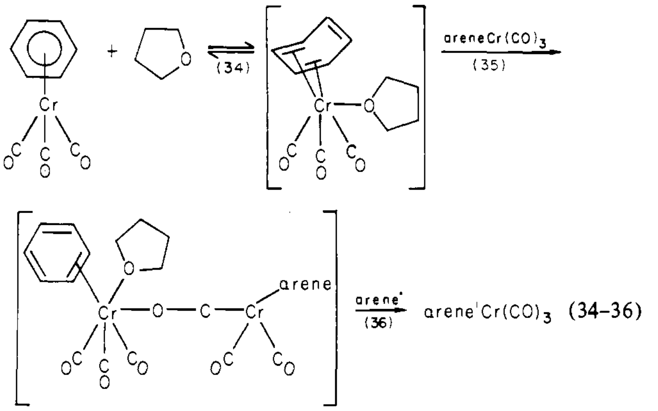
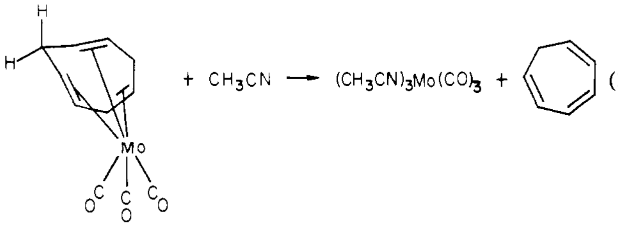
that these two catalysts are not competitive but somehow both participate at once. We tentatively suggest, in keeping with the discussion of the THF results above, that the (arene)carbonylchromium catalysts trap the reversibly formed THF adduct more efficiently than does arene itself.



(34-36)

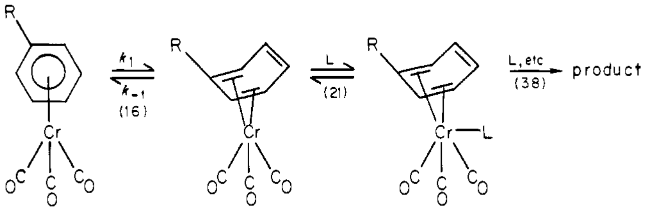
The intermediate species could also be $L_3Cr(CO)_3$ where the L's are both catalysts. This postulate implies a catalytic process which is second order in single catalysts, and such behavior has not yet been demonstrated in arene exchange. However, Al-Kathumi and Kane-Maguire[29] reported that a similar process (eq 37) is second order in acetonitrile.



(37)

Conclusions

Our results are consistent with a simple stepwise displacement of arenes in which there is essentially one mechanism involving a fluxional starting complex. The ligand L can be an arene, CO, or any of the catalysts mentioned above including the carbonyl of another (arene)tricarbonylchromium complex. This mechanism



(16, 21, 38)

can include the further reaction with L to give $L_2areneCr(CO)_3$ and finally $L_3Cr(CO)_3$. Any of these intermediates could react with another arene, making details of this mechanism look complicated. We suggest that all of the reactions studied could be represented by the stepwise, reversible reaction of an arene L leading to $L_3Cr(CO)_3$, where each intermediate can react with other electron pair donors.

This mechanism implies new processes such as neighboring group participation by an arene or other nucleophiles in arene exchange.[28] These processes and other catalytic reactions are under study.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE 81-20969) for support of this research.

Registry No. 1,5-COD, 111-78-4; THF, 109-99-9; $Cr(CO)_6$, 13007-92-6; PhCN, 100-47-0; (benzene)tricarbonylchromium, 12082-08-5; (*p*-xylene)tricarbonylchromium, 12129-27-0; (mesitylene)tricarbonylchromium, 12129-67-8; (hexamethylbenzene)tricarbonylchromium, 12088-11-8; (benzene)tricarbonylchromium (^{13}Co enriched), 76374-48-6; mesitylene, 108-67-8; pentanenitrile, 110-59-8; triphenylphosphine oxide, 791-28-6; pyridine, 110-86-1; ethyl acetate, 141-78-6; cyclohexanone, 108-94-1; di-*n*-butyl ether, 142-96-1; cyclohexane, 110-82-7; diglyme, 111-96-6.

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Organolanthanide and Organoyttrium Hydride Chemistry. 6. Direct Synthesis and ^1H NMR Spectral Analysis of the Trimetallic Yttrium and Yttrium–Zirconium Tetrahydride Complexes, $\{[(C_5H_5)_2YH]_3H\}\{Li(THF)_4\}$ and $\{[(CH_3C_5H_4)_2YH]_2[(CH_3C_5H_4)_2ZrH]H\}$[1]

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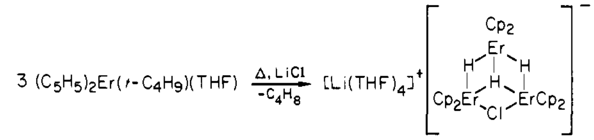
Contribution from the University of California, Irvine, Irvine, California 92717, and the University of Chicago, Chicago, Illinois 60637. *Received September 19, 1983*

Abstract: Improved syntheses for the trimetallic tetrahydride complexes $\{[(C_5H_5)_2LnH]_3H\}\{Li(THF)_4\}$ were investigated by studying the reactions of $[(C_5H_5)_2YH(THF)]_2$ with LiH, CH_3Li, and t-C_4H_9Li. The t-C_4H_9Li reaction generates the trimer, $\{[(C_5H_5)_2YH]_3H\}\{Li(THF)_4\}$, in 75% yield with $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)$ and $(C_5H_5)_3Y(THF)$ as byproducts. The reaction of $[(C_5H_5)_2YD(THF)]_2$ with t-C_4H_9Li forms the perdeuterio trimer, $\{[(C_5H_5)_2YD]_3D\}\{Li(THF)_4\}$. The latter synthesis indicates that the *tert*-butyl group does not provide an H^- ion for the trimer. A mechanism for formation of the trimer by in situ generation of a $(C_5H_5)_2YH_2^-$ intermediate which reacts with the dimeric hydride starting material to give the trimer is described. This mechanism was tested by reacting $[(CH_3C_5H_4)_2ZrH_2]_2$ with $[(CH_3C_5H_4)_2YH(THF)]_2$ to form the heterometallic tetrahydride $\{[(CH_3C_5H_4)_2YH]_2[(CH_3C_5H_4)_2ZrH]H\}$. The ^1H NMR spectra of $\{[(C_5H_5)_2YH]_3H\}\{Li(THF)_4\}$ and $\{[(CH_3C_5H_4)_2YH]_2[(CH_3C_5H_4)_2ZrH]H\}$ are presented and the HH, YH, and YY coupling constants are discussed on the basis of computer simulation of the spectra.

