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Organolanthanide and Organoyttrium Hydride Chemistry. 5. Improved Synthesis of $[(C_5H_4R)_2YH(THF)]_2$ Complexes and Their Reactivity with Alkenes, Alkynes, 1,2-Propadiene, Nitriles, and Pyridine, Including Structural Characterization of an Alkylideneamido Product[1]

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Abstract: Hydrogenolysis of $[(C_5H_5)_2YCH_3]_2$ in 10:1 toluene:THF or $[(CH_3C_5H_4)_2YCH_3]_2$ in 10:1 hexane:THF generates the corresponding complexes $[(C_5H_4R)_2YH(THF)]_2$ (**1a**, R = H; **1b**, R = CH_3) in high yield. **1a** and **1b** react with R′CN by 1,2-addition of Y–H to form $[(C_5H_4R)_2Y(N{=}CHR')]_2$ (**2**, R′ = CH_3; **3**, R′ = $C(CH_3)_3$). **3a** crystallizes from THF under pentane diffusion in space group $P\bar{1}$ with unit cell dimensions $a = 9.261$ (5) Å, $b = 10.398$ (6) Å, $c = 16.323$ (8) Å, $\alpha = 86.48$ (4)°, $\beta = 88.95$ (4)°, $\gamma = 70.29$ (4)°, and $Z = 2$ dimers for $D_c = 1.36$ g cm^{-3}. Least-squares refinement on the basis of 2532 observed reflections led to a final R value of 0.056. One of the two dimers in the unit cell has disorder in the *tert*-butyl group, but the other dimer is well-behaved. In the latter molecule, the two $(C_5H_5)_2Y$ units of the dimer are connected by asymmetrical N=CHR bridges with Y–N distances of 2.314 (9) and 2.382 (9) Å and YN=C angles of 109.8 (9) and 149.4 (9)°. **1a** and **1b** react (a) with $H_2C{=}CH_2$ and $CH_3CH{=}CH_2$ to form $(C_5H_4R)_2Y(CH_2CH_3)(THF)$ (**4**) and $(C_5H_4R)_2Y(CH_2CH_2CH_3)(THF)$ (**5**), respectively, (b) with $H_2C{=}C{=}CH_2$ to form $(C_5H_4R)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$ (**6**), (c) with $HC{\equiv}CC(CH_3)_3$ to form $[(C_5H_4R)_2YC{\equiv}CC(CH_3)_3]_2$ (**7**), (d) with $R''C{\equiv}CR''$ to form $(C_5H_4R)_2Y[C(R''){=}CHR''](THF)$ (**8**, R″ = C_2H_5; **9**, R″ = C_6H_5), (e) with pyridine in nonpolar solvents to form $[(C_5H_4R)_2YH(NC_5H_5)]_2$ (**10**), and (f) with pyridine in polar solvents to form the 1,2-isomer of $(C_5H_4R)_2Y(NC_5H_6)(NC_5H_5)$ (**11**), which rearranges to the 1,4-isomer, **12**. The new complexes were characterized by standard spectral and chemical methods. **1b** and **8b** are catalysts for activation of H_2 in alkyne hydrogenation reactions.

We recently have reported the synthesis of the first crystallographically characterized organolanthanide and organoyttrium hydride complexes[3-6] (eq 1–4; Ln = Y, Er, Lu; R = H, CH_3; X = H, Cl). These complexes provided the first opportunity to study

$$2(C_5H_4R)_2Ln(t\text{-}C_4H_9)(THF) + 2H_2 \rightarrow [(C_5H_4R)_2LnH(THF)]_2 + 2C_4H_{10} \qquad (1)^{3}$$

$$2(C_5H_4R)_2Ln(t\text{-}C_4H_9)(THF) \xrightarrow[-C_4H_8]{\Delta} [(C_5H_4R)_2LnH(THF)]_2 \qquad (2)^{4}$$

$$3(C_5H_5)_2Ln(t\text{-}C_4H_9)(THF) \xrightarrow[-C_4H_8]{\Delta,\ LiX} \{[(C_5H_5)_2LnH]_3X\}\{Li(THF)_4\} \qquad (3)^{4}$$

$$[(C_5Me_5)_2Sm](C_6H_5)C{=}C(C_6H_5)[Sm(C_5Me_5)_2] + 2H_2 \rightarrow [(C_5Me_5)_2SmH]_2 \qquad (4)^{5}$$

the reactivity of a lanthanide or yttrium hydrogen bond in a well-characterized molecular system. Since these complexes represent a new class of metal hydrides and since organometallic hydrides are key intermediates in a wide variety of stoichiometric and catalytic transformations involving unsaturated hydrocarbons, the reactivity of these hydrides with unsaturated substrates was of great interest. We describe here our investigations of the reactivity of this new type of metal–hydrogen bond with representative alkenes, alkynes, and nitriles as well as with 1,2-propadiene and pyridine.[1] We also report an improved synthetic route to these hydrides. The reactivity of the yttrium–hydrogen bond with isocyanides recently has been discussed.[11]

Yttrium was the metal chosen for this study since it not only provides diamagnetic complexes characterizable by ^{1}H and ^{13}C NMR spectroscopy, but it also provides additional NMR information via Y–H and Y–C coupling (100% abundant ^{89}Y has $I = {}^{1}/_{2}$).[12] In the past, isostructural and isochemical behavior has been observed for yttrium and the late lanthanides of similar radius.[13-17] Hence, the results described here for yttrium are expected to parallel reactivity for the later lanthanides.

Results and Discussion

Improved Synthesis of $[(C_5H_4R)_2LnH(THF)]_2$. As we began this and other continuing studies of the reactivity of the lan-

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(16) $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)$ and $\{[(C_5H_5)_2YH]_3H\}\{Li(THF)_4\}$ demonstrate analogous chemistry to that of Er and Lu complexes in ref 4: Evans, W. J.; Meadows, J. H., manuscript submitted for publication.

(17) Y^{3+}, 0.88 Å, Er^{3+}, 0.881 Å.[18] Structural studies by X-ray crystallography are also potentially more informative using yttrium particularly with respect to hydrogen positions, due to its smaller atomic number and more favorable absorption parameters.

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Table I. Variable-Temperature ^1H NMR Data (δ, ppm)

	T, K	$\overline{\mathit{CH_2}(CH_2)_2\mathit{CH_2}O}$	$\overline{CH_2(\mathit{CH_2})_2CH_2O}$	CH_3
$[(CH_3C_5H_4)_2YCH_3]_2/1.2$ THF	226	3.19	1.08	−0.91
	296	3.41	1.30	−0.86
	344	3.49	1.40	−0.83
THF	296	3.52	1.48	
$[(CH_3C_5H_4)_2YCH_3]_2$ only	296			−0.85

thanide- and yttrium-hydrogen bond, we sought to develop improved methods for preparing the $[(C_5H_4R)_2LnH(THF)]_2$ reagents. Although the cyclopentadienyl complexes, R = H, **1a**, can be prepared by hydrogenolysis in approximately 70% yield via eq 1, the yields of the methylcyclopentadienyl complexes, R = CH_3, **1b**, are lower, 30–50%. The latter result occurs because the $(CH_3C_5H_4)_2Ln(t\text{-}C_4H_9)(THF)$ precursors are not as thermally stable as the cyclopentadienyl analogues and competing decomposition reactions of the *tert*-butyl substrates diminish the yield.[4] Since the readily available methyl complexes $[(C_5H_4R)_2LnCH_3]_2$[14,19] and $(C_5H_4R)_2LnCH_3(THF)$ are more stable substrates, these complexes have been investigated to determine their utility as precursors to **1a** and **1b** via hydrogenolysis.

Our earlier studies of the hydrogenolysis of lanthanide-alkyl bonds[3,7] indicated that the degree of association and solvation of the alkyl complex was critical to achieving acceptable rates of reactivity for metal-hydrogen bond formation. The dimeric $[(C_5H_4R)_2LnCH_3]_2$ complexes in toluene were found to react very slowly (weeks) with H_2, whereas the monomeric $(C_5H_4R)_2Ln(t\text{-}C_4H_9)(THF)$ complexes reacted rapidly in toluene. In THF, however, $(C_5H_4R)_2Ln(t\text{-}C_4H_9)(THF)$ reacted slowly with H_2 at atmospheric pressure.[20] These observations indicated that an efficient hydrogenolysis required an unsolvated, terminal (i.e., nonbridged) lanthanide alkyl moiety.

The enhanced reactivity for H–H bond activation of a coordinatively unsaturated, nonbridged alkyl can be rationalized not only on steric grounds but also on an electronic basis. The metal in a bis(cyclopentadienyl)lanthanide alkyl is coordinatively unsaturated since it would prefer to form a bridged or solvated structure, and it is highly electrophilic, since the metal is very electropositive. The alkyl anion is also "coordinatively unsaturated" in the sense that it could form a bridge to another metal center and it is highly nucleophilic.[21] The two adjacent sites of high nucleophilicity and high electrophilicity, both with strong tendencies to further coordinate/react, seem ideally suited for the activation of a strong bond with little dipolar character.[22-26]

The possibility of generating such a reactive species from $[(C_5H_4R)_2LnCH_3]_2$ by adding less than stoichiometric amounts of a coordinating solvent was explored by studying the ^1H NMR spectrum of a mixture of $[(CH_3C_5H_4)_2YCH_3]_2$ with 1.2 mol of THF in toluene-d_8. The spectrum of $[(C_5H_5)_2YCH_3]_2$ in the absence of a noncoordinating solvent is invariant from −40 to 40 °C, exhibiting a well-resolved triplet for the methyl hydrogens due to coupling with the two yttrium atoms (J_{YH} = 3.6 Hz).[13] $[(CH_3C_5H_4)_2YCH_3]_2$ similarly exhibits a triplet. With small amounts of THF present, however, the Y–H coupling in $[(CH_3C_5H_4)_2YCH_3]_2$ is absent, which suggests that the environment of the methyl ligand is varying on the NMR time scale possibly by repeated bridge formation and breakage (eq 5).

$$[(CH_3C_5H_4)_2YCH_3]_2 + THF \rightleftarrows (CH_3C_5H_4)_2YCH_3(THF) + (CH_3C_5H_4)_2YCH_3 \quad (5)$$

The absence of coupling in the THF resonances may similarly be attributed to exchange of THF, in this case between the yttrium coordination sphere and bulk solvent. Further confirmation of this type of dynamic equilibrium was obtained by variable-temperature studies. Temperature-dependent shifts were observed for both the methyl and THF resonances in toluene-d_8 (Table I).

