Organometallics 1987, *6*, 295–301

Synthesis and X-ray Crystal Structure of μ,η^2-*N*-Alkylformimidoyl Complexes of Erbium and Yttrium: A Structural Comparison

William J. Evans,*[1] Timothy P. Hanusa, and James H. Meadows

Department of Chemistry, University of California, Irvine, California 92717

William E. Hunter and Jerry L. Atwood

Department of Chemistry, University of Alabama, University, Alabama 35486

Received April 8, 1986

The dimeric hydrides $[(C_5H_4R)_2Ln(\mu\text{-H})(THF)]_2$ (Ln = Er, Y; R = H, CH_3) react with *tert*-butyl isocyanide to form the complexes $[(C_5H_4R)_2Ln(\mu,\eta^2\text{-HC}{=}\text{NCMe}_3)]_2$. $[(C_5H_5)_2Y(\mu,\eta^2\text{-HC}{=}\text{NCMe}_3)]_2$ crystallizes in space group $P\bar{1}$ with a = 8.496 (5) Å, b = 8.549 (5) Å, c = 10.459 (6) Å, α = 77.13 (4)°, β = 86.58 (4)°, γ = 73.56 (4)°, V = 710.2 Å^3, and D_{calcd} = 1.42 g cm^{-3} for Z = 1 dimer/unit cell. $[(C_5H_5)_2Er(\mu,\eta^2\text{-HC}{=}\text{NCMe}_3)]_2$ crystallizes in space group $P\bar{1}$ with a = 10.909 (10) Å, b = 8.628 (2) Å, c = 16.632 (14) Å, α = 94.48 (5)°, β = 66.78 (6)°, γ = 87.84 (5)°, V = 1430 (2) Å^3, and D_{calcd} = 1.77 g cm^{-3} for Z = 2 dimers/unit cell. The structural features of the $HC{=}NCMe_3$ ligand are very similar in the two complexes. In both cases, this group bridges the two metal centers through the carbon atom, and the nitrogen atom is also within bonding distance of one of the metals. In the erbium complex, the two dimers in the unit cell differ principally in the orientation of the C_5H_5 rings with respect to each other.

Introduction

Yttrium, although not formally a lanthanide element, often is investigated along with the lanthanide metals since its chemistry can be quite similar.[2,3] The basis for the similarity lies in the fact that the 4f valence orbitals of the trivalent lanthanides have a limited radial extension[4] and do not appear to become significantly involved in bonding. Electrostatic and steric factors tend to dominate the chemistry of the comparatively ionic complexes of the trivalent lanthanides.[2,3,5,6] Hence, an electropositive trivalent metal ion with empty valence orbitals might be expected to mimic the behavior of a lanthanide ion of a similar radial size. Y^{3+} meets these requirements: it has a radial size very close to that of Er^{3+} and Ho^{3+},[7,8] it has a $4d^0$ electron configuration, and it has similar electronegativity.[9] To date, the chemical properties known for organometallic Y^{3+} complexes are very similar to those of the lanthanides later in the series, Ho^{3+}–Lu^{3+}.[2,3,10-29] X-ray crystal structures of the pairs $[(C_5H_5)_2Yb(\mu\text{-CH}_3)]_2$ and $[(C_5H_5)_2Y(\mu\text{-CH}_3)]_2$[13] and $[(CH_3C_5H_4)_2Er(\mu\text{-H})(THF)]_2$ and $[(CH_3C_5H_4)_2Y(\mu\text{-H})(THF]_2$[19] demonstrate that Y^{3+} complexes are also structurally similar.

In many respects, yttrium complexes are more desirable to study than erbium or holmium compounds, since their physical properties make them much easier to characterize definitively. Complexes of the diamagnetic Y^{3+} can be studied by NMR spectroscopy whereas this technique is not informative for Er^{3+} (μ_{eff} = 9.4–9.7 μ_B) or Ho^{3+} (μ_{eff} = 10.3–10.5 μ_B). Furthermore, the ^{89}Y isotope, which is 100% naturally abundant, has a nuclear spin of $I = {}^1/_2$. As a result, Y–H and Y–C coupling can often be observed in ^1H and ^{13}C NMR spectra and additional structural information can be obtained based on the coupling.[13,19-21,23,24,29] In addition, ^{89}Y NMR spectra can be obtained.[30] Yet another advantage of yttrium is that its

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0276-7333/87/2306-0295$01.50/0

lower atomic number vis-à-vis erbium or holmium can make it easier to locate hydrogen positions close to the metal in X-ray structural determinations.[19]

Given the many desirable features of Y^{3+}, it is tempting to study the chemistry of this element alone and to assume that the later lanthanides simply will behave in the same way. Despite repeated examples of the chemical similarity of these metals, it is possible that in some cases they will be found to differ. In the present study, we probed a potential situation of this type by comparing erbium and yttrium complexes in detail.