As part of our general investigation of the chemistry of complexes containing lanthanide–hydrogen and yttrium–hydrogen bonds,[3-7] we recently reported the synthesis of the novel trimetallic polyhydrides $\{[(C_5H_5)_2ErH]_3Cl\}\{Li(THF)_4\}$ (**1**) and $\{[(C_5H_5)_2$-

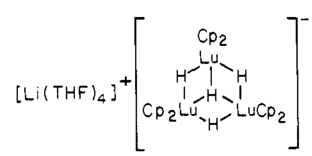
$\text{LuH}]_3\text{H}\}\{\text{Li(THF)}_4\}$ (**2**).[4] These complexes are unique in metal hydride chemistry since they are the first crystallographically characterized molecular trimetallic hydrides which contain a hydrogen atom inside and coplanar with a triangle of metal atoms.[8-10] Considering current interest in complexes containing hydrogen in metal clusters[8,11] and the fact that lanthanides are constituents in materials which have very high hydrogen storage capacity (e.g., LaNi_5[12,13]), it was desirable to develop high-yield syntheses of these complexes which would allow an extensive study of the chemistry of hydrogen in this new metallic coordination environment.

Complex **1** was originally obtained in 50% yield when $(C_5H_5)_2\text{Er}(t\text{-}C_4H_9)(\text{THF})$ underwent β-hydrogen elimination in the presence of LiCl (reaction 1).[4] Complex **2** was obtained in



(1)

12% yield from the product of the reaction of $[(C_5H_5)_2\text{LuCl}]_2$ with $t\text{-}C_4H_9\text{Li}$ in diethyl ether (reaction 2).[4] In reaction 2, an



(2)

unstable *tert*-butyl complex, possibly "$(C_5H_5)_2\text{Lu}(t\text{-}C_4H_9)(\text{Et}_2\text{O})$" or "$(C_5H_5)_2\text{Lu}(t\text{-}C_4H_9)\text{ClLi}(\text{Et}_2\text{O})_2$", presumably was formed. β-Hydrogen elimination from this species to form a hydride product which incorporated Li and H could generate the observed trimeric tetrahydride.

In this study, the high-yield synthesis of trimeric tetrahydride complexes analogous to **2** was our primary objective. Since the fully characterized dimeric hydrides, $[(C_5H_4R)_2\text{LnH(THF)}]_2$, (**3**) ($R = H, CH_3$; Ln = Lu[3], Er[3], Y[3], Tb[14]), can be readily prepared in 70–80% yield,[7] they were investigated as possible precursors to the trimeric hydrides. Yttrium was the metal of choice in this study, since it provides not only diamagnetic complexes characterizable by NMR spectroscopy but also additional structural information via Y–H coupling (100% abundant ^{89}Y has $I = {}^1/_2$).[3,6,7] In the past, isostructural and isochemical behavior have been observed for yttrium and the late lanthanides of similar radius.[15-18]

Analysis of the high-yield synthesis of $\{[(C_5H_5)_2\text{YH}]_3\text{H}\}\{\text{Li(THF)}_4\}$ described below suggested a general synthetic route to polymetallic polyhydride complexes similar to **1** and **2**. This idea has been tested experimentally and has led to the synthesis of the first heterometallic yttrium–zirconium complex.

Results and Discussion

Synthetic Strategy. The synthesis of the trimer $\{[(C_5H_5)_2\text{YH}]_3\text{H}\}\{\text{Li(THF)}_4\}$ (**2a**) from the dimer $[(C_5H_5)_2\text{YH(THF)}]_2$ (**3a**) in the simplest analysis requires cleavage of the dimer to form monomeric units which can either react with dimers to form trimers or directly aggregate to form the trimers. During the aggregation process an equivalent of LiH must be incorporated.

Cleavage of the hydride-bridged dimer requires replacement of the bridging hydride electron pair with some other two-electron donor, i.e., a base. For oxophilic metals like yttrium and the lanthanides, oxygen donor atom solvents capable of coordinating to the metal were obvious candidates. Tetrahydrofuran (THF) does not effect this cleavage, at least on the NMR time scale, since a clean triplet resonance arising from Y–H coupling is observed in both the ^{1}H and ^{89}Y NMR[20] spectra of **3a**. We have previously correlated loss of yttrium coupling with a dimer $\rightleftharpoons$ monomer equilibrium for $[(CH_3C_5H_4)_2\text{YCH}_3]_2$.[7] Oxygen-containing solvents more polar than THF can coordinate, but unfortunately they react further with **3a**. For example, ketones react to form alkoxides.[21] Nitrogen donor atom reagents such as pyridine and nitriles are also ineffective for the desired cleavage reaction, since they react to form hydropyridyl and alkylideneamido complexes, respectively,[7] by addition of Y–H across the unsaturated bonds.

An alternative approach to cleaving the dimers was to use anionic reagents. Since an equivalent of LiH had to be incorporated into the trimer following the cleavage, lithium reagents and particularly LiH were obvious choices.

Reaction of 3 with LiH. Reactions of **3a** with a stoichiometric amount of LiH (Li/Y = 0.33) and with excess LiH (Li/Y = 1.7) were examined. In each case, the infrared spectrum of the white powdery product lacked the prominent hydride absorption of **3a** at 1315 cm^{-1} and contained new absorptions at 1000–1100 cm^{-1}. These new absorptions occurred at energies distinctly lower than those of the hydride absorptions of the trimers **1** and **2** in the 1200–1250 cm^{-1} region.[4] Hence, although LiH does react with **3a**, the product hydride(s) is not the desired trimer.

One inherent problem in the above reaction is the low solubility of both reactants. The reaction of $[(CH_3C_5H_4)_2\text{YH(THF)}]_2$ (**3b**) with LiH was also examined to determine if the higher solubility of **3b** would allow a faster, perhaps cleaner reaction. Unfortunately, **3b** failed to react with LiH under a wide range of conditions. Hence, LiH does not appear to be a useful reagent for direct synthesis of trimeric hydrides from dimeric hydride precursors.

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(1) Presented in part at the Twelfth Sheffield-Leeds International Symposium on Organometallic, Inorganic and Catalytic Chemistry, Sheffield, England, March 1983, and the First Annual Texas A&M Industry–University Cooperative Chemistry Program, College Station, Texas, April 1983, Abstract 14.

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(21) Evans, W. J.; Meadows, J. H., in preparation.