These NMR results, taken with the previously described hydrogenolysis results for the methyl and *tert*-butyl complexes,[3,7] suggested that the equilibrium depicted in eq 6 was operative and

$$\begin{tikzcd}
(C_5H_4R)_2YCH_3(THF) \arrow[r, leftrightarrow] & (C_5H_4R)_2YCH_3 \arrow[r, leftrightarrow] \arrow[d, "H_2"] & {[(C_5H_4R)_2YCH_3]_2} \\
& {[(C_5H_4R)_2YH(THF)]_2} &
\end{tikzcd} \quad (6)$$

1a, R = H **1b**, R = CH_3

that this system might provide an effective route to the desired hydrides if conditions could be found that produced a satisfactory concentration of the reactive unsolvated monomeric species. This goal was successfully realized by using a mixed-solvent system.

When a 10:1 toluene:THF solvent mixture is used, $[(C_5H_5)_2YCH_3]_2$ generates $[(C_5H_5)_2YH(THF)]_2$ in ~70% yield via eq 6 when stirred at room temperature overnight under an excess of H_2 at 1 atm of pressure. The hydride so produced is completely insoluble in the supernatant solution and may be simply filtered away from the solution and washed with fresh hydrocarbon solvents to provide a product pure enough for subsequent reactivity studies.

To prepare $[(CH_3C_5H_4)_2YH(THF)]_2$ similarly via eq 6, a 10:1 hexane:THF solvent system is preferable, since this hydride is slightly soluble in aromatic solvents and moderately soluble in THF. The initially isolated product is completely insoluble in the mother liquor and again is of sufficient purity to permit subsequent reactivity studies without need of recrystallization. A yield of 70% is typical, and yields of 85% have been observed if the solution is stirred an additional day under a fresh supply of hydrogen.[27]

General Reactivity Considerations. The reactivity of the yttrium-hydrogen bond with various substrates was first studied on a small scale in an NMR tube containing THF-d_8. The methyl-substituted hydride $[(CH_3C_5H_4)_2YH(THF)]_2$, **1b**, was chosen for these studies since it is more soluble than **1a**. Most reactions were complete in less than 30 min. Samples involving less reactive substrates were monitored for 2–3 days or until the reaction was complete. Subsequent preparative-scale studies frequently involved the unsubstituted hydride, $[(C_5H_5)_2YH(THF)]_2$, **1a**, since the isolated products often were less soluble than the methyl-substituted analogues (a factor that aided in recrystallization efforts) and generally showed greater stability upon solvent removal. In some cases, the reaction products were sufficiently unstable in the absence of THF that only NMR data are reported. The fully characterized nitrile reaction products are described first, since they provide X-ray crystallographic data on the predominant mode of addition of **1** to unsaturated hydrocarbons.

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[21] The addition of polyamines to alkyllithium reagents similarly enhances reactivity by breaking up the $(RLi)_n$ clusters. In addition, the ionic character of the Li–C bond is thought to be increased upon chelation.[22,23]

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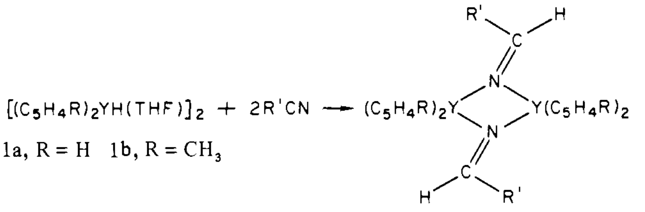
[27] The ether/alkane solvent system also allows the preparation of stable ytterbium(III) hydride complexes. Cf. ref 7.

Reactions with Nitriles. The hydrides **1a** and **1b** react rapidly with nitriles to form products that we characterize as dimeric alkylideneamido complexes (eq 7) as described below. Typically, addition of excess nitrile to a stirred slurry of **1a** in THF causes the suspended hydride to dissolve, giving a clear, colorless solution. The product can be isolated in quantitative yield as a white powder by removing the solvent. Complexometric metal analyses on **2a** and **3a** were consistent with the formulas $\{(C_5H_5)_2Y[N{=}C(H)CH_3]\}_2$ and $\{(C_5H_5)_2Y[N{=}C(H)C(CH_3)_3]\}_2$, respectively, according to eq 7. The preparative-scale reactions of **1b** with CH_3CN and $(CH_3)_3CCN$ to form **2b** and **3b**, respectively, gave oily products and were not examined further.



1a, R = H 1b, R = CH_3

2, R' = CH_3 3, R' = $C(CH_3)_3$

(7)

^1H NMR data on the nitrile reaction products are given in Table II. Assignment of the resonances was confirmed by synthesis of the deuterated analogues $\{(C_5H_5)_2Y[N{=}CDCH_3]\}_2$ (**2a'**) and $\{(C_5H_5)_2Y[N{=}C(D)C(CH_3)_3]\}_2$ (**3a'**) from $[(C_5H_5)_2YD(THF)]_2$ (**1a'**). The resonances at δ 7.87 for **2a** and δ 7.58 for **3a** in C_6D_6 and δ 8.30 for **2b** in C_4D_8O were assigned to the hydrogen added to the nitrile, $-N{=}C\mathit{H}R$, based on their absence in the spectra of **2a'** and **3a'**. These resonances in the acetonitrile products, **2a** and **2b**, are broad quartets due to coupling to the methyl group hydrogens and to two yttrium atoms. Irradiation of the methyl protons causes the quartet to collapse to a sharp triplet (J_{YH} = 3.0 Hz). In the spectrum of the $(CH_3)_3CCN$ product, **3a**, a triplet due to Y-H coupling is observed, as expected (J_{YH} = 1.5 Hz). The observed coupling to two yttrium atoms provides direct evidence that these products are dimeric in solution.

The IR spectra of **2a** and **3a** have strong absorptions at 1625 and 1655 cm^{-1}, respectively, assignable to $\nu_{N=C}$.[28] The spectrum of each complex also has a low-energy ν_{C-H} band at 2695 cm^{-1} for **2a** and 2610 cm^{-1} for **3a**. In the spectra of the deuterated analogues **2a'** and **3a'**, these absorptions shift to 2050 and 1980 cm^{-1}, respectively (ratio 1.31–1.32; cf. 1.36 calculated for a pure harmonic C–H oscillator) and are assigned to the C–H stretch of the $-N{=}C\mathit{H}R$ hydrogen.

Crystallographic Studies. In order to confirm the formulation of the nitrile reaction products and to precisely define the coordination geometry in the dimeric complex, an X-ray diffraction study was carried out on one of the nitrile products. Attempts to obtain suitable crystals of **2a** were unsuccessful, perhaps because the methyl substituent was not sterically bulky enough. However, diffusion of pentane into a saturated THF solution of the *tert*-butyl-substituted **3a** readily produced colorless prisms suitable for X-ray analysis.

As shown in Figures 1 and 2, the molecular structure confirms the formulation of **3a** as a dimeric alkylideneamido complex, which presumably is formed by addition of "$(C_5H_5)_2Y{-}H$" across the multiple bond of the nitrile. Important bond lengths and angles for this structure are presented in Table III and final fractional coordinates are given in the supplementary material. Two independent $\{(C_5H_5)_2Y[N{=}C(H)C(CH_3)_3]\}_2$ moieties are found in the unit cell, each of which exists as a dimer with its symmetry counterpart located across a center of inversion. Molecule "A" exhibits crystallographic disorder (see Experimental Section) in the *tert*-butyl groups, and many important bonding parameters cannot be extracted with reliability. However, molecule "B" is well-behaved, and its bond lengths and angles are discussed below.

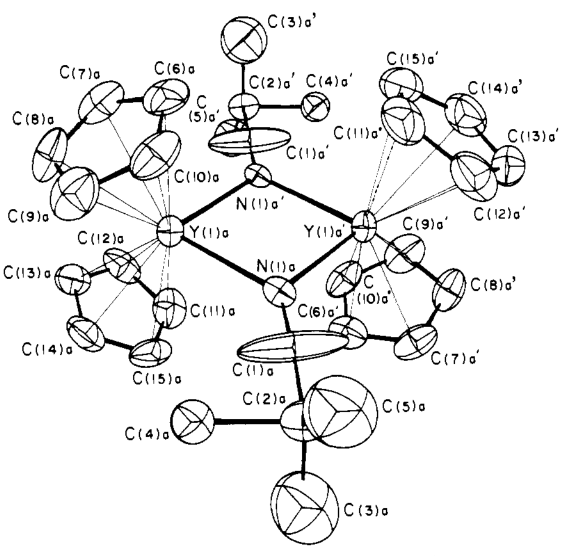


Figure 1. ORTEP plot of the molecular structure of $\{(C_5H_5)_2Y[N{=}C(H)C(CH_3)_3]\}_2$ (**3a**), molecule A.

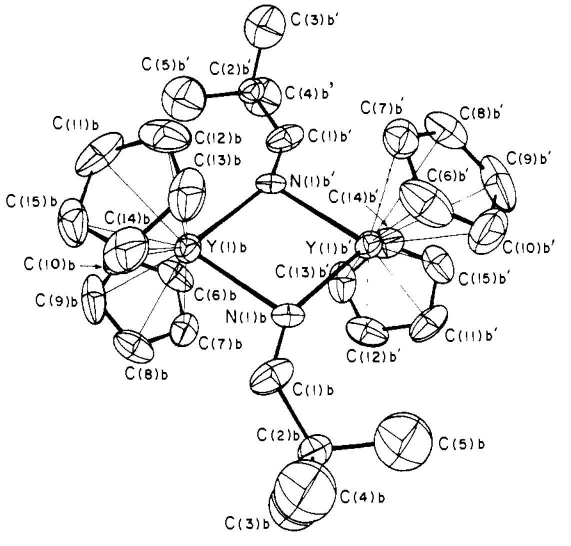


Figure 2. ORTEP plot of the molecular structure of $\{(C_5H_5)_2Y[N{=}C(H)C(CH_3)_3]\}_2$ (**3a**), molecule B.