The reaction of organolanthanide and organoyttrium hydrides with isocyanides has been examined to provide information on the early stages of the more complex lanthanide and yttrium hydride reduction of isoelectronic carbon monoxide.[31,32] The organoyttrium hydride complexes $[(C_5H_4R)_2Y(\mu\text{-H})(THF)]_2$ (R = H, CH_3) react with *tert*-butyl isocyanide to form dimeric *N*-alkylformimidoyl complexes as shown in eq 1 (R = H, CH_3).[24] An X-ray

$$[(C_5H_4R)_2Y(\mu\text{-H})(THF)]_2 + 2CNCMe_3 \xrightarrow{THF} [(C_5H_4R)_2Y(\mu,\eta^2\text{-HC=NCMe}_3)]_2 \quad (1)$$

crystal structure of $[(C_5H_5)_2Y(\mu,\eta^2\text{-HC=NCMe}_3)]_2$ showed that both C and N atoms of the formimidoyl ligand are within bonding distance of the same metal center while a short C–N distance indicative of multiple bonding is retained. This η^2-coordination of a multiply bonded organic group was unusual for metals of this type and was particularly unusual for trivalent lanthanides.[33] It is possible in this case that the η^2-coordination could involve the vacant 4d orbitals of Y^{3+}, orbitals which have the appropriate energy and radial extension for such an interaction. In contrast, for Er^{3+} the 4f orbitals and their 11 electrons have a limited radial extension and the 5d orbitals, approximately 6 eV above the ground state,[36,37] may be too high in energy for substantial interaction. Hence, an *N*-alkylformimidoyl ligand attached to Er^{3+} could have a different structure than in an Y^{3+} complex. Accordingly, we report here the synthesis and structure of $[(C_5H_5)_2Er(\mu,\eta^2\text{-HC=NCMe}_3)]_2$ and compare in detail its structure with that of the yttrium analogue.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, all syntheses and manipulations of these compounds were conducted under nitrogen with the rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques. The solvents were dried and degassed as previously described.[19] The yttrium starting materials were prepared according to the literature,[20] and the erbium hydride was prepared in identical fashion. Me_3CNC was dried over activated molecular sieves and degassed on a vacuum line before use. Physical measurements were made as previously described.[19,23]

$[(C_5H_5)_2Y(\mu,\eta^2\text{-HC=NCMe}_3)]_2$ (1). *tert*-Butyl isocyanide (75 mg, 0.90 mmol) dissolved in THF (3 mL) was added dropwise to a stirred suspension of $[(C_5H_5)_2Y(\mu\text{-H})(THF)]_2$ (254 mg, 0.43 mmol) in THF (20 mL). The hydride dissolved, and a yellow and then orange solution developed. The solution was stirred for 1 h, and solvent was removed to give an orange powder. The powder was washed with pentane (2 × 5 mL) and then extracted into toluene (30 mL), giving an amber solution. Solvent removal gave a yellow-green powder (205 mg, 0.68 mmol, 78%) which was >90% $[(C_5H_5)_2Y(\mu,\eta^2\text{-HC=NCMe}_3)]_2$ by ^1H NMR spectroscopy (vide infra). This material was recrystallized by cooling a saturated toluene/pentane solution to give colorless prisms of 1. Anal. Calcd for $YC_{15}H_{20}N$: Y, 29.35. Found: Y, 29.5. IR (KBr, cm^{-1}): 3075 w, 2960 w, 2870 w, 2765 w, 1760 w, 1645 w, 1540 m, 1455 m, 1385 w, 1360 s, 1290 m, 1225 w, 1188 s, 1008 s, 860 w, 760 s, 476 m, 448 m, 422 w, 360 m, 273 w. ^1H NMR (C_6D_6, 500 MHz): δ 9.29 (t, $^2J_{YH}$ = 1.5 Hz, HC=NCMe$_3$), 5.93 (s, C_5H_5), 0.98 (s, CMe_3). $^{13}C\{^1H\}$ NMR (50.31 MHz, 10/1 THF/C_6D_6, referenced to C_6D_6 at δ 128.0): δ 108.6 (s, C_5H_5), 29.4 (s, HC=NC(CH_3)$_3$), 60.6 (s, HC=NC(CH_3)$_3$), 217.0 (d of d, $^1J_{YC}$ = 35.0, $^1J'_{YC}$ = 5.1 Hz, HC=NC(CH_3)$_3$). The triplet structure of the formimidoyl hydrogen in the ^1H NMR spectrum may be due to (a) fortuitously equal coupling to both yttrium atoms (100% abundant ^{89}Y has $I = {}^1/_2$), (b) chemical exchange (not detected by variable temperature studies), or (c) inequivalent coupling to both yttrium atoms which appears equivalent due to additional Y–Y or H–H coupling. Explanation c is supported by the fact that the formimidoyl resonance has a filled-in triplet structure rather than an ideal binomial triplet structure and the fact that computer simulation, assuming inequivalent Y–H coupling but allowing for additional coupling, nicely reproduces this feature. Application of reasonable Y–Y and H–H coupling in the simulation of the ^{13}C spectrum showed no observable effect on the ^{13}C spectrum due to the larger values of Y–^{13}C coupling.

$[(C_5H_5)_2Y(\mu,\eta^2\text{-DC=NCMe}_3)]_2$ (2). In a manner similar to that described above, Me_3CNC was reacted with $[(C_5H_5)_2Y(\mu\text{-D})(THF)]_2$ to form $[(C_5H_5)_2Y(\mu,\eta^2\text{-DC=NCMe}_3)]_2$. IR (KBr, cm^{-1}): 3070 w, 2920 m br, 2020 w, 1745 w, 1640 w, 1528 m, 1456 m, 1380 w, 1355 s, 1225 w, 1188 s, 1045 w, 1000 s, 755 s, 455 m, 438 m, 403 m, 330 m, 270 w. The ^1H NMR spectrum of this complex was identical with that of the above complex except that the δ 9.29 resonance was absent.