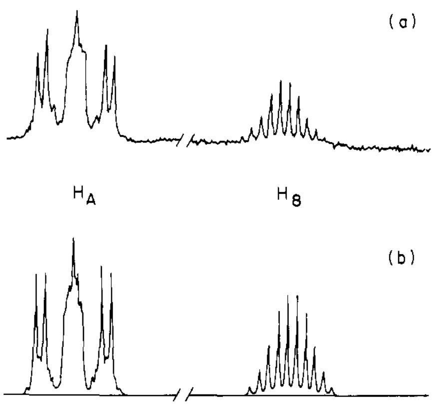
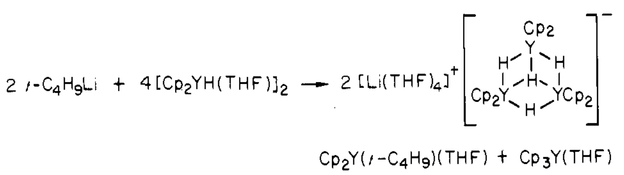


Figure 1. High-field portion of the 500-MHz ^1H NMR spectrum of $\{[(C_5H_5)_2YH]_3H\}\{Li(THF)_4\}$ (**2a**): (a) experimental spectrum in THF-d_8; (b) simulated spectrum using $^2J_{AB} = 8.5$ Hz, $^1J_{AY} = 29.7$ Hz, $^3J_{AY} = 1$ Hz, $^1J_{BY} = 17$ Hz, $J_{AA} = 4$ Hz, $J_{YY} = 4$ Hz, line width = 1.7 Hz, and $^1J_{AY} + {}^3J_{AY} = 30.7$ Hz.

Reaction of 3a with *t*-C_4H_9Li. *t*-C_4H_9Li was a second, reasonable choice for dimer cleavage. Acting as a Lewis base, the *tert*-butyl anion certainly could provide the electron pair believed necessary for cleavage of the dimer. The *tert*-butyl ligand was preferred over other alkyl groups such as methyl, since its steric bulk makes formation of a stable bridged species unlikely. This is a desirable feature since bridge formation might defeat the purpose of the cleavage reaction. The tendency of the *tert*-butyl group not to bridge is well-established in organolanthanide chemistry by the structural and chemical studies of $(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$.[3,22-24] *t*-$C_4H_9Li$ was also superficially favorable since it was the original source of lithium in trimers **1** and **2** and had the potential to generate LiH via β-hydrogen elimination.[25]

Addition of *t*-C_4H_9Li to **3a** in THF at −78 °C gives a yellow solution containing some suspended white **3a**. As the reactants warmed to −15 °C, the mixture developed into a clear, colorless solution. Solvent removal followed by washing with toluene gave a white powder identified as the trimer **2a** in 75% yield. The toluene extract contained the byproducts $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)$ (**4**) and $(C_5H_5)_3Y(THF)$[26] (**5**). The main features of this synthesis are shown in reaction 3 (Cp = C_5H_5). Variation of reaction stoichiometries indicated that a 1:3.7 Li:Y ratio was optimal for trimer production.



(3)

Characterization of $\{[(C_5H_5)_2YH]_3H\}\{Li(THF)_4\}$ (2a). The white toluene-insoluble product of reaction 3 had solubility properties similar to those of trimer **2**,[4] i.e., it was more soluble in THF than the dimeric starting material **3a**. Complexometric metal analysis, complete elemental analysis, and hydrolytic decomposition data also were similar to those obtained for **2** and were consistent with the formulation $\{[(C_5H_5)_2YH]_3H\}\{Li(THF)_4\}$ (**2a**). The infrared spectrum of **2a** lacked the ν_{Y-H} absorption of the starting material and contained several new absorptions. Four of the absorptions in the spectrum of **2a** were found to shift in a 1.40 ratio in the spectrum of the analogous deuteride (vide infra), ν_{Y-H} (ν_{Y-D}) = 1305 (930), 1170 (835), 850 (605), 667 (475) cm^{-1}, and hence were attributable to Y–H vibrations. Strong broad absorptions like that at 1170 cm^{-1} were previously observed for **1** and **2** in the 1200–1250 cm^{-1} region. For the dimers **3**, the ν_{Ln-H} absorptions for Ln = Y always have been observed at lower frequency than those of Ln = Er or Lu. A similar situation appears to exist for trimer hydrides.

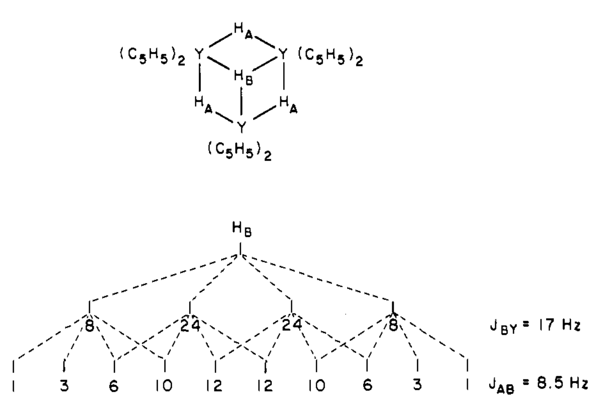


Figure 2. Schematic diagram of the proposed structure for **2a** and a possible splitting pattern for the central μ_3-hydrogen.

^1H NMR Spectrum of 2a. The 500-MHz ^1H NMR spectrum of **2a** is most informative with regard to structure. In addition to absorptions characteristic of C_5H_5 and coordinated THF, the spectrum contains a complex multiplet at δ 0.75 and a 10-line multiplet at δ −1.03 in a ratio of 3:1, respectively (Figure 1). These latter high-field resonances can be interpreted as the AB part of a 4 hydrogen 3 yttrium AA′A″BYY′Y″ system with all 7 nuclei having spin $^1/_2$. The 0.75-ppm A resonance is assignable to the μ_2-hydrides and the −1.03-ppm B resonance is assignable to the central μ_3-hydride as described below.

The μ_3-hydride resonance can be interpreted as resulting from the coupling of the B hydrogen to three equivalent A hydrogens and to three equivalent yttrium nuclei as depicted in Figure 2. Due to the clean appearance of this resonance, J_{AB} appears to be very close to one-half the J_{BY} value. Thus, the experimentally observed J value of ca. 8.5 Hz (8.3 Hz in the A region) suggests that $J_{AB} \sim 8.5$ Hz and $J_{BY} \sim 17$ Hz. The result of using these values to simulate this portion of the spectrum is seen in Figure 1.

The other resonance at 0.75 ppm, due to the three μ_2-hydrogen atoms, is more difficult to interpret. In the first-order approximation, a simple doublet of triplets due to coupling to the B hydrogen and effective coupling to only two of the yttrium nuclei might be anticipated. Although the observed resonance does have the general appearance of a doublet of triplets, it is marked by a distinct filling-in of the central lines. The filled-in inner resonance cannot be explained by residual long-range coupling to the third yttrium, since such coupling would also be observed in the outer resonances.