The bond distances and angles for the $(C_5H_5)_2Y$ part of the structure are unexceptional. The Y–C distances for the cyclopentadienyl carbons range from 2.63 (2) to 2.67 (1) Å, with ring averages of 2.636 (5) and 2.650 (9) Å. These averages are intermediate in the range of averages found in other $[(C_5H_5)_2LnX]_2$ structures where Ln = Y or Er:[17] $[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2$[29] (I), 2.616 (5) and 2.634 (5) Å; $[(C_5H_5)_2YCH_3]_2$[14] (II), 2.655 (6) Å; $\{(C_5H_5)_2Y[HC{=}NC(CH_3)_3]\}_2$[11] (III), 2.68 (1), 2.674 (7) Å. The ring-centroid–metal–ring centroid angle, 129.7°, is similarly intermediate: I, 130.2°; II, 128.9°; III, 127.2°.

The most interesting part of the structure is the alkylideneamido bridge which connects the two $(C_5H_5)_2Y$ moieties. The six atoms comprising the $C{=}NY_2N{=}C$ unit are completely planar. The N–C bond length of 1.25 (2) Å is quite reasonable for an sp^2 carbon–nitrogen double bond[30] and compares well with distances found in other structurally characterized complexes in which two metals are bridged by $N{=}CRH$ or $N{=}CR_2$ groups.[31-37]

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Table II. 500-MHz ^{1}H NMR Data

complex	solvent	chemical shift^a	assignment
$\{(C_5H_5)_2Y[N{=}C(H)CH_3]\}_2$ (**2a**)	C_6D_6	6.07 (s)	C_5H_5
		1.35 (d)	$N{=}C(H)CH_3$
		7.87 (br q) ($^3J_{HH}$ = 3.8)	$N{=}C(H)CH_3$
		($^3J_{YH}$ = 3.0)	
$\{(CH_3C_5H_4)_2Y[N{=}C(H)CH_3]\}_2$ (**2b**)	$C_4D_8O^b$	5.92 (s), 5.84 (s)	$C_5H_4CH_3$
		2.11 (s)	$C_5H_4CH_3$
		8.30 (q) ($^3J_{HH}$ = 4.0, $^3J_{YH}$ = 1.7)	$N{=}C(H)CH_3$
		1.83 (d) ($^3J_{HH}$ = 4.0)	$N{=}C(H)CH_3$
$\{(C_5H_5)_2Y[N{=}C(H)C(CH_3)_3]\}_2$ (**3a**)	C_6D_6	6.04 (s)	C_5H_5
		0.83 (s)	$N{=}C(H)C(CH_3)_3$
		7.58 (t) ($^3J_{YH}$ = 1.7)	$N{=}C(H)C(CH_3)_3$
$(CH_3C_5H_4)_2Y(CH_2CH_3)$ (**4b**)	$C_4D_8O^b$	5.80 (s), 5.79 (s)	$C_5H_4CH_3$
		2.10 (s)	$C_5H_4CH_3$
		1.20 (d of t)	CH_2CH_3
		($^3J_{HH}$ = 8.0, $^3J_{YH}$ = 1.4)	
		−0.38 (d of q)	CH_2CH_3
		($^2J_{YH}$ = 3.1, $^3J_{HH}$ = 8.0)	
$(CH_3C_5H_4)_2Y(CH_2CH_2CH_3)$ (**5b**)	$C_4D_8O^b$	5.81 (s)	$C_5H_4CH_3$
		2.11 (s)	$C_5H_4CH_3$
		0.86 (t) ($^3J_{HH}$ = 7.1)	$CH_2CH_2CH_3$
		1.52 (br q)	$CH_2CH_2CH_3$
		−0.28 (br d of t) ($^3J_{HH}$ = 8.1; $^2J_{YH}$ = 3.3)	$CH_2CH_2CH_3$
$(C_5H_5)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$ (**6a**)	C_6D_6	5.92 (s)	C_5H_5
		2.87 (d) ($^3J_{HH}$ = 12.1)	CH_2CHCH_2
		6.46 (p)	CH_2CHCH_2
		3.28, 1.20 (m)	THF
$(CH_3C_5H_4)_2Y(\eta^3\text{-}CH_2CHCH_2)$ (**6b**)	$C_4D_8O^b$	5.71 (s), 5.70 (s)	$C_5H_4CH_3$
		2.07 (s)	$C_5H_4CH_3$
		6.25 (p) ($^3J_{HH}$ = 12.2)	CH_2CHCH_2
		2.58 (d) ($^3J_{HH}$ = 12.2)	CH_2CHCH_2
$[(CH_3C_5H_4)_2YC{\equiv}CC(CH_3)_3]_2$ (**7b**)	C_6D_6	6.31 (s), 6.24 (s)	$C_5H_4CH_3$
		2.20 (s)	$C_5H_4CH_3$
		0.99 (s)	$C(CH_3)_3$
$(C_5H_5)_2Y[C(CH_2CH_3){=}C(H)CH_2CH_3](THF)$ (**8a**)		6.11 (s)	C_5H_5
b a c d e		1.28 (t) ($^3J_{HH}$ = 7.5)	CH_3 a
		2.72 (q)	CH_2 b
	C_6D_6	4.90 (t) ($^3J_{HH}$ = 5.9)	H c
		2.24 (p)	CH_2 d
		1.06 (t) ($^3J_{HH}$ = 7.5)	CH_3 e
		3.26, 1.13 (m), concn dep	THF
$(CH_3C_5H_4)_2Y[C(CH_2CH_3){=}C(H)CH_2CH_3]$ (**8b**)		5.79 (s), 5.77 (s)	$C_5H_4CH_3$
b a c d e		2.07 (s)	$C_5H_4CH_3$
		0.97 (t) ($^3J_{HH}$ = 7.6)	CH_3 a
	$C_4D_8O^b$	2.40 (q)	CH_2 b
		4.77 (t) ($^3J_{HH}$ = 5.7)	H c
		2.02 (p)	CH_2 d
		0.92 (t) ($^3J_{HH}$ = 7.5)	CH_3 e
$(C_5H_5)_2Y[C(C_6H_5){=}C(H)C_6H_5](THF)$ (**9a**)	C_6D_6	6.09 (s)	C_5H_5
a		7.28 (d); 7.01 (d) (J = 7.1)	H_o; H'_o
		7.10 (t); 7.27 (t)	H_m; H'_m
		6.95 (t), 6.93 (t)	$H_{p,p'}$
		6.40 (s)	H a
		3.10, 0.98 (m)	THF
$[(CH_3C_5H_4)_2YH(NC_5H_5)]_2$ (**10b**)	C_6D_6	6.22 (s), 6.11 (s)	$C_5H_4CH_3$
		2.11 (s)	$C_5H_4CH_3$
		3.08 (t) ($^1J_{YH}$ = 27.0)	Y-H-Y
		8.75, 6.86, 6.58 (m)	NC_5H_5
$(CH_3C_5H_4)_2Y(NC_5H_6)$ (**11b**)	$C_4D_8O^b$	5.93 (s), 5.91 (s)	$C_5H_4CH_3$
		2.10 (s)	$C_5H_4CH_3$
		3.71 (d) ($^3J_{HH}$ = 4.3)	$\overline{NCH_2CHCHCHCH}$
		4.51 (m)	$\overline{NCH_2CHCHCHCH}$
		5.74 (m)	$\overline{NCH_2CHCHCHCH}$
		4.65 (t) ($^3J_{HH}$ = 5.7)	$\overline{NCH_2CHCHCHCH}$
		6.77 (d) ($^3J_{HH}$ = 6.3)	$\overline{NCH_2CHCHCHCH}$
$(C_5H_5)_2Y(NC_5H_6)(NC_5H_5)$ (**12a**)	C_6D_6	6.01 (s)	C_5H_5
		6.75 (d) ($^3J_{HH}$ = 7.3)	$\overline{NCHCHCH_2CHCH}$
		4.51 (m)	$\overline{NCHCHCH_2CHCH}$
		3.64 (s)	$\overline{NCHCHCH_2CHCH}$
		8.35, 6.88, 6.57	NC_5H_5

[a] Chemical shifts (in δ, ppm) are referenced to residual hydrogen in benzene-d_6 at δ 7.15 or to residual hydrogen in THF-d_8 at δ 3.58. Coupling constants are in Hz. Integrated intensities match those expected. Small non-first-order coupling (~2 Hz) is frequently observed in the resonances of the $CH_3C_5H_4$ ring protons. [b] In spectra run in C_4D_8O, multiplets due to C_4H_8O at 3.61 and 1.73 ppm are observed.

Table III. Bond Lengths (Å) and Angles (Deg) for Molecule B of $\{(C_5H_5)_2Y[N{=}C(H)C(CH_3)_3]\}_2$ (3a)

atoms	distance	atoms	distance
Y(1)-Y(1)	3.617 (2)	Y(1)-C(1)	3.04 (1)
Y(1)-C(6)	2.63 (2)	Y(1)-C(7)	2.64 (2)
Y(1)-C(8)	2.63 (2)	Y(1)-C(9)	2.64 (3)
Y(1)-C(10)	2.63 (2)	Y(1)-C(11)	2.64 (2)
Y(1)-C(12)	2.67 (1)	Y(1)-C(13)	2.64 (2)
Y(1)-C(14)	2.64 (1)	Y(1)-C(15)	2.65 (2)
Y(1)-Cnt(1)	2.378 (1)	Y(1)-Cnt(2)	2.386 (1)
Y(1)-Ave(1)	2.636 (5)	Y(1)-Ave(2)	2.650 (9)
Y(1)-N(1)	2.382 (9)	Y(1)-N(1)′	2.314 (9)
C(1)-C(2)	1.48 (2)	C(1)-N(1)	1.25 (2)
C(2)-C(3)	1.49 (3)	C(2)-C(4)	1.50 (3)
C(2)-C(5)	1.52 (3)	C(6)-C(7)	1.35 (3)
C(6)-C(10)	1.32 (3)	C(7)-C(8)	1.34 (3)
C(8)-C(9)	1.34 (3)	C(9)-C(10)	1.34 (4)
C(11)-C(12)	1.36 (4)	C(11)-C(15)	1.39 (3)
C(12)-C(13)	1.35 (3)	C(13)-C(14)	1.35 (3)
C(14)-C(15)	1.33 (4)		

atoms	angle	atoms	angle
Cnt(1)-Y(1)-Cnt(2)	129.7	Cnt(1)-Y(1)-N(1)	107.4
Cnt(2)-Y(1)-N(1)	108.0	Cnt(1)-Y(1)-N(1)′	110.0
Cnt(2)-Y(1)-N(1)′	110.5	N(1)-Y(1)-N(1)′	79.3 (3)
C(2)-C(1)-N(1)	135 (1)	C(1)-C(2)-C(3)	111 (1)
C(1)-C(2)-C(4)	111 (1)	C(3)-C(2)-C(4)	113 (1)
C(1)-C(2)-C(5)	112 (1)	C(3)-C(2)-C(5)	105 (1)
C(4)-C(2)-C(5)	105 (2)	C(7)-C(6)-C(10)	107 (2)
C(6)-C(7)-C(8)	108 (2)	C(7)-C(8)-C(9)	108 (2)
C(8)-C(9)-C(10)	107 (2)	C(6)-C(10)-C(9)	110 (2)
C(12)-C(11)-C(15)	106 (2)	C(11)-C(12)-C(13)	109 (2)
C(12)-C(13)-C(14)	107 (2)	C(13)-C(14)-C(15)	110 (2)
C(11)-C(15)-C(14)	108 (2)	Y(1)-N(1)-Y(1)′	100.7 (3)
Y(1)-N(1)-C(1)	109.8 (9)	Y(1)′-N(1)-C(1)	149.4 (9)