$[(CH_3C_5H_4)_2Y(\mu,\eta^2\text{-HC=NCMe}_3)]_2$ (3). *tert*-Butyl isocyanide (112 mg, 1.35 mmol) dissolved in THF (5 mL) was added dropwise to $[(CH_3C_5H_4)_2Y(\mu\text{-H})(THF)]_2$ (408 mg, 0.64 mmol) dissolved in THF (15 mL). During the addition the solution color changed from yellow to a scarlet red color. After being stirred for 1 h, the solution was evaporated to an orange paste that became a green-brown powder upon further drying. The powder was washed with pentane (2 × 5 mL) to give a green filtrate and tan powder. The ^1H NMR spectrum of the tan powder showed it to be primarily $[(CH_3C_5H_4)_2Y(\mu,\eta^2\text{-HC=NCMe}_3)]_2$ (312 mg, 0.94 mmol, 74%). The material was purified by cooling a saturated toluene/hexane solution to −78 °C which produced a white amorphous powder. This powder was recrystallized by vapor diffusion of hexane into a toluene solution at −5 °C to give colorless prisms of 3. Anal. Calcd for $YC_{17}H_{24}N$: Y, 26.87. Found: Y, 27.1. IR (KBr, cm^{-1}): 3070 w, 2900 m br, 2720 w, 1685 w, 1580 w, 1532 m, 1455 m, 1358 s, 1286 s, 1190 s, 1025 s, 930 m, 870 w, 820 s, 750 s, 618 m, 569 w, 466 w, 440 w, 414 w, 320 w. A THF solution IR spectrum of this complex also showed an unshifted band at 1532 cm^{-1} assigned to ν(C=N). ^1H NMR ($C_6D_5CD_3$, 270 MHz): δ 9.46 (t, $^2J_{YH}$ = 1.5 Hz, HC=), 5.95, 5.82, 5.60 ($C_5H_4CH_3$), 2.20 (s, $C_5H_4CH_3$), 1.11 (s, CMe_3). $^{13}C\{^1H\}$ NMR (50.31 MHz, 10/1 THF/C_6D_6 solution): δ 15.5 s, $\overline{C_4H_4C}CH_3$; 107.0 s, 109.4 s, 109.6 s, 110.5 s, $\overline{C_4H_4C}CH_3$; 119.6 s, $\overline{C_4H_4C}CH_3$; 29.7 s, HC=NC(CH_3)$_3$; 61.1 s, HC=NC(CH_3)$_3$; 218.1 (d of d), $^1J_{YC}$ = 35.5 Hz, $^1J'_{YC}$ = 4.7 Hz, HC=NC(CH_3)$_3$. The ^{13}C spectrum of $[(CH_3C_5H_4)_2Y(\mu,\eta^2\text{-HC=NCMe}_3)]_2$ in C_6H_6 is identical with that above. While this complex is slightly more soluble in THF than C_6H_6, it has less stability in THF. In THF solution green impurities are observed to form during an overnight period.

$[(C_5H_5)_2Er(\mu,\eta^2\text{-HC=NCMe}_3)]_2$ (4). *tert*-Butyl isocyanide (60 mg, 0.72 mmol) dissolved in THF (10 mL) was added dropwise

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Table I. Crystal Data for $[(C_5H_5)_2Y(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$ (1) and $[(C_5H_5)_2Er(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$ (4)

	1	4
compd	$YNC_{15}H_{20}$	$ErNC_{15}H_{20}$
mol wt	303.23	381.59
space group	$P\bar{1}$	$P\bar{1}$
cell consts		
a, Å	8.496 (5)	10.909 (10)
b, Å	8.549 (5)	8.628 (2)
c, Å	10.459 (6)	16.632 (14)
α, deg	77.13 (4)	94.48 (5)
β, deg	86.58 (4)	66.78 (6)
γ, deg	73.56 (4)	87.84 (5)
V, Å^3	710.2	1430 (2)
Z	1 (dimer)	2 (dimers)
ρ(calcd), g cm^{-3}	1.42	1.77
μ(calcd), cm^{-1}	42.20	59.25
transmsn factor range	0.98–1.29	0.063–0.165 calcd
radiatn	0.71073 Å; graphite	0.71073 Å; graphite
max crystl dimens, mm	0.20 × 0.35 × 0.30	0.55 × 0.35 × 0.30
scan width	0.8 + 0.2 tan θ	−1.2° in 2θ from $K\alpha_1$ to +1.2° from $K\alpha_2$
std reflctns	200, 020, 002	423, 2-54, 361
decay of standards	<3%	5%
reflctns measd	1972	5358
2θ range, deg	0–46	5–50
obsd reflctns, $I \geq 3\sigma(I)$	1729	4355
no. of parameters varied	154	307
GOF	1.11	1.631
R	0.035	0.035
R_w	0.042	0.047

through an addition funnel to a suspension of $[(C_5H_5)_2Er(\mu\text{-}H)(THF)]_2$ (212 mg, 0.29 mmol) in THF (20 mL) in a Schlenk flask cooled to −78 °C. The cold bath was removed, and the pink suspension was allowed to warm with stirring. When the vessel reached 0 °C, the suspended material dissolved to give a lemon yellow solution. The yellow solution was allowed to warm further to room temperature and then was evaporated to dryness. The solids were washed with hexane and extracted with toluene. Solvent was removed from the light orange toluene extract by rotary evaporation to give a pink-orange microcrystalline solid (107 mg, 0.28 mmol, 49%). IR (KBr, cm^{-1}): 3075 w, 2970 m, 2860 w, 2720 w, 1535 w, 1450 m, 1435 m, 1380 w, 1355 s, 1290 m, 1185 s, 1000 s, 870 w, 770 s, 750 s, 475 w, 420 w. Pink prisms suitable for x-ray diffraction were obtained by diffusion of hexane vapor into a toluene solution and cooling the mixture to 10 °C.