However, the A resonance can be rationalized in terms of a non-first-order analysis due to experimentally unobservable couplings (cf. the ^1H NMR spectrum of diborane[27]). A series of computer simulations of this region of the spectrum with variations in the values of J_{AA} and J_{YY} was performed, and the closest fit to the experimental spectrum is presented in Figure 1. The experimentally observed parameters $J_{AB} = 8.5$, $J_{AY} = 29.7$, and $J_{BY} = 17$ Hz were used in this series of calculations. The best match of calculated to experimental results occurs when the values for J_{AA} and J_{YY} are both ca. 4 Hz. The signs of J_{AA} and J_{YY} were found to be independent of those for the other specified parameters, but they must possess the same sign. In contrast, the relative signs

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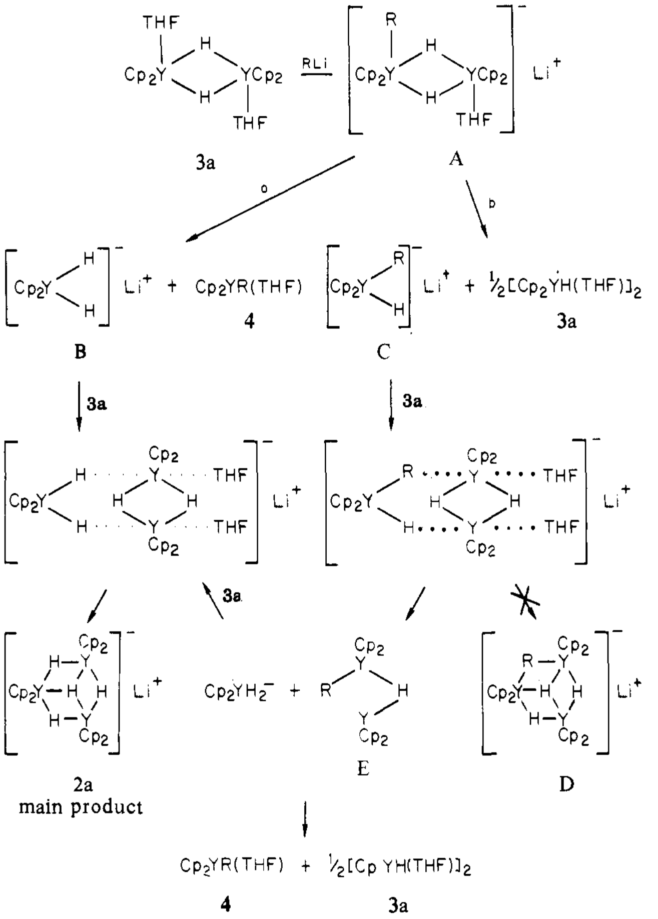
Scheme I



of J_{AB} and J_{BY} do not significantly affect the fit of the spectrum. The B resonance remains unaffected by any choice of J_{AA} or J_{YY}. Although it was not possible to demonstrate that these assignments are unique, we were unable to find any other combination of parameters that gave a better simulation.

Consistent with the above assignments, application of a decoupling pulse to the B resonance caused the A resonance to collapse to a broad triplet $J_{AY} \sim 30$ Hz (cf. $J_{HY} \sim 27$ Hz for **3a**[3]). Application of the pulse to the A protons was less effective in revealing the decoupled structure of B—probably due to the 3:1 ratio and the larger value of J_{AY}. These assignments are also consistent with the ^1H NMR spectrum of the crystallographically characterized lutetium analogue, **2**, for which 3:1 doublet:quartet signals having $J_{AB} = 7.3$ Hz are observed.[4]

Synthesis of {[$(C_5H_5)_2YD$]$_3$D}{Li(THF)$_4$}. Since the formation of **2a** occurred under mild conditions and in THF, it seemed unlikely that the LiH incorporated with the three Cp_2YH units could arise from thermal decomposition of *t*-C_4H_9Li or a *t*-C_4H_9Y complex.[25] Consistent with this, reaction of [$(C_5H_5)_2YD(THF)$]$_2$ (**3a′**) with *t*-C_4H_9Li generated the perdeuterio analog of **2a**, {[$(C_5H_5)_2YD$]$_3$D}{Li(THF)$_4$} (**2a′**). Hence, the *tert*-butyl reagent does not serve as the source of the hydride ion that is incorporated into the trimer.

Mechanistic Considerations. The formation of perdeuterio **2a′** can be rationalized by the reaction sequence shown in Scheme I (Cp = C_5H_5; R = *t*-C_4H_9).[28] Initial attack of *t*-C_4H_9Li on the dimer **3a** may proceed by displacement of the THF of solvation. Similar reactivity is observed in the reaction of **3a** with C_5H_5N. In that case, THF is displaced to form [$(C_5H_5)_2YH(NC_5H_5)$]$_2$ before Y–H addition to C_5H_5N occurs to produce hydropyridyl products.[7]

The resulting dimeric anion A[28] is likely to be unstable with respect to sterically less crowded species and is likely to fragment.[29] The fragmentation of the dimer constitutes the cleavage reaction originally desired in the trimer synthesis strategy. Fragmentation of A could occur in two ways: (a) to give the dihydride anion $(C_5H_5)_2YH_2^-$ (B) and $(C_5H_5)_2YR(THF)$ (**4**), an observed reaction byproduct when R = *t*-C_4H_9, or (b) to give the alkyl hydride anion $(C_5H_5)_2YRH^-$ (C) and $(C_5H_5)_2YH$ which would dimerize to starting material **3a**. Both fragmentation routes seem reasonable and hence both are discussed below.

If pathway a is followed, it is reasonable that the dihydride anion B can itself act as the base which attacks dimer **3a**. Although without kinetic data one cannot comment on whether the reaction is S_N1 or S_N2 in character, one can envisage displacement of the two THF molecules and formation of two new Y–H connections. Formation of an additional internal Y–H connection generates the observed trimer **2a**.

If pathway b is followed and if C attacks **3a** as discussed for B above, formation of a stable trimeric structure D is unlikely for the R = *tert*-butyl case since this would involve a *tert*-butyl group in a bridging position.[22,24] If an intermediate leading to D would form, it is possible that the *tert*-butyl group could simply exchange with the hydride ligand of **3a** to form $(C_5H_5)_2YH_2^-$ (B) and $(C_5H_5)_2RYHY(C_5H_5)_2$ (E).[30] Since the *tert*-butyl group is unlikely to bridge in E, E could fragment to the observed byproduct, **4**, and $(C_5H_5)_2YH$, which would dimerize to starting material, **3a**. Ligand redistribution reactions are common in organolanthanide chemistry[31] and precedent for such reactivity also exists with main group 3 alkyl and hydride complexes of boron and aluminum.[24,32-34] The formation of $R_2BH_2^-$ and $R_2BR'_2{}^-$ products from the reaction of $[R_2BH]_2$ with R′Li is particularly relevant.[32] Indeed, the formation of the byproduct $(C_5H_5)_3Y(THF)$ suggests ligand redistribution is occurring in this system.

The overall analysis presented in Scheme I is consistent with the reactivity of CH_3Li with **3a** as described below.