The two independent Y–N distances are significantly different, 2.314 (9) and 2.382 (9) Å, but both must be regarded as short compared to the distance expected for a =N:→Y linkage, which would appear to be minimally 2.5 Å.[38,39] For comparison, the Y–C bond distances in the 3-center, 2-electron methyl-bridged dimer $[(C_5H_5)_2YCH_3]_2$ are 2.553 (10) and 2.537 (9) Å.[14,39] These distances are consistent with a bonding scheme for nitrogen comprised of a nitrogen–carbon double bond with the third valence of nitrogen involved in a 3-center Y–N–Y bridge. The Y–Y distance of 3.617 (2) Å is similar to that found in other erbium[17] and yttrium bridged dimers: I, 3.657 (2) Å;[29] II,[14] 3.599 (8) Å; III, 3.607 (1) Å;[11] **1b**, 3.664 (1) Å;[3] $[(CH_3C_5H_4)_2ErH(THF)]_2$, 3.616 (5) Å.[3]

The alkylideneamido bridge is not located symmetrically between the two $(C_5H_5)_2Y$ moieties as evidenced by the Y(1)b–N(1)b–C(1)b and Y(1)b′–N(1)b–C(1)b angles: 109.8 (9) and 149.4 (9)°, respectively. This asymmetry is reminiscent of that found in the bridged alkynides $[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2$[29] (ErC≡C, 115 (2)°; Er′C≡C, 149 (2)°) and $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$[40] (SmC≡C, 151 (1)°; Sm′C≡C, 112 (1)°), although the reason for the effect may be different. The Y(1)b–C(1)b distance of 3.04 (1) Å is well beyond the range for an Y–C interaction. The analogous distances in the bridged alkynides were found to be around 3.2 Å.

Crystallographic data on only one other μ-η^1-N=CHR complex are available for comparison with the angular asymmetry found in **3a**. In $HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9[P(CH_3)_2C_6H_5]$,[31] the asymmetry is less: the analogous MN=C angles are 131.8 (10)° and 142.5 (10)°, with the larger angle on the side of the non-hydrogen substituent as in **3a**. μ-η^1-N=CR$_2$ complexes display even less asymmetry: $Al_2[N{=}C(C_6H_5)(C_6H_4Br)](C_6H_5)_4$[33] has Al–N–C angles of 129.2° and 133.7°; $Mn_2[\mu\text{-}\eta^1\text{-}N{=}C(CF_3)_2](CO)_7$[34] has Mn–N–C angles of 139.72 (57)° and 142.71 (56)°; $Al_2[N{=}C(CH_3)_2]_2(CH_3)_4$[35] has identical Al–N–C angles. The substantially greater asymmetry found in **3a** can arise in several ways. The direction of asymmetry of the alkylideneamido bridge is such that it provides more room for the *tert*-butyl substituent. The asymmetry is also in the direction that puts the N=C(*H*)C(CH$_3$)$_3$ hydrogen closer to the yttrium center. Since lowered ν_{CH} frequencies assignable to this hydrogen are observed in the infrared spectrum of **3a** (vide supra), an Y–H–C interaction could contribute to this asymmetric structural conformation. The observed asymmetry is also consistent with the presence of a stereochemically active lone pair of electrons on nitrogen. Conformational effects of this type by nitrogen lone pairs in —N=CR$_2$ ligands have been observed by NMR in monometallic systems.[41,42] The NMR spectrum of **3a** indicates no asymmetry in solution, however.

The structure of **3a** clearly establishes that the Y–H moiety engages in 1,2-addition across a multiple unsaturated bond. The question of whether this is a cis or trans addition cannot be determined because the complex dimerized. Although a variety of metal hydride reductions of nitriles are described in the literature,[31,36,37,43-45] apparently none of the boron,[44] aluminum,[43] or early transition-metal systems[45] useful in organic synthesis have provided crystallographically characterized products. In this sense, **3a** provides a structural prototype for these hydride reductions.

Reactions with Alkenes. Both **1a** and **1b** react with terminal monosubstituted alkenes at room temperature in THF to form the corresponding alkyl complexes (eq 8). The rate of reaction

$$[(C_5H_4R)_2YH(THF)]_2 + 2R'CH{=}CH_2 \rightarrow 2(C_5H_4R)_2Y(CH_2CH_2R')(THF) \quad (8)$$

$$\mathbf{4},\ R' = H \qquad \mathbf{5},\ R' = CH_3$$

is observed to correlate with the steric bulk of the substrate. Ethene reacts quantitatively at room temperature with **1b** in THF

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(32) $Fe_2[\mu\text{-}\eta^1\text{-}N{=}C(p\text{-}CH_3C_6H_5)_2](CO)_6$, N=C = 1.24 (2) and 1.29 (2) Å: Bright, D.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1967**, 245–246.

(33) $Al_2[\mu\text{-}N{=}C(C_6H_5)(C_6H_4Br)]_2(C_6H_5)_4$, N=C = 1.282 (15) Å: McDonald, W. S. *Acta Crystallogr., Sect. B* **1969**, *25*, 1385–1391.

(34) $Mn_2[\mu\text{-}\eta^1\text{-}N{=}C(CF_3)_2](CO)_7$, N=C = 1.256 (9) and 1.259 (9) Å: Churchill, M. R.; Lin, K.-K. G. *Inorg. Chem.* **1975**, *14*, 1675–1680.

(35) $Al_2[\mu\text{-}N{=}C(CH_3)_2]_2(CH_3)_4$, N=C = 1.273 (3) Å: Seale, S. K.; Atwood, J. L. *J. Organomet. Chem.* **1974**, *73*, 27–34.

(36) $Re_2(\mu\text{-}\eta^1\text{-}N{=}CHCH_3)(CO)_6[(C_6H_5)_2PCH_2P(C_6H_5)_2]H$ has an anomalously long[31] reported C=N distance of 1.39 (10) Å: Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 171–173.

(37) $[C_5(CH_3)_4(C_2H_5)]_2Ta_2(\mu\text{-}\eta^2\text{-}N{=}CHCH_3)Cl_4H$ [Churchill, M. R.; Wasserman, H. J.; Belmonte, P. A.; Schrock, R. R. *Organometallics* **1982**, *1*, 559–561] and $HFe_3(\mu_3\text{-}\eta^2\text{-}N{=}CHCH_3)(CO)_9$ [Andrews, M. A.; van Buskirk, G.; Knobles, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7245–7254] are not comparable since η^2 coordination is involved.

(38) Complex, metal–N distance (Å), metal radius minus Y^{3+} radius (Å)[17] (reference): $(C_5H_5)_3YbNC_4H_4NYb(C_5H_5)_3$, 2.61 (1), –0.022 (Baker, E. C.; Raymond, K. N. *Inorg. Chem.* **1977**, *16*, 2710–2714). $[C_5(CH_3)_5]_2Yb(NC_5H_5)_2$, 2.586 (7) and 2.544 (6), 0.05 (Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A., *Inorg. Chem.* **1982**, *21*, 2647–2649). $La(bpy)_2(NO_3)_3$, 2.665 (10) and 2.659 (9), 0.181 (Al-Karaghauli, A. R.; Wood, J. S. *Inorg. Chem.* **1972**, *11*, 2293–2299). $Eu(terpy)_3(ClO_4)_3$, 2.57 (1)–2.62 (1), 0.07 (Frost, G. H.; Hart, F. A.; Heath, C.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1969**, 1421–1422). $Eu(phen)(acac)_3$, 2.645(12) and 2.641(8), 0.07 (Watson, W. H.; Williams, R. J.; Stemple, N. R. *J. Inorg. Nucl. Chem.* **1972**, *34*, 501–508). $Ho(thd)_3(4\text{-picoline})_2$, 2.53 (3), 0.014 (Horrocks, W. DeW., Jr.; Sipe, J. P., III; Luber, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 5258–5260). $\{Sm[2.2.2\text{-crypt}]NO_3\}[Sm(NO_3)_5(H_2O)]$, 2.748 (5), 2.779 (6), 0.084 (Burns, J. H. *Inorg. Chem.* **1979**, *18*, 3044). Comparisons using the radii of Shannon (Shannon, R. D., *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767) similarly indicate the Y–N bond in **3a** is short compared to known N:→Ln distances.

(39) An Y–N distance of 2.325 (4) Å has been observed in the formimidoyl complex $\{(C_5H_5)_2Y[\mu\text{-}\eta^2\text{-}HC{=}NC(CH_3)_3]\}_2$, in which the two yttrium atoms are bridged by the formimidoyl carbon at distances of 2.545 (5) and 2.561 (5) Å and each yttrium is within bonding distance of one nitrogen atom. The C=N bond distance is 1.275 (6) Å.[11]

(40) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709.

(41) Collier, M. R.; Lappert, M. F.; McMeeking, J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 689–694.

(42) Cf.: Sufferford, C.; Wade, K. *J. Chem. Soc. A* **1970**, 2010–2017.

(43) Rabinovitz, M. In "The Chemistry of the Cyano Group"; Rappoport, Z., Ed.; Wiley: New York, 1970; Chapter 7.

(44) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972.