X-ray Crystallography of $[(C_5H_5)_2Y(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$. A single crystal measuring 0.40 × 0.35 × 0.10 mm was sealed under N_2 in a thin-walled glass capillary. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 reflections (25° > 2θ > 20°) accurately centered on the diffractometer are given in Table I. Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. This method has been previously described.[12] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[38]

Calculations were carried out with the SHELX system of computer programs.[39] Neutral atom scattering factors for Y, N, and C were taken from Cromer and Waber,[40] and the scattering for yttrium was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[41] Scattering factors for H were from ref 42.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[(C_5H_5)_2Y(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
Y(1)	0.56754 (6)	0.47469 (6)	0.83716 (5)	0.024
Cp(1)	0.7373 (8)	0.6467 (8)	0.6662 (6)	0.052
Cp(2)	0.7306 (7)	0.7050 (7)	0.7827 (7)	0.050
Cp(3)	0.8258 (7)	0.5776 (8)	0.8763 (6)	0.054
Cp(4)	0.8908 (7)	0.4396 (8)	0.8199 (7)	0.053
Cp(5)	0.8385 (8)	0.4834 (9)	0.6907 (7)	0.063
Cp(6)	0.453 (1)	0.3382 (8)	0.6700 (6)	0.064
Cp(7)	0.3510 (8)	0.3283 (8)	0.7782 (8)	0.064
Cp(8)	0.442 (1)	0.2137 (8)	0.8803 (7)	0.065
Cp(9)	0.5990 (9)	0.1536 (7)	0.8365 (7)	0.054
Cp(10)	0.6062 (9)	0.2295 (9)	0.7070 (7)	0.065
N(1)	0.3408 (5)	0.7079 (5)	0.8048 (4)	0.028
C(1)	0.3352 (7)	0.6797 (6)	0.9297 (5)	0.032
C(2)	0.2213 (7)	0.8483 (7)	0.7157 (5)	0.035
C(3)	0.3196 (9)	0.9507 (8)	0.6278 (7)	0.063
C(4)	0.1375 (8)	0.7682 (8)	0.6341 (7)	0.057
C(5)	0.092 (1)	0.9569 (9)	0.7904 (7)	0.067
H(1)	0.6794	0.7101	0.5819	0.080
H(2)	0.6700	0.8194	0.7948	0.080
H(3)	0.8427	0.5835	0.9688	0.080
H(4)	0.9632	0.3287	0.8643	0.080
H(5)	0.8681	0.4098	0.6258	0.080
H(6)	0.422	0.4119	0.5814	0.080
H(7)	0.2326	0.3915	0.7807	0.080
H(8)	0.401	0.1822	0.9713	0.080
H(9)	0.6900	0.0662	0.8892	0.080
H(10)	0.7055	0.2114	0.6499	0.080
H(11)	0.2469	1.0338	0.5585	0.080
H(12)	0.3773	1.0014	0.6694	0.080
H(13)	0.4095	0.8798	0.5822	0.080
H(14)	0.0787	0.8629	0.5586	0.080
H(15)	0.0635	0.7029	0.6878	0.080
H(16)	0.2368	0.6891	0.5808	0.080
H(17)	0.039	0.8808	0.8489	0.080
H(18)	0.025	1.0482	0.7266	0.080
H(19)	0.172	1.0138	0.8357	0.080

The position of the yttrium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the metal atom revealed the positions of the non-hydrogen atoms. Least squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.066$. All non-hydrogen atoms were refined with anisotropic thermal parameters.

The final agreement factors were $R = 0.035$ and $R_w = 0.042$. A final difference Fourier showed no feature greater than 0.6 e Å^{-3}. The weighting scheme was based on unit weights, a choice made on the basis of the manner in which the data were collected.[12] 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 Table II.

X-ray Crystallography of $[(C_5H_5)_2Er(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$. General procedures for data collection and reduction have been described previously.[32,43,44] A well-formed pink parallelepiped measuring 0.30 × 0.33 × 0.55 mm was sealed under N_2 in a glass capillary and mounted on a Syntex $P2_1$ diffractometer. Lattice parameters were determined at 24 °C from the angular settings of 15 computer-centered reflections measured from 4° ≤ 2θ ≤ 21°. Relevant crystal and data collection parameters for the present study are given in Table I.

During the data collection, the intensities of three standard reflections measured every 100 reflections decreased by 5%; a correction for decay and absorption (by Gaussian integration) was later applied. A combination of Patterson and difference Fourier techniques provided the locations of all non-hydrogen atoms, which were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The unique hydrogen atom in the HC=NCMe$_3$ ligand, H(1), was the first hydrogen atom to