Reaction of CH_3Li with 3a. If CH_3Li rather than *t*-C_4H_9Li is used as the reagent to cleave the dimer, a clean reaction to form **2a** does not result. Instead, an oil is obtained. Pentane extraction of the oil gives a product with properties consistent with $(C_5H_5)_2YMe_2Li(THF)_2$.[30,35] Little of the original reaction product was toluene soluble and the THF extraction gave a white powder which appeared to contain some **2a** by IR spectroscopy. The spectrum was not clean, however, and appeared to contain other low-frequency absorptions attributable to other aggregated species. Since the smaller methyl ligand can bridge, several oligomeric complexes containing bridging methyl groups such as complex D in Scheme I are conceivable and may be present. Bridged dimers such as $(C_5H_5)_2RYHY(C_5H_5)_2$ (E) may also be present when R = CH_3. The CH_3Li reaction may be further complicated by ligand redistribution of $[(C_5H_5)_2YRH]^-Li^+$ (C) to form $[(C_5H_5)_2YH_2]^-Li^+$ (B) and the observed $[(C_5H_5)_2Y(CH_3)_2]^-Li^+$, a reaction which is likely to be more favorable for R = CH_3 than for R = *t*-C_4H_9.[30,35] Because the CH_3Li reaction was rather complex, it was not studied further. However, it does provide supporting evidence for the importance of the nonbridging *tert*-butyl group in providing a clean reaction according to Scheme I.

Direct Synthesis of a Heterotrimetallic Polyhydride {[$(CH_3C_5H_4)_2YH$]$_2$[$(CH_3C_5H_4)_2ZrH$]H} (5). If the above mechanistic

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[28] Numbered species in this scheme are known complexes. All other species including species labeled with letters are unisolated postulated intermediates. These formulas are not meant to specify precisely the degree of THF solvation.

(29) In analogy to the reaction of pyridine with 3a, in which both THF molecules are displaced, it is possible that A loses a second THF by reaction with a second equivalent of *t*-C_4H_9Li before fragmentation occurs.

(30) It is also possible that 2 equiv of C could undergo ligand exchange to form B and $(C_5H_5)_2YR_2^-$, a product observed in the R = CH_3 case (vide infra).

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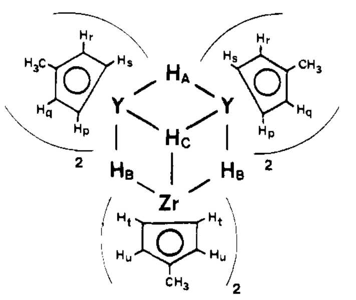

Figure 3. Schematic diagram of the proposed structure of $\{[(CH_3C_5H_4)_2YH]_2[(CH_3C_5H_4)_2ZrH]H\}$ (**5**).

analysis is correct, a variety of reagents analogous to $(C_5H_5)_2YH_2^-$ may be able to participate in similar reaction sequences. To test this hypothesis, the reaction of a dihydride complex of a metal other than yttrium with an yttrium dimer was studied. $[(CH_3C_5H_4)_2ZrH_2]_2$[36] was chosen as the reagent. The methylcyclopentadienyl derivative was preferable to the unsubstituted cyclopentadienyl analogue[37] since it was more soluble and had a greater potential to furnish monomeric $(ring)_2ZrH_2$ moieties. The $CH_3C_5H_4$ derivative was chosen over the $C_5(CH_3)_5$ analogue[38] for this initial study, since permethylated $\{[C_5(CH_3)_5]_2MH\}_3H$ complexes may be less stable for steric reasons.[39] $[(CH_3C_5H_4)_2YH(THF)]_2$ was chosen as the yttrium reagent so that exchange of cyclopentadienyl rings would not be a problem.

Dropwise addition of $[(CH_3C_5H_4)_2YH(THF)]_2$ to a suspension of $[(CH_3C_5H_4)_2ZrH_2]_2$ in THF gives a clear solution after 5 min. Removal of solvent after further stirring gives a residue containing a product, **5**, which can be extracted with hexane. Complete elemental analysis and hydrolytic decomposition data on **5** were consistent with the formulation $\{[(CH_3C_5H_4)_2YH]_2[(CH_3C_5H_4)_2ZrH]H\}$, which is analogous to that of **2** and **2a** except a Zr^{4+} is replacing an Y^{3+} and a Li^+ cation. The solubility of **5** in hexane is consistent with its neutral formulation and the presence of $CH_3C_5H_4$ rings. The identity of **5** as a trimetallic tetrahydride analogous to **2** and **2a** is best established from the ^1H NMR spectrum discussed below.

^1H NMR Spectrum of 5. The 250-MHz ^1H NMR spectrum of **5** consists of six resonances of equal area arising from the ring protons of the $CH_3C_5H_4$ units, two singlets with an intensity ratio of 2:1 assignable to the methyl protons of the cyclopentadienyl rings, and two high-field multiplets centered at δ −1.57 and −2.99 with an area ratio of 3:1, respectively. The ^1H NMR spectrum of **5** was essentially the same at 500 MHz. The observation of only two methyl group resonances is consistent with a trimetallic Y_2Zr core in which a mirror plane passes through the zirconium and renders the two yttrium centers identical (Figure 3). Even with rapid rotation, however, the ring protons on the $CH_3C_5H_4$ ligands attached to yttrium atoms would remain nonequivalent and would yield four distinct resonances. The protons at the 2,5 and 3,4 positions of the $CH_3C_5H_4$ rings attached to zirconium would then form diastereotopic pairs, thus producing the two other peaks.

The two high-field multiplets (Figure 4) are attributable to three μ_2-hydrides and a single μ_3-hydride in a structure analogous to **2** and **2a**. The hydridic protons and the two yttrium atoms form an ABB′CYY′ spin system, with $I = {}^1/_2$ for all nuclei (the natural abundance of ^{91}Zr ($I = {}^5/_2$) is only 11.2% and no Zr–H coupling was observed). The lower molecular symmetry of **5** relative to **2a** increased the number of independent chemical shifts and coupling constants to be derived, but computer simulation of the spectrum (Figure 4) still yielded a satisfactory analysis (final root mean square error of the coupling constants was 0.57 Hz).

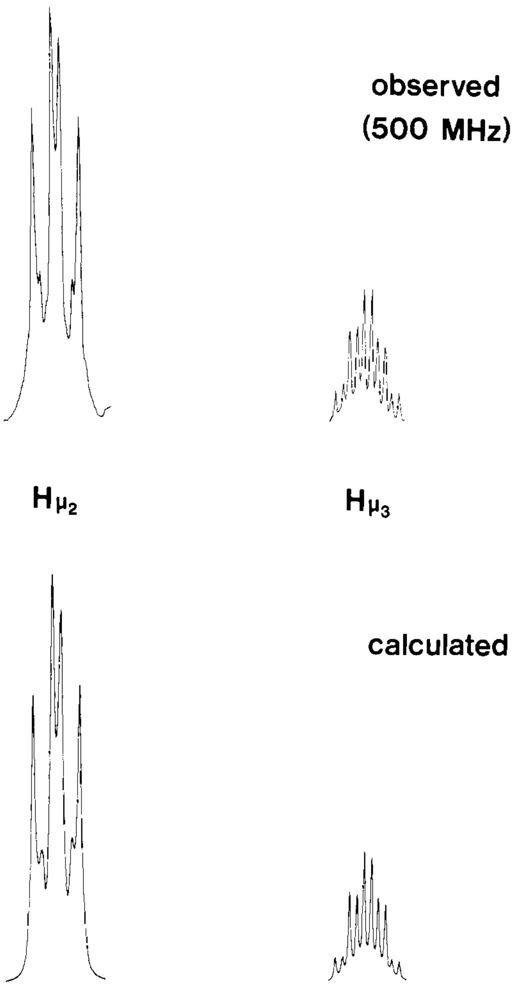

Figure 4. High-field resonances of the 500-MHz ^1H NMR spectrum of $\{[(CH_3C_5H_4)_2YH]_2[(CH_3C_5H_4)_2ZrH]H\}$ (**5**): (a) observed spectrum in C_6D_6; (b) simulated spectrum using $^2J_{AC}$ = 14.9 Hz, $^1J_{AY}$ = 20 Hz, $^1J_{BY}$ = 15 Hz, $^3J_{BY}$ = 2 Hz, $^1J_{CY}$ = 14.9 Hz, J_{AB} = 1 Hz, J_{BB} = 5 Hz, J_{YY} = 3.5 Hz, and line width = 2.9 Hz.