(45) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340.

in less than an hour to form the ethyl complex, $(CH_3C_5H_4)_2Y(CH_2CH_3)(THF)$ (**4b**), whereas the propene reaction requires up to 10 h to generate $(CH_3C_5H_4)_2Y(CH_2CH_2CH_3)(THF)$ (**5b**). Neither 2-methylpropene nor *cis*-3-hexene was observed to react with **1b** under the same conditions even after 3 days. In the propene reaction, the direction of the 1,2-addition of the Y–H moiety is as expected based on both polarization[46] and steric arguments. The alkyl products had limited stability upon solvent removal and were characterized only by NMR spectroscopy (Table II).[47]

The ^1H NMR spectrum of **4b** is interesting in that Y–H coupling is exhibited by the methyl hydrogen resonance ($^3J_{Y-H} = 1.4$ Hz) as well as by the methylene resonance ($^2J_{Y-H} = 3.1$ Hz). $^3J_{YH}$ for this methyl resonance is similar to the three-bond YN=CH coupling observed for **2** and **3**, 1.7–3.0 Hz (vide supra). This ^1H NMR spectrum clearly demonstrates the unique potential of organoyttrium complexes to reveal information not obtainable in analogous organolanthanide complexes that lack either diamagnetism or a high abundance nucleus with $I = {}^1/_2$.

One other interesting feature of the ^1H NMR spectrum of **4b** is the appearance of new resonances after approximately 1 day in the presence of excess ethene. A new α proton resonance is generated at slightly lower field than in pure **4b**, and other resonances consistent with an *n*-butyl group are also observed. Decoupling experiments are also consistent with the existence of an *n*-butyl complex presumably arising as the first step in a Ziegler–Natta type of polymerization. Such reactivity has previously been observed for yttrium alkyls, e.g., $[(RC_5H_4)_2YCH_3]_2$ and $[C_5(CH_3)_4(C_2H_5)]_2Y(n\text{-}C_4H_9)$, at 70–100 °C[49] as well as for lanthanide complexes.[48-50]

Reactions with 1,2-Propadiene. Another example of 1,2-addition of Y–H to a carbon–carbon double bond is the rapid reaction of **1a** and **1b** with 1,2-propadiene to form the corresponding allyl complexes **6a** and **6b** (eq 9). A trihapto coordination mode is observed for the allyl moiety based on strong IR absorptions at 1540 cm^{-1} and the ^1H NMR spectra of both complexes (Table II).

$$[(C_5H_4R)_2YH(THF)]_2 + 2\ H_2C{=}C{=}CH_2 \rightarrow 2\ \underset{\textbf{6}}{(C_5H_4R)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)} \quad (9)$$

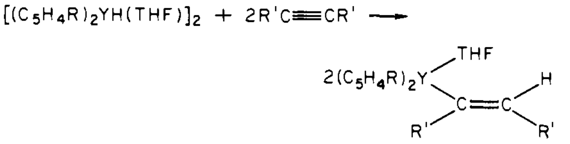
The previously reported cyclopentadienyllanthanide allyl complexes, $(C_5H_5)_2Ln(\eta^3\text{-}C_3H_5)$ (Ln = Sm, Ho, Er), have similar IR absorptions, but no NMR data were presented.[51] In contrast to these lanthanide complexes, which were reported as solvate free, we find that THF persists in the yttrium allyls, both in the solid and in arene solution. Attempts to displace the THF from **6a** by heating results in decomposition.

Reactions with Alkynes. The reaction of **1a** and **1b** with terminal alkynes does not involve Y–H addition across the unsaturated carbon–carbon bond. Instead metalation at the acidic terminal position occurs to generate hydrogen and an alkynide complex, **7** (eq 10). The reaction proceeds rapidly and is indicative of the hydridic nature of this class of metal–hydrogen complexes.

$$[(C_5H_4R)_2YH(THF)]_2 + 2HC{\equiv}CC(CH_3)_3 \rightarrow \underset{\textbf{7}}{[(C_5H_4R)_2YC{\equiv}CC(CH_3)_3]_2} + 2H_2 \quad (10)$$

Such metalation of C–H bonds in terminal alkynes by lanthanide methyl and lanthanide *tert*-butyl moieties has previously been reported.[29,52] The erbium analogue of **7a**[29] and the samarium analogue of **7b**[40] have been shown by X-ray diffraction to have asymmetric, electron-deficient alkynide-bridged structures, and similar structures are likely for the yttrium complexes. The ^1H NMR spectra of **7a** and **7b** (Table II) exhibit simple cyclopentadienyl patterns, indicating that a single, rigid asymmetric structure is not maintained in solution at room temperature [a similar situation is observed for **3a** (vide supra)]. No long-range Y–H coupling is observed in this case. Complex **7a** has also been prepared by ionic metathesis from $LiC{\equiv}CC(CH_3)_3$ and $(C_5H_5)_2YCl$[53] and by metalation from $HC{\equiv}CC(CH_3)_3$ and $(C_5H_5)_2YCH_3(THF)$.[54]

Cyclopentadienyl hydrides react with internal alkynes by adding Y–H across the multiple bond to form alkenyl complexes (eq 11).



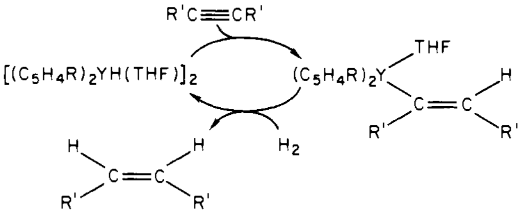
(11)

8, R′ = C_2H_5 9, R′ = C_6H_5

These reactions are considerably slower than the terminal alkyne reactions. As with alkene substrates, the rates appear to depend on steric factors. Up to 16 h is required for **1b** to react with 3-hexyne to form **8b**, whereas no reaction product is observed after 2 days using diphenylethyne as a substrate. The less sterically encumbered **1a** reacts with 3-hexyne to form **8a** in 4 h and requires 12 h to react with diphenylethyne at 40 °C to form **9a**. The reactions are essentially quantitative except for the **1a**/$C_6H_5C{\equiv}CC_6H_5$ system, for which a detectable side product (<10%) is observed. The competing reaction may be a metalation of the phenyl ring that occurs at the higher reaction temperature, since 5–10% diphenylethyne is recovered upon hydrolysis.

The ^1H NMR data on **8** and **9** (Table II) are consistent with a THF-solvated alkenyl complex as shown in eq 11. Chemical evidence suggests the yttrium hydride bond adds cis to the alkyne to generate the *cis*-alkenyl complex. Hydrolysis of **9a** forms *cis*-stilbene and hydrogenolysis of **8b** forms *cis*-3-hexene and generates the starting hydride **1b**.

Catalytic Studies. The synthesis of the alkenyl complexes taken with the hydrogenolysis reaction described above constitutes a catalytic cycle for hydrogenation of 3-hexyne (eq 12). We have been interested in precisely defining such a reaction sequence since we first discovered f-element-catalyzed homogeneous activation of molecular hydrogen using alkyne hydrogenation as the model reaction.[55-57] In those studies, complexes of formula $(ErC_9H_{15})_n$, YbC_6H_{10}, and SmC_6H_{10}, prepared by co-condensation of the appropriate metal atoms with 3-hexyne, were found to effect catalytic hydrogenation of 3-hexyne to 3-hexene that was >90% cis. Although that research provided the first evidence suggesting the existence of molecular lanthanide hydride complexes, no hydrides were isolated. With the availability of complexes **1a** and **1b**, the reasonable catalytic hydrogenation mechanism of (a) cis addition to substrate followed by (b) hydrogenolysis of a metal–carbon bond could be tested. As described above, catalytic hydrogenation does proceed in this way. The fact that the catalysis



(12)

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(46) Roberts, J. D.; Caserio, M. C. "Basic Principles of Organic Chemistry"; 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1977; pp 377–380.

(47) NMR evidence for Lu–H addition to alkenes[10] and chemical evidence for Sm–H addition to alkenes[5] recently has been presented.

(48) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507–6508.

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can be effected sequentially, **1b** → **8b** → **1b** + *cis*-3-hexene, as well as starting from **1b** plus 3-hexyne and hydrogen, is consistent with the relatively slow rates observed, ~2.5 × 10^{-3} turnovers/min/metal center.[58]

Reaction with Pyridine. Another test of the reactivity of a hydride complex is its potential to reduce aromatic compounds. Since the organoyttrium hydrides studied here do not appear to react with unactivated benzene rings under mild conditions, their reactivity with aromatic compounds activated by a heteroatom such as nitrogen was investigated.

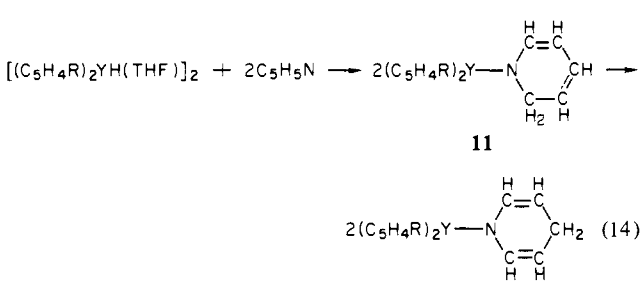
Organoyttrium hydrides **1a** and **1b** react with pyridine via displacement of THF from the coordination sphere, followed by 1,2-hydride addition and subsequent isomerization in excess pyridine to the 1,4-pyridyl product. The course of these reactions is more complex than those previously discussed due to the formation of the pyridine adducts and the limited stability of the pyridyl products.

In nonpolar solvents such as pentane, **1a** and **1b** were observed to react with excess pyridine to form base adducts $[(C_5H_4R)_2YH(C_5H_5N)]_2$ (**10**) by displacement of THF (eq 13).

$$[(C_5H_4R)_2YH(THF)]_2 + 2C_5H_5N \rightarrow \underset{\mathbf{10}}{[(C_5H_4R)_2YH(C_5H_5N)]_2} + 2THF \quad (13)$$

1a reacts over a few hours to form **10a**, whereas the reaction of **1b** to give **10b** is somewhat slower. The products maintain the dimeric $Y(\mu\text{-}H)_2Y$ bridged structure as evidenced by retention of the triplet hydride resonance in the ^1H NMR spectrum of **10b** (J_{Y-H} = 27 Hz) and by the presence of a bridged hydride absorption in the IR spectrum of **10a** with a maximum at 1265 cm^{-1}. This is shifted from the 1315-cm^{-1} maximum in **1a**, but it is still in the region observed for doubly bridged hydrides involving these metals.[3-5]

Polar solvents promote addition of Y–H to the ring. Addition of pyridine to **1b** in THF in an NMR tube is sufficiently fast to prevent observation of a pyridine adduct intermediate. The hydride resonance rapidly disappears with concurrent formation of a spectrum consistent with the 1,2-addition product, the assignment of which was substantiated by decoupling experiments. The 1,2-addition product subsequently rearranges to the 1,4-isomer (eq 14). Fifty percent conversion is observed after 2 days. The reactions of **1b** and **1b′** with pyridine-d_5 confirmed that hydrogen originally attached to the metal was transferred to the 2 position on pyridine.



