_{44}SU$: C, 55.8; H, 6.24; S, 4.51. Found: C, 52.7; H, 6.32; S, 4.65. IR 1575 m, 1300 w, 1272 m, 1198 w, 1168 w, 1155 ms, 1070 mw, 1052 w, 1040 w, 1021 m, 970 m, 838 m, 798 m, 788 m, 772 ms, 765 s, 739 s, 720 m, 698 m, 678 mw, 611 m, 482 w, 418 w, 238 mw cm^{-1}. The EI mass spectrum showed a weak parent ion at *m/e* = 710 amu.

$(Me_3CC_5H_4)_4U_2(\mu\text{-}SPh)_2$. To $(Me_3CC_5H_4)_3U$ (1.07 g, 1.78 mmol) dissolved in hexane (15 mL) and cooled to −25 °C was added, via syringe, thiophenol (0.18 mL, 1.8 mmol). The solution color turned from green to red upon addition. After ca. 2 min a green precipitate began forming. The suspension was stirred for an additional 15 min, and then the precipitate was allowed to settle. The hexane was removed by filtration, and the remaining green microcrystalline solid was washed with hexane (2 × 10 mL, −25 °C). The solid was extracted with toluene (45 mL, −30 °C). This caused the solution color to become red. The solution was filtered, and the filtrate was concentrated to ca. 30 mL. Cooling to −20 °C afforded dark green crystals (0.25 g, 24%), mp 112–113 °C (dec). Anal. Calcd for $C_{48}H_{62}S_2U_2$: C, 48.9; H, 5.30; S, 5.44. Found: C, 48.5; H, 5.05; S, 4.24. IR 1570 m, 1405 w, 1300 w, 1272 m, 1200 w, 1186 w, 1165 w, 1150 m, 1118 w, 1075 m, 1062 w, 1038 m, 1018 m, 970 w, 912 mw, 845 w, 821 m, 812 w, 772 m, 763 s, 757 mw, 740 s, 718 mw, 690 s, 672 m, 481 mw, 453 w, 424 w, 239 mw cm^{-1}. ^1H NMR (C_6D_6, 28 °C) δ 6.28 (4 H, $\nu_{1/2} \approx 50$ Hz), −0.87 (1 H), −1.92 (2 H, d, J = 6.8 Hz), −7.58 (4 H, $\nu_{1/2} \approx 58$ Hz), −17.63 (18 H, $\nu_{1/2} \approx 13$ Hz), −21.07 (2 H). The NMR solution color gradually turned red with time. The ^1H NMR spectrum contained resonances due to $(Me_3CC_5H_4)_3USPh$; the integrated intensity of the latter resonances grew with time relative to those of $(Me_3CC_5H_4)_4U_2(\mu\text{-}SPh)_2$.

$(Me_3CC_5H_4)_3U$. *tert*-Butyllithium (0.52 mL of a 2.5 M pentane solution, 1.3 mmol) was added to $(Me_3CC_5H_4)_3UCl$[17] (0.85 g, 1.3 mmol) in tetrahydrofuran at −70 °C. An immediate color change from brown to red was observed. The solution was allowed to warm to room temperature, and the green solution was stirred at that temperature for 1 h. The volatile material was removed under reduced pressure, and the green residue was extracted with hexane (10 mL). The extract was filtered, the volume of the filtrate was decreased to ca. 5 mL; cooling to −80 °C afforded dark green crystals in 90% (0.72 g) yield, mp 80–81 °C. IR 3080 w, 1274 s, 1258 m, 1198 m, 1187 w, 1150 s, 1040 s, 1015 m, 901 m, 802 s, 750 vs, 695 w, 665 m, 455 m cm^{-1}. The EI mass spectrum contained a molecular ion at 601 amu, though satisfactory elemental analysis could not be obtained. ^1H NMR (C_6D_6, 29 °C) −21.0 (9 H, $\nu_{1/2}$ = 7 Hz), −24.2 (2 H, $\nu_{1/2}$ = 16 Hz), 9.04 (2 H, $\nu_{1/2}$ = 16 Hz).