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Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[(C_5H_5)_2Er(HC{=}NCMe_3)]_2$

atom	x/a	y/b	z/c	10^4U_{eq},[a] Å^2
Er(1)	0.34640 (2)	0.05239 (3)	0.49041 (1)	317 (2)
Cp(1)A	0.3324 (11)	0.3554 (9)	0.4774 (6)	744 (81)
Cp(2)A	0.3689 (8)	0.3406 (8)	0.5461 (7)	703 (81)
Cp(3)A	0.2589 (10)	0.2891 (8)	0.6150 (5)	675 (74)
Cp(4)A	0.1584 (9)	0.2722 (9)	0.5843 (6)	740 (77)
Cp(5)A	0.2054 (12)	0.3158 (10)	0.5011 (7)	812 (101)
Cp(6)A	0.3700 (10)	−0.0103 (10)	0.3260 (5)	663 (76)
Cp(7)A	0.2375 (9)	0.0000 (10)	0.3750 (6)	674 (80)
Cp(8)A	0.2051 (8)	−0.1219 (11)	0.4270 (5)	696 (75)
Cp(9)A	0.3193 (11)	−0.2133 (8)	0.4097 (5)	685 (81)
Cp(10)A	0.4251 (8)	−0.1449 (10)	0.3468 (5)	671 (69)
N(1)	0.2868 (5)	−0.0927 (5)	0.6095 (3)	364 (37)
C(1)A	0.4102 (6)	−0.1009 (6)	0.5933 (4)	367 (43)
C(2)A	0.1827 (6)	−0.1654 (8)	0.6833 (4)	481 (50)
C(3)A	0.0900 (12)	−0.0383 (11)	0.7424 (7)	1211 (109)
C(4)A	0.2397 (11)	−0.2577 (15)	0.7336 (8)	1160 (119)
C(5)A	0.1139 (12)	−0.2766 (13)	0.6452 (8)	1030 (114)
H(1)A[b]	0.4382	−0.1662	0.6344	
Er(2)	0.35076 (2)	0.49241 (3)	0.09689 (1)	307 (2)
Cp(1)B	0.1165 (8)	0.6438 (10)	0.1740 (8)	781 (82)
Cp(2)B	0.1544 (11)	0.6678 (13)	0.0907 (8)	885 (107)
Cp(3)B	0.2554 (14)	0.7613 (14)	0.0710 (8)	1179 (120)
Cp(4)B	0.2787 (12)	0.7906 (12)	0.1455 (13)	1114 (143)
Cp(5)B	0.1926 (15)	0.7188 (13)	0.2080 (6)	937 (110)
Cp(6)B	0.2769 (9)	0.3623 (10)	0.2453 (5)	668 (69)
Cp(7)B	0.3998 (10)	0.4151 (10)	0.2324 (5)	720 (87)
Cp(8)B	0.4957 (8)	0.3210 (10)	0.1596 (5)	635 (72)
Cp(9)B	0.4266 (9)	0.2165 (9)	0.1294 (5)	600 (69)
Cp(10)B	0.2923 (8)	0.2412 (9)	0.1818 (5)	624 (72)
N(2)	0.3158 (5)	0.3512 (5)	−0.0140 (3)	353 (37)
C(1)B	0.4349 (6)	0.3826 (7)	−0.0636 (4)	362 (44)
C(2)B	0.2306 (6)	0.2578 (7)	−0.0475 (4)	421 (49)
C(3)B	0.0964 (9)	0.2544 (14)	0.0274 (6)	903 (91)
C(4)B	0.2134 (8)	0.3374 (10)	−0.1223 (5)	656 (72)
C(5)B	0.2989 (10)	0.0951 (9)	−0.0822 (7)	849 (98)
H(1)B[b]	0.4690	0.3403	−0.1332	

[a] $U_{eq} = {}^1/_3$ (trace of orthogonalized $\mathbf{U}_{ij}$ matrix). [b] Atom not refined.

be located on a difference map. Other hydrogen atoms were either located from difference maps or placed in ideal geometries by using C–H = 0.95 Å. B_H was set equal to 1.0 + B_{iso} of the connecting atom. Hydrogen positions were not refined.

A final difference map contained no recognizable features. There were several ripple peaks of 3–4 e Å^{-3} height near the metal atom; the largest was of height 4.07 e Å^{-3} at a distance of 1.00 Å from the erbium atom. The final values of the positional parameters are given in Table III.

Results and Discussion

Synthesis. The neutral dimeric lanthanide and yttrium hydride complexes $[(C_5H_4R)_2Ln(\mu\text{-}H)(THF)]_2$ (Ln = Y, Er; R = H, CH_3) react with a wide variety of unsaturated organic substrates.[15,24,31] In most cases 1,2-metal hydride addition across the multiple bond is observed. Hence, alkenyl products result from alkyne reactions, alkyl complexes from alkene reactions, and alkylideneamido compounds from nitrile reactions.[15] The hydrides $[(C_5H_5)_2Y(\mu\text{-}H)(THF)]_2$, $[(C_5H_5)_2Y(\mu\text{-}D)(THF)]_2$, $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$, and $[(C_2H_5)_2Er(\mu\text{-}H)(THF)]_2$ react with *tert*-butyl isocyanide to form products 1–4, respectively, which are characterized as *N*-alkylformimidoyl complexes as described below.

Color changes during each reaction indicated that new products were forming, and ^{1}H and ^{13}C NMR spectroscopy on the yttrium products and IR spectroscopy on all the products suggested formimidoyl formation. IR absorptions at 1540, 1528, 1532, and 1535 cm^{-1} for 1, 2, 3, and 4, respectively, are consistent with a C–N multiple bond.[45,46] An absorption at 2765 cm^{-1} for 1 which shifted to 2020 cm^{-1} in the deuteriated analogue 2 is reasonable for a CH (CD) stretch in a formimidoyl ligand (ν_{CH}:ν_{CD} = 1.37).[45,46] Comparison of the ^{1}H NMR spectra of 1 and 2 confirmed that the δ 9.29 resonance arises from hydrogen in the hydride starting material, since it was absent in the deuteride reaction product. The Y–H and Y–C couplings in the NMR spectra of the yttrium complexes indicated that these complexes are dimeric in THF as well as in arene solvents. Since some organolanthanide dimers such as $[(C_5H_5)_2Ln(\mu\text{-}CH_3)]_2$[13,20] and $[(C_5H_5)_2Ln(\mu\text{-}Cl)]_2$[47,48] readily dissociate in THF to form solvated monomers, the latter result suggests that the formimidoyl ligand forms a relatively strong bridge between the metals (cf. the alkynide complexes $[(C_5H_4R)_2Ln(\mu\text{-}C{\equiv}CR)]_2$[49,50]).