11

(14)

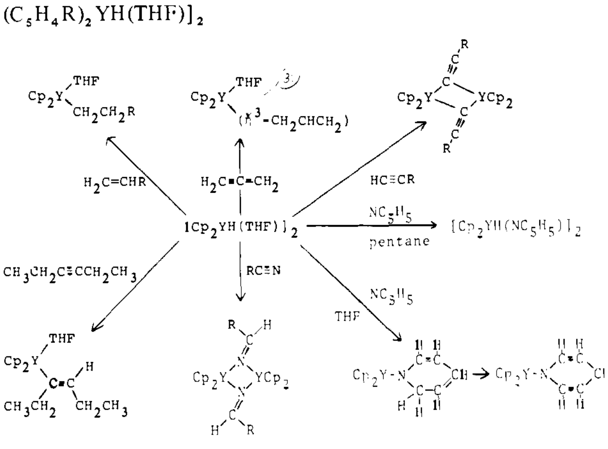
12

Attempts to isolate **11b** failed due to its instability upon solvent removal. **11a** is more stable with respect to this decomposition, but **1a** is sufficiently insoluble that appreciable isomerization of **11a** to **12a** occurs during the time necessary to effect reaction.

Complete conversion of the 1,2-isomer **11a** to the 1,4-isomer required 5 days in THF with a 10-fold excess of pyridine. The yellow powder isolated was identified as the 1,4-isomer of $(C_5H_5)_2Y(NC_5H_6)(NC_5H_5)$ by ^1H NMR spectroscopy. The pyridine in this complex is very labile and must be present during recrystallization to prevent decomposition.

The reactions of **1a** and **1b** with substituted pyridines were also briefly examined. ^1H NMR examination of the reaction of **1b** with a 4-fold excess of 4-methylpyridine in THF-d_8 indicated that the 1,2-pyridyl product was rapidly formed. After 2 days the 1,2-pyridyl was still the main product, with no evidence of formation of the 1,4-isomer. Apparently, the methyl group is effectively blocking the isomerization reaction. Reaction of 4-methylpyridine with **1a** was attempted on a preparatory scale, but the 1,2-pyridyl complex could not be isolated without decomposition.

Scheme I. Summary of Reactivity of the Y–H Bond in $[(C_5H_4R)_2YH(THF)]_2$



Precedent for the type of 1,2- and 1,4-addition of Y–H to pyridine as observed here exists in previous studies of $LiAlH_4$,[59] MgH_2,[60] and ZnH_2[61] reductions of pyridine.

Conclusion

We have demonstrated a clean, high yield synthesis of the dimeric hydrides **1a** and **1b**, which further illustrates the principle that high reactivity can be achieved with yttrium and lanthanide alkyls when attached to a coordinatively unsaturated, unsolvated metal center.[3] Our studies of the reactivity of the organoyttrium hydrides with unsaturated hydrocarbons demonstrate that a rich organometallic chemistry is available through the Y–H bond (Scheme I). The observed reactivity of the dimeric **1a** and **1b** indicates the Y–H bond is hydridic and has reactivity related to that of B–H, Al–H, and early transition metal-hydrogen bonds. 1,2-Addition to unsaturated bonds is the most common mode of reactivity in the absence of acidic hydrogens on the substrate. This reactivity toward addition combined with the demonstrated viability of hydrogenolysis under mild conditions in organoyttrium chemistry[3,5] provides a mechanistic rationale for the observed catalytic activity of these hydrides in hydrogenation reactions. As demonstrated by the crystallographic study of **3a**, these dimeric lanthanide hydrides and the addition reactivity they display may provide access to structural information on metal hydride reaction products not easily obtainable with other metals having analogous reactivity.

We expect the chemistry of the analogous cyclopentadienyl and methylcyclopentadienyl hydrides of the late lanthanides of comparable size, $[(C_5H_4R)_2LnH(THF)]_2$ (Ln = Lu, Er),[3] to be similar to that described here for **1a** and **1b**. The samarium hydride $[(C_5Me_5)_2SmH]_2$, **IV**, which we previously described,[5] may display different chemistry since the cyclopentadienyl ligands are significantly different and the metal is much larger in radius.[62,63]

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(58) Much faster f element based homogeneous hydrogenation cataysts have subsequently been discovered.[5]

(59) Lansbury, P. T.; Peterson, J. O. *J. Am. Chem. Soc.* **1961**, *83*, 3537–3538; **1962**, *84*, 1756–1757; **1963**, *85*, 2236–2242.

(60) Ashby, E. C.; Goel, A. B. *J. Organomet. Chem.* **1981**, *204*, 139–145.

(61) Dekoning, A. J.; Boersma, J.; Vander Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *186*, 159–172.

(62) For example, $[(C_5Me_5)_2SmH]_2$ is unstable in THF and $(C_2H_5)_2O$ and the Sm–H readily exchanges with the pentamethylcyclopentadienyl hydrogens (observed with the deuterium analogue). It does have catalytic activity in hydrogenation reactions like **1a** and **1b**, however.[5]

(63) Results communicated as this manuscript was nearing completion on $[(C_5Me_5)_2LuH]_n$,[64] and $(C_5Me_5)_2ScH$[65] also support this contention.

(64) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276–277. Watson, P. L., Industrial Associates Conference on Catalysis, California Institute of Technology, Pasadena, CA, March 16, 1983; 185th National Meeting of the American Chemical Society, Seattle, WA, March 1983, INOR 189. *Chem. Eng. News*, April 11, **1983**, pp 46–47.

In addition to studying the variation in reactivity of Ln–H and Y–H bonds as a function of the metal and coligands in these dimers, we are studying the extension of our dimeric hydride chemistry to the yttrium and lanthanide hydride bonds in trimeric complexes.[4,16] The dimeric hydrides **1a** and **1b** are also reactive with multiply bonded carbon–oxygen systems including CO, ketones, and transition-metal carbonyls, and this reactivity will be described in a subsequent paper.

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 by using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-43 Dri-Lab) techniques.

Physical Measurements. Infrared spectra were obtained as KBr pellets prepared in the glovebox and protected from the atmosphere outside the box by attaching O-ring sealed NaCl plates to the pellet holder. The IR measurements were obtained on a Perkin-Elmer 283 spectrophotometer. ^{1}H NMR spectra were obtained on either a Bruker HX-270 or the 500 MHz DS-1000 spectrometer constructed at the University of Chicago. ^{13}C NMR spectra were obtained on a Bruker HX-90E. Gas chromatographic analyses were performed on a Hewlett-Packard 5830A thermal conductivity gas chromatograph equipped with a 6 ft × $^1/_4$ in. column of 4-Å molecular sieves pulverized to 40/60 mesh (used at −140 °C) and a 6 ft × $^1/_4$ in. column of 20% tricresyl phosphate on 60/80 Chromosorb W treated with dimethyldichlorosilane. Complexometric metal analyses were obtained as previously described.[29]

Materials. Toluene was predried with alumina and distilled from sodium. THF was distilled from potassium benzophenone ketyl. Pentane and hexane were washed with sulfuric acid, dried over $MgSO_4$, refluxed over finely divided $LiAlH_4$, and vacuum transferred. Deuterated NMR solvents were vacuum transferred from potassium benzophenone ketyl. Hydrogen (Matheson, Prep grade) was purified by passage through an Alltech Oxytrap. Deuterium, ethene, propene, and 1,2-propadiene (Union Carbide-CP grade) were used as received. 3-Hexyne, acetonitrile, and 2,2-dimethylpropanonitrile were dried over molecular sieves activated by heating overnight under vacuum. Pyridine was predried over KOH and distilled from BaO. Diphenylethyne was used as received. KBr was ground to a fine powder and heated to 120 °C overnight under vacuum. CH_3Li was obtained from Aldrich and the concentration was checked before use.[66] Anhydrous yttrium trichloride was prepared from the hydrate (Research Chemicals) by the method of Taylor and Carter.[67] NaC_5H_4R and $[(C_5H_4R)_2YCl]_2$ (R = H, CH_3) were obtained as previously described.[3] We include here our synthesis of $[(C_5H_5)_2YCH_3]_2$,[14] which is a modification of that originally reported for the analogous organolanthanides.[19]

$[(C_5H_5)_2YCH_3]_2$. $[(C_5H_5)_2YCl]_2$ (3.663 g, 7.20 mmol) was dissolved in THF (80 mL) in a Schlenk flask equipped with a stirbar. CH_3Li (8.0 mL of a 1.8 M solution, 14.4 mmol) in diethyl ether was added via syringe to the THF solution at −40 °C. The suspension readily cleared and the solution was allowed to warm overnight. Solvent was removed in vacuo and the residue was extracted twice with toluene (2 × 100 mL). Removal of impurities was facilitated by heating toluene solutions of the product to 60 °C. A white microcrystalline powder of $[(C_5H_5)_2YCH_3]_2$ (3.1 g, 6.5 mmol, 90%) was obtained upon removal of toluene from the final extract. In practice, toluene extractions are repeated until the product has a single CH_3 resonance and no THF in its ^{1}H NMR spectrum. Usually, low-halide CH_3Li permits fewer extractions than when CH_3Li stabilized as a LiBr complex is used.