As was observed in the case of **2a**, the μ_3-hydride resonance in **5** is a 10-line multiplet, but the intensities and spacings of the lines in **5** give it the appearance of a quintet of doublets. The computer simulation found this effect to arise from the accidental equivalence of J_{CY} and J_{BC}: beginning with spectra using coupling constants based on those in **2a**, successive iterations lowered J_{CY} and raised J_{BC} until they both equaled 14.9 Hz. The identical coupling of the μ_3-hydride to four $I = {}^1/_2$ centers generates a quintet, which when further split by the unique Y–H–Y hydride (J_{AC} = 7.6 Hz) produces the experimentally obtained pattern.

As was found for **2a**, the multiplet assigned to the doubly bridging hydrides in **5** is not amenable to such first-order analysis. The simulated spectrum established that the chemical shifts of the Y–H–Y and the Y–H–Zr hydrides were identical within error (in the best fit they differ by <0.01 ppm), but as with **2a**, second-order effects are responsible for much of the appearance of the resonance. In general, most of the coupling constants are somewhat smaller than those found for **2a**; in particular, J_{AY} was lowered to 15 Hz and J_{BY} fell to 20 Hz in **5** (cf. J_{AY} = 29.7 Hz in **2a**). J_{YY} and J_{BB} are 3.5 and 5 Hz, respectively (cf. 4 Hz for both constants in **2a**). In addition, the fit was improved by the inclusion of $^3J_{BY}$ with a value of 2 Hz. The appearance of the spectrum is unaffected not only by the choice of sign for J_{YY}, as in **2a**, but also by the signs of J_{AY} and J_{AC}. The relative signs of J_{BB} and J_{AC}, however, must be the same.

Conclusion. The development of a high-yield synthesis of the trimeric yttrium polyhydride, **2a**, from the dimeric hydride, **3a**, permits ready access to this novel class of complexes. This syn-

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(39) Preliminary studies involving C_5Me_5 complexes have yielded new complexes of limited thermal stability.

thesis should allow the full exploration of the physical, chemical, and catalytic properties of trimers containing hydrogen in a planar tricoordinate metal environment. Equally important, this synthesis suggests that (a) alkyllithium reagents, and particularly t-C_4H_9Li, may have important and general utility in the synthesis of associated metal complexes and (b) dimeric organolanthanide complexes may be readily converted to polymetallic species by reaction with L_nMX_2 reagents such as $(C_5H_5)_2YH_2^-$. The synthesis of the heterotrimetallic yttrium–zirconium complex is the first example confirming this contention. Since a wide variety of L_nMX_2 reagents are available with main group metals, transition metals, and actinide metals as well as in the lanthanide series and since X may also be varied from hydride to halide, alkoxide, alkyl, etc., a wide range of new types of polyhydride complexes appears to be accessible. We are currently investigating the generality of Scheme I in its broadest sense in the periodic table.

Experimental Section

All of the complexes described below are extremely air and moisture sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted with rigorous exclusion of air and water with Schlenk, vacuum line, and glove box (Vacuum/Atmosphere HE-43 Dri-Lab) techniques. Physical measurements and purification of many reagents have been described previously.[3] LiH and CH_3Li (low halide) were obtained from Aldrich. $[(C_5H_5)_2YH(THF)]_2$ (**3a**) was prepared as previously described[7] and $[(CH_3C_5H_4)_2YH(THF)]_2$ was prepared analogously. $[(CH_3C_5H_4)_2ZrH]_2$ was prepared according to literature methods.[36] Elemental analysis was performed by Analytische Laboratorien, Engelskirchen, Germany. The 500-MHz ^1H NMR spectrum of **5** was obtained at the Southern California Regional NMR Facility at CalTech. Computer simulations of the ^1H NMR spectrum of **2a** were done with the NTCSIM program of the Nicolet Corporation. The ^1H NMR spectrum of **5** was simulated with use of the PANIC program of the Bruker Corporation.

Reaction of LiH with 3a. (a) Li/Y = 0.33. **3a** (115 mg, 0.20 mmol) was stirred with LiH (1.0 mg, 0.13 mmol) in THF (15 mL) overnight. The suspension was heated to reflux briefly and stirred at room temperature for 2 days. Solvent was removed by rotary evaporation, and the IR spectrum of the material showed a decrease in the main hydride band of **3a** with broad bands in the 1000–1100 cm^{-1} region. The material was extracted with THF to give a yellow solution which was evaporated to dryness. Extraction with Et_2O gave a colorless solution which was evaporated to dryness. An IR of this material showed no 1170 cm^{-1} or higher-energy hydride bands, but it had a broad absorption in the 1000–1060 cm^{-1} region. Attempts to recrystallize this material by slow pentane diffusion into a THF/hexane solution at −8 °C failed to give well-formed crystals.

(b) Li/Y = 1.7. **3a** (58.4 mg, 0.10 mmol) was stirred in THF (20 mL) with LiH (2.7 mg, 0.34 mmol) for 1 h. The hydride readily went into solution. After solvent removal the material had an IR spectrum essentially unchanged from that for **3a**. The material was stirred overnight in a 5:1 toluene:THF solution, evaporated to dryness, and extracted with THF. After solvent removal a white powder was obtained having strong, broad IR bands in the 1000–1100 cm^{-1} region with the prominent hydride band of **3a** essentially absent. The fingerprint region of this spectrum was dominated by a strong, tailing base line. No band at 1040 cm^{-1} due to Li-coordinated THF was observed.