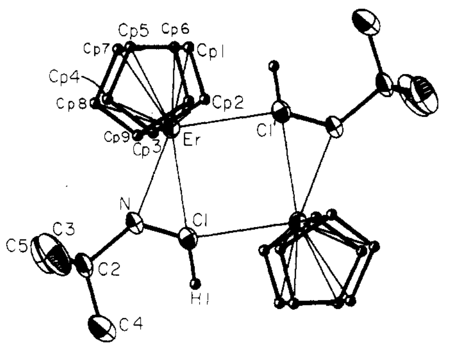

Figure 1. ORTEP drawing of one of the independent molecules in the unit cell of $[(C_5H_5)_2Er(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$ with nearly eclipsed C_5H_5 rings. For clarity, cyclopentadienyl and *tert*-butyl hydrogen atoms have been omitted and the cyclopentadienyl carbon atoms and the remaining hydrogen atom have been given arbitrary thermal parameters.

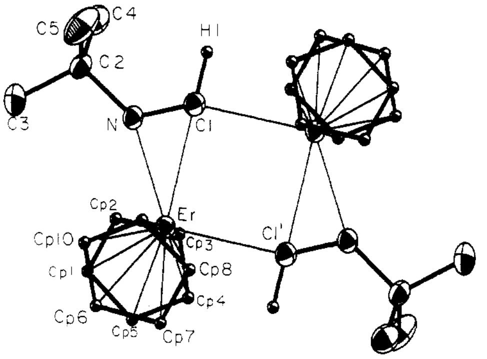

Figure 2. ORTEP drawing of one of the independent molecules in the unit cell of $[(C_5H_5)_2Er(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$ with nearly staggered C_5H_5 rings. For clarity, cyclopentadienyl and *tert*-butyl hydrogen atoms have been omitted and the cyclopentadienyl carbon atoms and the remaining hydrogen atom have been given arbitrary thermal parameters.

X-ray Crystal Structures of $[(C_5H_5)_2Y(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$ (1) and $[(C_5H_5)_2Er(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$ (4). Complex 1 crystallizes in the triclinic space group $P\bar{1}$ with one centrosymmetric dimer in the unit cell. Compound

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Table IV. Bond Distances (Å) in $[(C_5H_5)_2Ln(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$

	1 (Ln = Y)	**4a** (Ln = Er)	**4b** (Ln = Er)
Ln–Ln	3.607 (1)	3.607 (1)	3.582 (4)
Ln–C(1)	2.545 (5)	2.527 (6)	2.544 (6)
Ln–C(1)	2.561 (5)	2.534 (6)	2.490 (6)
Ln–N	2.325 (4)	2.312 (5)	2.296 (5)
Ln–Cp(1)	2.676 (6)	2.644 (7)	2.605 (8)
Ln–Cp(2)	2.659 (6)	2.640 (7)	2.616 (8)
Ln–Cp(3)	2.663 (6)	2.647 (7)	2.642 (9)
Ln–Cp(4)	2.677 (6)	2.638 (8)	2.629 (10)
Ln–Cp(5)	2.697 (6)	2.650 (8)	2.622 (8)
Ln–Cnt(1)	2.399	2.371	2.365
Ln–Ave(1)	2.68 (1)	2.644 (7)	2.623 (9)
Ln–Cp(6)	2.667 (6)	2.653 (7)	2.633 (7)
Ln–Cp(7)	2.667 (6)	2.646 (7)	2.640 (7)
Ln–Cp(8)	2.674 (6)	2.638 (7)	2.672 (7)
Ln–Cp(9)	2.683 (6)	2.651 (7)	2.655 (7)
Ln–Cp(10)	2.680 (6)	2.641 (7)	2.640 (7)
Ln–Cnt(2)	2.403	2.370	2.372
Ln–Ave(2)	2.674 (7)	2.646 (7)	2.648 (7)
C(1)–N	1.275 (6)	1.262 (8)	1.288 (7)
C(2)–N	1.504 (6)	1.505 (7)	1.489 (7)
C(2)–C(3)	1.508 (8)	1.47 (1)	1.51 (1)
C(2)–C(4)	1.521 (8)	1.48 (1)	1.54 (1)
C(2)–C(5)	1.525 (8)	1.49 (1)	1.52 (1)
Cp(1)–Cp(2)	1.408 (9)	1.36 (1)	1.32 (1)
Cp(2)–Cp(3)	1.385 (9)	1.41 (1)	1.34 (2)
Cp(3)–Cp(4)	1.396 (9)	1.39 (1)	1.37 (2)
Cp(4)–Cp(5)	1.384 (9)	1.36 (1)	1.31 (2)
Cp(5)–Cp(1)	1.393 (9)	1.35 (1)	1.33 (2)
Cp(6)–Cp(7)	1.39 (1)	1.35 (1)	1.37 (1)
Cp(7)–Cp(8)	1.38 (1)	1.38 (1)	1.42 (1)
Cp(8)–Cp(9)	1.37 (1)	1.37 (1)	1.38 (1)
Cp(9)–Cp(10)	1.370 (9)	1.40 (1)	1.38 (1)
Cp(10)–Cp(6)	1.39 (1)	1.42 (1)	1.38 (1)
C(1)–H(1)		1.04	1.09