$[(C_5H_4CH_3)_2YCH_3]_2$. $[(C_5H_4CH_3)_2YCl]_2$ (1.784 g, 3.16 mmol) was suspended in diethyl ether (30 mL) in a Schlenk flask equipped with a magnetic stir bar. CH_3Li (3.5 mL of a 1.8 M solution, 6.3 mmol) in diethyl ether was syringed into the flask. A colorless solution soon formed. The solution was stirred for 8 h, solvent was removed in vacuo, and the remaining paste was taken into the glovebox. The residue was extracted with hexane (2 × 50 mL). LiCl was most effectively removed by heating these solutions just to reflux and allowing them to cool to room temperature before filtration. Usually, the product (1.4 g, 2.65 mmol, 84%) was pure by ^{1}H NMR after two such extractions.

$[(C_5H_5)_2YH(THF)]_2$ (1a). $[(C_5H_5)_2YCH_3]_2$ (1.253 g, 1.34 mmol) was dissolved in a toluene–THF solution (30 mL:3 mL) in a 250-mL round-bottom flask equipped with a Fischer–Porter greaseless seal, a high-vacuum Teflon stopcock, and a stir bar. The reaction vessel was attached to a vacuum line, cooled to −78 °C, and evacuated. An atmospheric pressure of H_2 was established and the stopcock closed. The solution was stirred vigorously for 40 h. After filtration and washing with toluene and pentane, white **1a** was isolated (1.318 g, 2.26 mmol, 84% yield).

Table IV. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compound	$\{(C_5H_5)_2Y[N{=}C(H)C(CH_3)_3]\}_2$
M_r	303.27
space group	$P\bar{1}$
cell constants, *a*, Å	9.261 (5)
b, Å	10.398 (6)
c, Å	16.323 (8)
α, deg	86.48 (4)
β, deg	88.95 (4)
γ, deg	70.29 (4)
cell vol, Å^3	1476.95
molecules/unit cell	2 dimers
ρ(calcd), g cm^{-3}	1.36
μ(calcd), cm^{-1}	40.58
radiation	Mo Kα
max. crystal dimensions (mm)	0.45 × 0.45 × 0.20
scan width	0.8 + 0.2 tan ∂
standard reflections	400, 040, 004
decay of standards	<3%
reflections measured	3597
2θ range	1–44
observed reflections	2532
no. of parameters varied	281
GOF	2.20
R	0.056
R_w	0.064

$[(C_5H_4CH_3)_2YH(THF)]_2$ (1b). $[(CH_3C_5H_4)_2YCH_3]_2$ (1.367 g, 1.30 mmol) was dissolved in a hexane–THF solution (40 mL:4 mL) in a 250-mL round-bottom flask equipped with a Fischer–Porter seal, a high-vacuum Teflon stopcock, and a stir bar. An atmospheric pressure of H_2 was added as described above, and the solution was stirred overnight for 10 h. The flask was refilled with H_2 and the solution was stirred for 24 h longer. Filtration in a glovebox gave a white powder, which was washed with hexane and extracted with THF. After solvent removal, white microcrystalline **1b** was obtained (1.422 g, 2.22 mmol, 85%).

$\{(C_5H_5)_2Y[N{=}C(H)CH_3]\}_2$ (2a). **1a** (71 mg, 0.12 mmol) was suspended in THF (10 mL) in a flask in the glovebox. CH_3CN (0.2 mL, 4 mmol) was added by pipet to the stirred suspension and the hydride rapidly dissolved. The clear, colorless solution was evaporated to a white powder of **2a** (46 mg, 0.09 mmol, 75%), which is moderately soluble in THF and slightly soluble in benzene. Anal. Calcd for $YC_{12}H_{14}N$: Y, 34.08. Found: Y, 33.8. IR (KBr, cm^{-1}) 3920 (w), 3350 (w), 3070 (m), 2960 (m), 2805 (m), 2695 (m), 1760 (w), 1633 (s), 1445 (m), 1385 (w), 1345 (m), 1258 (w), 1088 (w), 1003 (s), 770 (s, br), 545 (s), 430 (w), 323 (s).

$\{(C_5H_5)_2Y[N{=}C(D)CH_3]\}_2$ (2a′). The reaction of CH_3CN with $[(C_5H_5)_2YD(THF)]_2$ (**1a′**) was conducted as described above for **2a** to form **2a′** in comparable yield. IR (KBr, cm^{-1}) 3070 (m), 2960 (m), 2890 (m), 2050 (m), 1765 (w), 1625 (s), 1430 (m), 1347 (m), 1258 (m), 1078 (w), 1005 (s), 885 (w), 770 (s), 535 (s), 430 (w), 308 (m).

$\{(C_5H_5)_2Y[N{=}C(H)C(CH_3)_3]\}_2$ (3a). 2,2-Dimethylpropanonitrile (0.25 mL, 2.3 mmol) was added to a stirred suspension of **1a** (97 mg, 0.17 mmol) in THF (10 mL). **1a** dissolved to give a colorless, clear solution that was evaporated to a microcrystalline powder. Quantitative formation of **3a** was indicated by ^{1}H NMR spectroscopy. Anal. Calcd for $YC_{15}H_{20}N$: Y, 29.35. Found: Y, 28.8. IR (KBr, cm^{-1}) 3080 (w), 2950 (s), 2860 (m), 2620 (w, br), 1755 (w), 1655 (s), 1633 (m), 1465 (m), 1440 (w), 1360 (m), 1257 (w), 1205 (m), 1055 (w), 1010 (s), 875 (w), 770 (s).

$\{(C_5H_5)_2Y[N{=}C(D)C(CH_3)_3]\}_2$ (3a′). The reaction of $(CH_3)_3CCN$ with **1a′** as described above for **3a** produced **3a′** in comparable yield. IR (KBr, cm^{-1}) 3080 (m), 2940 (s), 2860 (m), 1980 (m), 1637 (s), 1460 (m), 1440 (w), 1357 (m), 1255 (w), 1218 (w), 1200 (w), 1060 (w), 1007 (s), 855 (w), 770 (s, br).

X-ray Data Collection, Structure Determination, and Refinement for 3a. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table IV.

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(65) Thompson, M. E.; Bercaw, J. E., Industrial Associates Conference on Catalysis, California Institute of Technology, Pasadena, CA, March 1983; 185th National Meeting of the American Chemical Society, Seattle, WA, March 1983 (INOR 235).

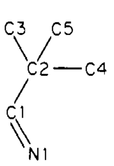
(66) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–168.

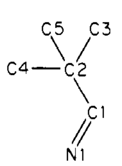
(67) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387–391.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. This method has been previously described.[13] A summary of data collection parameters is given in Table IV. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[68]

Calculations were carried out with the SHELX system of computer programs.[69] Neutral atom scattering factors for Y, N, and C were taken from Cromer and Weber,[70] and the scattering for yttrium was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[71] Scattering factors for H were from ref 72.

The positions of the yttrium atoms of the two independent $[(C_5H_5)_2Y(NCHC(CH_3)_3)]_2$ units were revealed by the inspection of a Patterson map. A difference Fourier map phased on the metal atoms revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.091$. All non-hydrogen atoms except the methyl carbon atoms of the *tert*-butyl groups were refined with anisotropic thermal parameters.[73] Of the two independent units, disorder was encountered for molecule A. The model that gave the best results is based on the superposition of the two structures shown.





The atoms most affected are C(1) and C(3). Clearly, all the atoms of the *tert*-butyl group suffer to some extent, but only the disorder of the C(1) and C(3) methyl groups could be resolved. They were treated with occupancy factors of 0.50, and these were not varied. Carbon atom C(1) was refined anisotropically, and the evidence of the disorder is clear from Figure 1. Unfortunately, it was not possible to resolve this position into its components. The remaining atoms of the *tert*-butyl group show high thermal motion, but refined satisfactorily with (large) isotropic temperature factors. Molecule B, Figure 2, is not disordered, and the discussion of bond lengths and angles focuses on this structure.

The final agreement factors are $R = 0.056$ and $R_w = 0.064$. A final difference Fourier showed no feature greater than 0.8 $e^-/Å^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in the supplementary material.[73]

Reaction of 1a with C_2H_4. A suspension of **1a** (98 mg, 0.17 mmol) in THF (10 mL) was placed in a glass tube equipped with a high-vacuum Teflon stopcock and a stir bar. Excess C_2H_4 was added to the stirred suspension. After 1 h, the hydride had dissolved. Removal of solvent and trituration with pentane gave a white powder that developed a yellow color upon exposure to the desolvating conditions of the glovebox. Upon addition of C_6D_6 to this product, a white precipitate was observed (probably hydride). The ^1H NMR spectrum of the soluble material differed from that of the ethyl complex originally observed in the preliminary NMR experiments. THF was observed in the spectrum, indicating that the unstable material isolated was a THF adduct.

Reaction of 1b with C_2H_4. **1b** was treated with C_2H_4 in THF as described above for **1a**. Reaction occurred in approximately 30 min. Removal of solvent gave a colorless oil, which quickly turned yellow in the glovebox. Attempts to isolate a powder by trituration with pentane gave a tacky yellow powder having a very complex ^1H NMR spectrum. Reaction of **1b** with C_2H_4 in nonpolar solvents, e.g., pentane, was observed to be very slow.

$(C_5H_5)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$ (6a). **1a** (107 mg, 0.18 mmol) was suspended in THF (10 mL) in a reaction tube equipped with a high-vacuum Teflon stopcock and a stir bar. The tube was attached to a vacuum line, evacuated, warmed to room temperature, and filled with 1,2-propadiene to atmospheric pressure. The suspension was stirred overnight to give a clear, colorless solution. The solution was evaporated to a slightly off-white powder of **6a** (96 mg, 0.29 mmol, 80%). IR (KBr, cm^{-1}) 3900 (w), 3060 (m), 2955 (m), 2880 (m), 2700 (w), 1890 (w), 1755 (w), 1650 (w), 1540 (s), 1450 (m), 1435 (m), 1337 (w), 1235 (m), 1190 (m), 1005 (s), 915 (w), 865 (s), 770 (s), 662 (m), 557 (m), 420 (w).

$(C_5H_5)_2Y(C(CH_2CH_3){=}CHCH_2CH_3)(THF)$ (8a). 3-Hexyne (0.5 mL, 4.4 mmol) was added to **1a** (320 mg, 0.55 mmol) in THF (20 mL). The hydride dissolved with stirring over a 4-h period. The clear, colorless solution was evaporated to a colorless oil. After trituration with pentane, white microcrystalline **8a** was obtained (372 mg, 0.99 mmol, 90%). Anal. Calcd for $YC_{20}H_{29}O$: Y, 23.77. Found: Y, 24.8. IR (KBr, cm^{-1}) 3075 (w), 2950 (s), 2860 (m), 2820 (m), 1755 (w), 1640 (w), 1560 (w), 1448 (m), 1365 (w), 1295 (w), 1260 (m), 1175 (w), 1010 (s), 860 (m), 760 (s). Slow recrystallization of **8a** was most successful when a pentane solution of **8a** was allowed to concentrate by vapor diffusion of the pentane into hexane in the other arm of an H-tube assembly at 0 °C.