Reaction of t-C_4H_9Li with 3a. Synthesis of $\{[(C_5H_5)_2YH]_3H\}\{Li(THF)_4\}$ (2a). **3a** (776 mg, 1.33 mmol) was suspended in THF (30 mL) in a Schlenk flask equipped with a glass-encased stir bar. t-C_4H_9Li (46.0 mg, 0.72 mmol) (**3a**/t-C_4H_9Li = 1.85) dissolved in pentane (20 mL) was added dropwise from an addition funnel to the suspension maintained at −78 °C. A yellow color developed immediately and persisted until the suspension had warmed to −15 °C. After the solution was stirred overnight, a white flocculant precipitate (**2a**) and a trace of some crystalline material were observed in the pale yellow saturated solution. The solution was evaporated to dryness, taken into a drybox, and extracted with toluene (2 × 10 mL). The remaining insoluble product was extracted with THF (a trace, 5 mg, was insoluble) and concentrated to microcrystalline, white **2a** (643 mg, 0.67 mmol, 75% yield based on Y). Slow recrystallization may be effected by pentane diffusion into a saturated THF/hexane solution at −8 °C. Anal. Calcd for $Y_3C_{46}H_{66}O_4Li$: C, 57.74; H, 6.90; Y, 27.90; Li, 0.73; total, 93.28. Found: C, 55.31; H, 6.31; Y, 37.40; Li, 0.75; total, 99.77. Calcd for the unsolvated THF-free $\{[(C_5H_5)_2YH]_3H\}Li$, i.e., $Y_3C_{30}H_{34}Li$: C, 53.92; H, 5.09; Y, 39.95; Li, 1.04; total, 100.00. In the past, loss of THF has also complicated complete elemental analysis of the crystallographically characterized trimers **1** and **2**.[4] The observed Li/Y ratio of 0.26 of **2a** is similar to the 0.28 found for **2**.[4] The analysis of unsolvated **2a** may be high in C and H due to incorporation of pentane into the lattice. We have seen NMR evidence for pentane or toluene incorporation into crystalline samples of **2a** depending upon the crystallization solvent system. Hydrocarbon incorporation may be the reason that a suitable model for the X-ray diffraction data on **2a** has not been refined to an acceptable limit.[40] Decomposition of **2a** with H_2O gave 0.80 mol of H_2 per yttrium atom (cf. 0.8 mol of H_2 per Lu in **2**): IR (KBr) 3090 (w), 2970 (m), 2880 (m), 1620 (w), 1460 (w), 1438 (w), 1305 (m, br), 1258 (w), 1170 (s, br), 1040 (s), 1010 (s), 885 (m), 860 (m), 850 (m), 840 (m), 770 (s), 730 (m), 667 (m), 385 cm^{-1} (w, br); ^1H NMR (500 MHz, THF-d_8) δ 5.92 (s, C_5H_5), 3.62 (m, C_4H_9O), 1.77 (m, C_4H_8O), 0.75 (m, μ_2-H), −1.03 (m, μ_3-H); $^{13}C\{^1H\}$ NMR (22.63 MHz, THF-d_8) δ 106.30 (C_5H_5), 67.40, 25.32 (C_4H_8O).

Removal of solvent from the toluene extract of the crude reaction product gives a yellow oil and an off-white powder. The IR spectrum of this product shows that some trimer was extracted, but it also contains lowered (C–H) stretches at 2760, 2730, and 2670 which are characteristic of $(C_5H_5)_2Ln(t\text{-}C_4H_9)(THF)$.[22] A ^1H NMR (C_6D_6) spectrum of this material indicated that $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)$ comprised ~30% of the sample. $(C_5H_5)_3Y(THF)$ was also observed and comprised ~40% of the NMR sample.

Synthesis of $\{[(C_5H_5)_2YD]_3D\}\{Li(THF)_4\}$ (2a′). The synthesis of **2a′** was analogous to that of **2a** except that the deuteride, $[(C_5H_5)_2YD(THF)]_2$, was used as the starting material. The product had a ^1H NMR spectrum which was identical with that of **2a** except that the high-field hydride resonances were missing: IR (KBr) 3080 (w), 2950 (w), 2880 (m), 1745 (w), 1620 (w), 1460 (w), 1440 (w), 1260 (w), 1170 (w), 1040 (m), 1010 (s), 930 (m), 915 (m), 880 (m), 835 (m, br), 770 (s), 605 (m), 475 (m), 385 cm^{-1} (w, br).

Reaction of 3a with CH_3Li. **3a** (205 mg, 0.35 mmol) was suspended in THF (20 mL) in a Schlenk flask. CH_3Li (0.70 mmol) in Et_2O was added via syringe to the suspension stirred at −78 °C. The colorless suspension became a colorless solution at ca. −15 °C. After being stirred overnight the solution was evaporated to a pasty white oil and taken into the glove box. The oil was sequentially extracted with pentane, toluene, and THF. Rotary evaporation of the pentane fraction gave a white microcrystalline powder. The IR and ^1H NMR spectra of this powder were consistent with the formulation $(C_5H_5)_2Y(CH_3)_2Li(THF)_2$, but this product was not investigated further.[35]

Evaporation of the toluene fraction left little material. Evaporation of the THF fraction gave a white powder with an IR spectrum showing two broad bands at 1305 and 1170 cm^{-1}, indicative of a trimeric species, and a THF absorption characteristic of an anionic species.[4,17] These bands were not well-defined, however, and an attempt was made to eliminate lithium salts such as LiH or CH_3Li by heating a saturated THF/toluene solution (cf. the synthesis of **1**[4]). This led, however, to an amorphous white powder exhibiting no evidence of the previous absorptions, but containing broad maxima at 1240 and 1090 cm^{-1}. While some **2a** may be present in this product, the IR spectrum indicates other species (probably trimeric but containing bridging methyl ligands) dominate. This reaction was not studied further.

Synthesis of $\{[(CH_3C_5H_4)_2YH]_2[(CH_3C_5H_4)_2ZrH]H\}$ (5). A solution of $[(CH_3C_5H_4)_2YH(THF)]_2$ (0.555 g, 0.87 mmol) in THF (10 mL) was added dropwise over a 5-min interval to a magnetically stirred suspension of $[(CH_3C_5H_4)_2ZrH_2]_2$ (0.218 g, 0.43 mmol) in THF (30 mL). The suspension became clear during the addition, and the resulting solution was stirred at room temperature for 2 h. The solvent was removed by rotary evaporation, and the residue was extracted with hexanes to obtain the product. More thorough extraction with boiling hexanes (3 × ca. 75 mL) gave a higher yield of the same product. After the solution was filtered, the extracts were combined and evaporated to dryness, leaving crude $\{[(CH_3C_5H_4)_2YH]_2[(CH_3C_5H_4)_2ZrH]H\}$ (**5**) (0.208 g, 32% based on Y). Recrystallization from hot hexanes yields colorless crystals, mp 100–105 °C dec. Anal. Calcd for $Y_2ZrC_{36}H_{46}$: C, 57.82; H, 6.20; Y, 23.78; Zr, 12.20. Found: C, 56.22; H, 5.87; Y, 22.50; Zr, 12.05. As in the case of **2** and **2a**, the elemental analysis of **5** was not as complete as possible. However, the observed Y/Zr ratio of 1.92 was close to the expected value of 2. Decomposition of **5** with D_2O produced an amount of gas corresponding to 0.98 hydrides per metal center. Since the trimeric tetrahydrides **2** and **2a** have had hydrolytic hydrogen yields[4] of 0.8 hydride per metal center, this yield is still consistent with the stoichiometric ratio of 1.33 hydride ligands per metal center. IR (KBr) 3103 (w), 2941 (m), 2876 (m), 1593 (w), 1472 (m), 1299 (s, br), 1214 (m), 1035 (m), 962 (w), 933 (w, sh), 853 (m, sh), 821 (s, sh), 782 (s), 754 cm^{-1} (s); ^1H NMR (250 MHz, C_6D_6) δ 6.31 (m, 4, $CH_3C_5H_4$), 6.19 (m, 4, $CH_3C_5H_4$), 6.15 (m, 4, $CH_3C_5H_4$), 6.08 (m, 4, $CH_3C_5H_4$), 5.89 (m, 4, $CH_3C_5H_4$), 5.52 (m, 4, $CH_3C_5H_4$), 2.22 (s, 6, $CH_3C_5H_4$), 1.70 (s, 3, $CH_3C_5H_4$), −1.57 (m, 3, μ_2-H), −2.99 (m, 1, μ_3-H). The ^1H NMR