X-ray Studies. Air-sensitive crystals of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$ (I) with dimensions 0.22 × 0.25 × 0.25 mm and $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}OCHMe_2)_2$ (II) with dimensions 0.18 × 0.15 × 0.30 mm were sealed inside 0.3-mm quartz capillaries. A modified Picker FACS-I automated diffractometer using graphite-monochromated Mo Kα radiation [$\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å] was used to collect θ–2θ scan data, 7663 and 7397 scans for the thiolate (I) and the alkoxide (II), respectively, to a 2θ limit of 50° using a scan width of (1.50 + 0.693 tan θ)° for I and (1.40 + 0.693 tan θ)° for II on 2θ. Three standard reflections were measured every 250 reflections; the intensities decayed 2% for I and 6% for II and were corrected accordingly. The data were corrected for Lorentz and polarization effects and absorption (analytical method);[18] the absorption corrections ranged from 1.23 to 1.36 for I and from 1.34 to 1.50 for II.

Cerium positions were located with the use of three-dimensional Patterson maps; subsequent least-squares refinements and electron density maps revealed the location of the other atoms. The structure was refined by full-matrix least-squares methods using anisotropic thermal parameters on the non-hydrogen atoms, with the exception of the disordered C19 in II. The estimated positional parameters of the hydrogen atoms on the cyclo-

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pentadienyl rings and the hydrogen atom on C19 of I were included with isotropic thermal parameters but were not allowed to vary. The central isopropoxide carbon atom, C19 of II, refined with anisotropic thermal parameters to a long ellipsoidal shaped atom, which strongly suggested disorder; this atom was assumed to be disordered and refined as two isotropic half-atoms. Scattering factors[19] were adjusted for anomalous dispersion. The positional parameters in Tables II and III, and crystal data are in Table IV.

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Supplementary Material Available: Tables of thermal parameters, additional distances and angles, calculated hydrogen positions, and the least-squares planes (10 pages); listings of the observed structure factors (14 pages). Ordering information is given on any current masthead page.

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Electronic Structure of Bis(dimethylmethylenephosphoranyl)dihydroborato(1−) Main-Group and Transition-Metal Complexes. A Case Study Involving Theoretical Pseudopotential ab Initio Calculations and UV Photoelectron Spectroscopy

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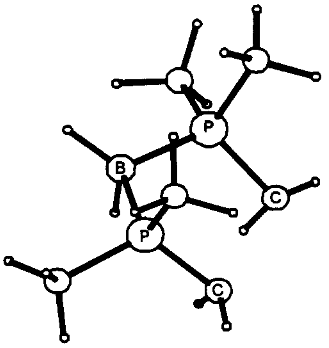
This contribution describes a study that uses He I/He II UV photoelectron spectroscopy and theoretical ab initio pseudopotential calculations to investigate the electronic structure of a large series of bis(dimethylmethylenephosphoranyl)dihydroborato(1−) [(L)$^-$] complexes. The series includes the pseudotetrahedral complexes $(CH_3)_2M(L)$ (M = Al, Ga) and $M(L)_2$ (M = Be, Cd, Hg), as well as the square-planar $M(L)_2$ (M = Ni, Pd, Pt) complexes. All complexes represent unusual examples of tetracoordinated alkyls and, in the case of homoleptic $M(L)_2$ complexes of d^8 transition-metal M(II) ions (M = Ni, Pt, Pd), are almost unique examples of square-planar alkyls. Reorganization energies in the ionic state as well as relativistic corrections in the case of the heavy atom in the $Pt(L)_2$ complex have been taken into account to interpret the photoelectron spectra. The theoretical results provide a convincing description of the metal–ligand bonding in these complexes. In the case of the $(CH_3)_2M(L)$ complexes both theoretical and experimental results indicate that their uppermost MOs can be described in terms of symmetry combinations of the ligand ylidic and methyl lone pairs perturbed by the metal subshells. This is also true in the case of the group II metal complexes. The metal–ligand bonding appears much more intriguing in the square-planar d^8 metal complexes, in which the metal d subshells lead to severe perturbations not only of ligand ylidic lone pairs but also of the deep σ MOs. Detailed assignments of the photoelectron spectra are proposed on the basis of both theoretical and experimental results. A tentative comparison of bonding between the phosphorus ylide under study and the more usual hydrocarbyl complexes has been carried out.

Introduction

In recent years the bis(dimethylmethylenephosphoranyl)dihydroborate uninegative anion [(L)$^-$] has been recognized as a novel, powerful ligand (I).[1] It has proven capable of stabilizing stoichiometries and coordination environments uncommon within usual homoleptic hydrocarbyls, thus forming stable metal-to-carbon σ-bonds with almost all the metals of the periodic table.[1] These, so called "onium-stabilized alkyls" possess equivalent Me_2PCH_2 groups and, hence, symmetrical bonding of lig-



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