Hydrogenolysis of 8a. **8a** (118 mg, 0.31 mmol) was dissolved in toluene (3 mL) in a reaction tube equipped with a high-vacuum Teflon stopcock and a stir bar. The vessel was attached to a vacuum line, cooled to −196 °C, evacuated, and warmed to room temperature. One atmosphere of H_2 was placed over the solution and the solution was stirred at 0 °C. A white precipitate soon developed. After stirring overnight the volatile liquids were collected under vacuum and analyzed by GC to confirm the presence of *cis*-3-hexene. The remaining white precipitate (65 mg, 0.11 mmol, 70%) was reslurried in THF and identified by IR as being **1a**. No attempt was made to drive the hydrogenolysis to completion.

Catalytic Hydrogenation of 3-Hexyne by 1b. **1b** (48.5 mg, 0.076 mmol) was dissolved in THF (10 mL) in a glass reaction tube equipped with a stir bar. 3-Hexyne (1.0 mL, 8.85 mmol, 3-hexyne/Y = 58) was transferred on a vacuum line to the solution. The tube was filled with 1 atm of H_2, and hydrogen uptake was monitored for 5 days. The initial turnover rate based on H_2 uptake observed was 0.003/min and the average over 5 days was 0.0025/min. The solution was analyzed by GC to contain *cis*-3-hexene and unreacted 3-hexyne.

$(C_5H_5)_2Y[C(C_6H_5){=}CH(C_6H_5)](THF)$ (9a). **1a** (206 mg, 0.35 mmol) was suspended in THF (15 mL) in a Pyrex reaction tube equipped with a magnetic stir bar. Diphenylethyne (540 mg, 3.03 mmol) was added, and the tube was evacuated to the solvent vapor pressure and sealed with a high-vacuum Teflon stopcock. The suspension was heated to 40 °C with vigorous stirring overnight. The orange solution was taken into a drybox and evaporated to an orange oil that was washed with pentane (2 × 10 mL) to remove excess diphenylethyne (a result confirmed by ^1H NMR) leaving pink-orange **9a** (274 mg, 0.58 mmol, 82%). Anal. Calcd for $YC_{28}H_{29}O$: Y, 18.93. Found: 18.2. IR (KBr, cm^{-1}) 3600 (m), 2960 (m), 2885 (m), 1760 (w), 1660 (w), 1585 (s), 1485 (s), 1475 (s), 1440 (s), 1300 (w), 1170 (m), 1148 (s), 1065 (w), 1005 (s), 918 (m), 855 (s), 770 (s), 695 (s). Several attempts at recrystallizing **9a** by cooling or by vapor diffusion gave orange starburst-like crystals. **9a** appears to be more stable in noncoordinating solvents than **8a**. **9a** may also be synthesized at room temperature, but 4 days are required for complete reaction.

Hydrolysis of 9a. **9a** (93 mg, 0.20 mmol) was decomposed in vacuo with degassed H_2O. The residue was extracted with diethyl ether and the extract was dried with $MgSO_4$. Filtration and rotary evaporation gave a light yellow oil identified as *cis*-stilbene by ^1H NMR spectroscopy and by mass spectrometry. The presence of diphenylethyne (5–10%) was also confirmed by both techniques.

$[(C_5H_5)_2YH(NC_5H_5)]_2$ (10a). Pyridine (73 mg, 0.92 mmol) was added to **1a** (95 mg, 0.16 mmol) suspended in pentane (10 mL). The suspension was stirred for 4 h. After filtration and washing with pentane, **10a** was obtained as a pale yellow powder (71 mg, 0.12 mmol). The material was essentially free of THF based on elemental analysis and IR spectroscopy. Anal. Calcd for $YC_{15}H_{16}N$: Y, 29.74. Found: Y, 29.4. Hydrolysis: 0.84 mol H_2/g atom Y. IR (KBr, cm^{-1}) 3080 (w), 3060 (w), 2950 (w), 1640 (w), 1595 (s), 1483 (s), 1440 (s), 1265 (s, br), 1210 (m), 1150 (w), 1063 (m), 1035 (m), 1010 (s). 1005 (s), 872 (m), 858 (m), 840 (w), 780 (s), 750 (s), 700 (s), 632 (m), 614 (m).

$[(C_5H_4CH_3)_2YH(NC_5H_5)]_2$ (10b). Excess pyridine (275 mg, 3.48 mmol) was added to **1b** (130 mg, 0.20 mmol) suspended in pentane (15 mL) and the suspension was stirred 8 h. After filtration and washing with pentane, **10b** was obtained as a yellow powder (74 mg, 0.11 mmol). The ^1H NMR spectrum of **10b** indicated virtually complete displacement of THF by pyridine. Anal. Calcd for $YC_{17}H_{20}N$: Y, 27.20. Found: Y, 27.2. Hydrolysis: 0.91 mmol of H_2/g-atom of Y.

$(C_5H_5)_2Y(NC_5H_6)(NC_5H_5)$ (12a). **1a** (120 mg, 0.21 mmol) was suspended in THF (3 mL). Excess pyridine (365 mg, 4.62 mmol) was added to give an immediate yellow color. After stirring overnight a deep orange solution was obtained. Stirring was continued for 5 days to give **12a** free of the 1,2-isomer. Attempted recrystallization of **12a** by vapor diffusion of pentane into a saturated pyridine/hexane solution at −8 °C resulted in an orange oil and yellow supernatant liquid. If this system was allowed to rapidly warm to room temperature, tacky yellow prisms

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were obtained. Attempts to obtain better crystals by slower recrystallization were unsuccessful.

Reaction of 1a with 4-Methylpyridine. 4-Methylpyridine (153 mg, 1.65 mmol) was added to **1a** (138 mg, 0.24 mmol) suspended in THF (5 mL), and the yellow suspension was stirred overnight. Solvent was removed and the yellow powder was extracted with toluene, giving a yellow-orange solution and a white powder. The white powder was identified as unreacted **1a** by its IR spectrum. The yellow-orange solution was evaporated to an orange powder. This material had no hydride band in its IR spectrum. When the orange powder was dissolved in C_6D_6 a white precipitate formed (probably hydride), and the spectrum obtained had a complex cyclopentadienyl region and no pyridyl resonances.

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Registry No. 1a, 80642-73-5; **1a′**, 80642-74-6; **1b**, 80658-44-2; **2a**, 88181-77-5; **2a′**, 88181-78-6; **2b**, 88200-37-7; **3a**, 88181-79-7; **3a′**, 88181-80-0; **4a**, 88181-86-6; **4b**, 88181-87-7; **5a**, 88181-88-8; **5b**, 88181-89-9; **6a**, 88181-81-1; **6b**, 88181-90-2; **7b**, 88181-91-3; **8a**, 88181-82-2; **8b**, 88181-92-4; **9a**, 88181-83-3; **10a**, 88181-84-4; **10b**, 88200-38-8; **11b**, 88181-93-5; **12a**, 88181-85-5; $[(C_5H_5)_2YCl]_2$, 57398-67-1; $[(C_5H_5)_2YCH_3]_2$, 60997-40-2; $[(C_5H_4CH_3)_2YCl]_2$, 80642-81-5; $[(C_5H_4CH_3)_2YCH_3]_2$, 72556-67-3; 3-hexyne, 928-49-4; *cis*-3-hexene, 7642-09-3; *cis*-stilbene, 645-49-8.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters, and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

Synthesis, Binding Sites, and Spectroscopic Characterizations of Succinamic Acid and Succinimide Platinum Blues

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Abstract: By using K_2PtCl_4 and succinamic acid or succinimide new mixed-valent platinum blues have been obtained. By using ^{13}C NMR spectroscopy the compound, prepared from succinimide, has been identified as a succinamic acid blue, hydrolysis of the imide occurring during the course of the reaction. These compounds have been characterized by UV–visible spectral measurements, Ce(IV) oxidative titrations, XPS, and ESR spectroscopies. From the whole set of data so obtained the succinamic acid blues may be considered as a limiting case between class II and class III mixed-valence complexes.

The so-called "platinum blues" have attracted considerable attention for several years. In fact they are exceptional for their intense blue color in contrast to the yellow or colorless nature of most platinum complexes. Although blue platinum compounds were reported since 1908[1] and have been subject to extensive studies,[2] their nature remained elusive until single crystals of *cis*-diammineplatinum α-pyridone blue were prepared.[3] Extensive studies on this compound were carried out to determine the solid-state structure,[4] magnetic[4] and X-ray photoelectron spectroscopic[5] behavior, and chemical and spectroscopic properties in aqueous solution.[6] From these studies it has been inferred that at least three properties are shared by most of the platinum blues in solution as well as in the solid state: mixed valency, oligomerization, and amidate bridging. More recently arguments favoring a strong electronic delocalization along the platinum chains have been deduced from optical studies, and it has been suggested that the platinum blues are best described as class II–class III borderline or as delocalized class III mixed-valent compounds (according to Robin and Day's classification[7]) in which there is extensive delocalization but, at least in the case of the phthalimide blues,[8] inequivalent metal sites.

Table I. Elemental Analyses Data of Platinum Succinamic Acid and Succinimide Blues

	% C	% H	% N	% Pt	% Cl	% K
found for B						
batch 1	11.0	2.8	3.3	45.0	12.6	ϵ
batch 2	10.8	2.6	3.5	44.5	12.5	0.1
calcd for $[PtC_4O_3NH_6Cl_{1.5}\cdot 3H_2O]_n$	11.47	2.87	3.35	46.64	12.71	
found for (C)	12.3	2.7	3.6	50.9	4.5	0.3
calcd for $[PtC_4O_5NH_6Cl_{0.5}\cdot(OH)\cdot 2H_2O]_n$	12.57	2.88	3.67	51.10	4.64	

However, much of the interest devoted to these products stems in the fact that pyrimidine and amide blues were found to have a high index of antitumor activity and a low associated nephrotoxicity.[9-11]

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