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(40) Atwood, J. L.; Hunter, W. E., personal communication.

spectrum was invariant from −40 to +25 °C when measured in toluene-d_8.

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Registry No. 2a, 90762-81-5; **2a′**, 90742-67-9; **3a**, 80642-73-5; **4** (R = t-C_4H_9), 80642-66-6; **5**, 90742-68-0; $[(C_5H_5)_2YD(THF)]_2$, 80642-74-6; $[(C_5H_5)_2Y(CH_3)_2Li(THF)_2$, 90742-70-4; $[(CH_3C_5H_4)_2YH(THF)]_2$, 80658-44-2; $[(CH_3C_5H_4)_2ZrH_2]_2$, 77965-67-4; $(C_5H_5)_3Y(THF)$, 79533-63-4.

The Design of Multianionic Chelating Ligands for the Production of Inorganic Oxidizing Agents. Osmium Coordination Chemistry That Provides Stable Potent Oxidizing Agents and Stable Potent Reducing Agents

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Abstract: The design of multianionic chelating ligands for use in producing new oxidizing agents is discussed. Two potentially tetradentate tetraanionic ligands, 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane (H_4CHBA-Et (**1**)) and 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene (H_4CHBA-DCB (**2**)) were synthesized and found to coordinate to osmium as tetradentate tetraanions. X-ray crystal structures of two osmium(IV) complexes of this ligand class are reported: octahedral Os(η^4-CHBA-Et)$(py)_2$ (**5**) has axial pyridine ligands with the tetradentate tetraanion coordinated to the equatorial positions, whereas in Os(η^4-CHBA-DCB)(bpy) (**15**) the bpy ligand occupies one axial and one equatorial position with one phenolic donor in an axial position and the remaining donors of the tetradentate tetraanion coordinated equatorially. Ligand **1** forms osmium complexes in oxidation states II, III, IV, and VI. Attempted electrooxidation of the osmium(IV) complex, **5**, to an osmium(V) complex results in oxidation of the tetradentate tetraanion at the ethylene unit bridging the amide nitrogen atoms. In the presence of alcohol or water this oxidation proceeds in a stepwise manner and several key intermediates have been isolated, independently synthesized, and characterized. The first intermediate isolated results from dehydrogenation of the ligand bridge. In the second intermediate, the unsaturated bridge has been oxidized to a 1,2 diether. Finally, cleavage of the carbon–carbon bond and dealkylation of the two ethereal oxygen atoms yields two bidentate ligands bound through phenolic and organic imido donors. The cleavage product is produced as two diastereomers which differ in the coordination geometry at the metal. Both isomers have been characterized by X-ray crystal structure determinations. The diastereomeric distribution is determined primarily by the nature of the alcohol employed. The ligand oxidation can be prevented by replacement of the ethylene unit of **1** with the dichlorophenylene moiety of **2**. Osmium complexes of **2** have been produced in oxidation states II, III, IV, VI, and presumably the very rare state V. The apparent osmium(V) complexes are stable but are potent oxidizing agents with potentials for the V/IV couples ranging from ca. 1.31 to 1.65 V vs. NHE. The complex $[Os(\eta^4\text{-CHBA-DCB})(t\text{-Bupy})_2]^+$ forms as an apparent mixture of two diastereomers. The stable osmium(II) complexes of both ligands **1** and **2** are potent reducing agents.

The variety of useful inorganic oxidizing agents presently available is limited by the lack of appropriate oxidation resistant ligands. We have initiated an attempt to prepare a series of strongly oxidizing complexes by designing and synthesizing new oxidation-resistant ligands. Most suitable known ligands are monodentate species in which the donor atom is electronegative (e.g., O^{2-}, Cl^-, F^-). Noteworthy exceptions include the η^2-peroxo and η^4-porphyrinato dianionic ligands.[2,3] Our approach has been to prepare multianionic chelating ligands that are capable of forming stable strongly oxidizing complexes and to investigate the coordination chemistry of the ligands and the reaction chemistry of their metal complexes. Many classical oxidizing agents (e.g., CrO_3, $KMnO_4$) exhibit poor chemoselectivity when oxidizing organic substrates. For some reactions a fundamental reason for this behavior is that additional metal-based oxidizing agents are formed during the redox process which oxidize the organic substrate in a manner different from the initial oxidizing agent. An example is the chromic acid oxidation of cyclobutanol in which chromium(VI) cleanly oxidizes cyclobutanol to cyclobutanone, but the chromium(IV) generated in this process also attacks the cyclobutanol and produces ring cleavage. The final inorganic product is chromium(III).[4] We believe that in searching for selective transition-metal oxidizing agents it is highly desirable to seek or design systems which allow one to *control oxidation state changes* at the metal site during an oxidation process. In particular, we wish to generate complexes that will undergo a single oxidation reaction with a specific organic substrate to give a

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[2] For recent examples of the use of highly oxidized porphyrin complexes in oxidation reactions see: (a) Groves, J. T.; Watanabe, Y.; McMurry, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4489. (b) Groves, J. T.; Takahashi, T. *Ibid.* **1983**, *105*, 2073. (c) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *Ibid.* **1983**, *105*, 3510. (d) Smegal, J. A.; Hill, C. L. *Ibid.* **1983**, *105*, 3515.

[3] The extremely oxidized complexes $[Fe(bpy)_3]^{4+}$ and $[Ru(bpy)_3]^{4+}$ have recently been produced electrochemically in liquid SO_2 showing that aromatic ligands are capable of forming observable complexes that are potent oxidizing agents. Gaudiello, J. G.; Sharp, P. R.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6373. Stable very highly oxidizing complexes have recently been reported. Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 2689.

[4] Benson, D. "Mechanisms of Oxidation by Metal Ions"; Elsevier: New York, 1976, pp 178–193.