Table V. Bond Angles (deg) in $[(C_5H_5)_2Ln(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$

	1 (Ln = Y)	**4A** (Ln = Er)	**4B** (Ln = Er)
C(1)–Ln–C(1)′	90.1 (2)	90.0 (2)	89.3 (1)
C(1)–Ln–N	29.9 (1)	29.8 (2)	30.3 (1)
C(1)–Ln–Cnt(1)	115.3	114.9	115.6
C(1)′–Ln–Cnt(1)	97.9	97.8	100.1
N–Ln–Cnt(1)	107.2	107.7	106.0
Cnt(1)–Ln–Cnt(2)	127.2	126.5	127.6
C(1)–Ln–Cnt(2)	114.7	115.6	113.4
C(1)′–Ln–Cnt(2)	97.4	98.7	97.8
N–Ln–Cnt(2)	107.6	107.1	106.8
Ln–C(1)–N	65.4 (3)	65.6 (3)	64.1 (3)
Ln–C(1)–N	155.3 (4)	155.6 (4)	154.8 (4)
Ln–C(1)–Ln	89.9 (1)	90.0 (2)	90.7 (2)
C(3)–C(2)–C(4)	109.8 (5)	109.5 (9)	108.4 (5)
C(3)–C(2)–C(5)	110.8 (6)	112.0 (9)	112.0 (7)
C(4)–C(2)–C(5)	109.3 (8)	116.1 (8)	109.6 (6)
C(3)–C(2)–N	107.2 (5)	107.3 (6)	107.6 (5)
C(4)–C(2)–N	106.7 (4)	113.3 (6)	109.0 (5)
C(5)–C(2)–N	113.0 (5)	108.6 (6)	109.0 (5)
Ln–N–C(1)	84.6 (1)	84.6 (3)	85.6 (4)
Ln–N–C(2)	151.0 (3)	150.9 (4)	151.6 (4)
C(1)–N–C(2)	124.3 (4)	124.6 (5)	122.8 (5)
Cp(2)–Cp(1)–Cp(5)	107.1 (6)	108.5 (8)	109.6 (9)
Cp(1)–Cp(2)–Cp(3)	108.0 (6)	107.5 (8)	108 (1)
Cp(2)–Cp(3)–Cp(4)	108.2 (6)	106.7 (7)	107 (1)
Cp(3)–Cp(4)–Cp(5)	107.9 (6)	107.4 (8)	108 (1)
Cp(1)–Cp(5)–Cp(4)	108.7 (6)	109.8 (9)	108 (1)
Cp(7)–Cp(6)–Cp(10)	107.8 (6)	107.0 (7)	109.3 (8)
Cp(6)–Cp(7)–Cp(8)	107.3 (6)	109.9 (7)	107.1 (7)
Cp(7)–Cp(8)–Cp(9)	108.7 (6)	108.4 (7)	107.1 (7)
Cp(8)–Cp(9)–Cp(10)	108.0 (6)	107.3 (7)	109.0 (8)
Cp(6)–Cp(10)–Cp(9)	108.2 (6)	107.3 (7)	107.6 (7)
N(1)–C(1)–H(1)		115.1	115.8

4 crystallizes in the same space group but has two crystallographically independent centrosymmetric dimers in a unit cell. We shall call these **4A** and **4B**. ORTEP drawings of **4A** and **4B** are shown in Figures 1 and 2. Bond length and angle data are given in Tables IV and V, respectively.

The coordination spheres around the metal atoms in all three structures are quite similar. Hence, the observed coordination mode of the μ,η^2-$HC{=}NCMe_3$ ligand in these complexes cannot be attributed to special 4d orbital effects in the yttrium case. In each complex, the metal is surrounded by two cyclopentadienyl rings, a formimidoyl carbon–nitrogen unit bonded edge-on, and a bridging carbon atom (C(1)′) from the other formimidoyl ligand in the dimer. The two metal atoms in these dimers plus C(1), C(1)′, N(1), N(1)′, C(2), and C(2)′ are planar to within 0.007 Å in **1**, to within 0.003 Å in **4A**, and to within 0.004 Å in **4B**.

These complexes are formally similar to traditional transition-metal-bent metallocene complexes with three additional ligands,[51] e.g., $(C_5H_5)_2MH_3$ (M = Nb, Ta).[52] However, the arrangement of the three additional ligating atoms C(1), N(1), and C(1)′ in **1**, **4A**, and **4B** is rather asymmetrical compared to that of the $(C_5H_5)_2ML_3$ complexes. For example, the C(1)′–Ln–C(1) angles in **1**, **4A**, and **4B** are 90.1 (2)°, 90.0 (2)°, and 89.3 (1)°, respectively, whereas the C(1)–Ln–N angles are 29.9 (1)°, 29.8 (2)°, and 30.3 (2)°, respectively. This asymmetry results because C(1) and N(1) are connected by a short bond and because the complex is a bridged dimer. For comparison, the analogous angles in $[(CH_3C_5H_4)_2ZrH(\mu\text{-}H)]_2$[53] are 70 (1)° ($H_t$–Zr–$H_b$) and 60 (1)° ($H_b$–Zr–$H_b$); in $[(CH_3C_5H_4)_2Y(THF)(\mu\text{-}H)]_2$,[19] H–Y–H is 66 (3)° and H–Y–O(THF) is 71 (2)°.

The (ring centroid)–metal–(ring centroid) angles in **1**, **4A**, and **4B** of 127.2°, 126.5°, and 127.6°, respectively, are in the range commonly found for $(C_5H_5)_2LnL_x$ complexes (x = 2, 3).[23] The Ln–C(η^5) distances are also in the normal range.

Although the overall structure and the orientation of the formimidoyl ligands are similar in **1**, **4A**, and **4B**, the relative positions of the cyclopentadienyl rings as measured by the twist angle are found to vary.[54] Complex **1** has a 6.4° twist angle, which is closer to an eclipsed arrangement (0°) than to a staggered structure (36°). **4A** is even closer to eclipsed with a 2.2° twist angle. In the same unit cell, however, **4B** has a 36.2° twist angle![55] Evidently, *very* small differences in crystal packing forces can affect the orientation of these rings. This suggests that the orientation of cyclopentadienyl rings in complexes of this type cannot be reliably used to make conclusions on intramolecular structure and bonding.

The $HCNCMe_3$ ligands in **1**, **4A**, and **4B** have C–N bond lengths of 1.275 (6), 1.262 (8), and 1.288 (7) Å, respectively, in the range reasonable for carbon–nitrogen double bonds.[56] These distances are intermediate between the 1.24 (1) Å length found in the monometallic η^1-complex $Ru(\eta^1\text{-}HC{=}NC_6H_4CH_3)(CO)[P(C_6H_5)_3]_2(CH_3CO_2)$[57] and

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[52] Wilson, R. D.; Koetzle, T. F.; Hunt, D. W.; Kuick, A.; Tipton, L. D.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775–1781.

[53] Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889–2894.

[54] The twist angle is defined as the dihedral angle between planes such as Cp(1)–(ring 1 centroid)–(ring 2 centroid) and (ring 1 centroid)–(ring 2 centroid)–Cp 6.

[55] In comparison, $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$ has a twist angle of 7.1°; $[(C_5H_5)_2Yb(\mu\text{-}CH_3)]_2$ has a twist angle of 9.7°.

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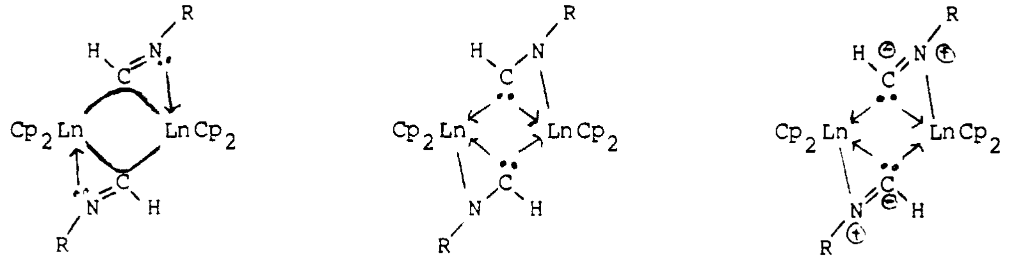
[57] Clark, G. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2556–2560.


A B C

Cp = C_5H_5 R = $C(CH_3)_3$

Figure 3. Formal bonding schemes for $[(C_5H_5)_2Ln(\mu,\eta^2\text{-}HCNCMe_3)]_2$ (Ln = Y, Er). The curved line represents a three-center, two-electron bond.

the 1.415 (11) and 1.32 (10) Å distances found in the trimetallic η^2-complexes $Os_3(\mu_3,\eta^2\text{-}HC{=}NC_6H_5)(CO)_9H$ and $Os_3(\mu_2,\eta^2\text{-}HC{=}NC_6H_5)(CO)_9[P(OCH_3)_3]H$,[58] in which the formimidoyl carbon and nitrogen atoms are bound to three and two different osmium atoms, respectively. The C–N distances are comparable to the 1.266 (12) and 1.287 (13) Å C–N distances found in the η^1-alkanimidoyl complexes $(CH_3CNC_6H_4)Mo(C_5H_5)(CO)_2[P(OCH_3)_3]$[59] and $(CH_3CNC_6H_4Cl)PtI[P(C_6H_5)_3]_2$[60] and slightly longer than the 1.233 (6) and 1.25 (2) Å C–N lengths in the η^2-alkanimidoyl compounds $(\eta^2\text{-}CH_3CNC_6H_5)Mo(C_5H_5)(CO)_2$[59] and $(C_5H_5)_3U[\eta^2\text{-}C(Me){=}N(C_6H_{11})]$.[35] The C–N bond length in $(C_5H_5)_3U[\eta^2\text{-}C(CHPPh_2Me)N(C_6H_{11})]$[34] is much longer, 1.39 (4) Å, and this complex is not a close analogue of 1 and 4.

For the erbium complexes, the X-ray crystal data were of sufficient quality to permit location of the unique hydrogen atom H(1).[61] In **4A**, it is within 0.023 Å of being coplanar with Er(1), N(1), C(1), and C(2); in **4B**, it is within 0.051 Å of this four-atom plane. The N(1)–C(1)–H(1) angles in **4A** and **4B** are 115.1° and 115.7°, respectively. Hence, the hydrogen position is also roughly consistent with sp^2 hybridization at the bridging carbon atom C(1).

The Y–C(1) and Y–C(1)′ distances of 2.545 (5) and 2.561 (5) Å in 1 are slightly longer than the Er–C(1) and Er–C(1)′ distances in **4A** and **4B**: 2.527 (6), 2.534 (6), 2.544 (6), and 2.490 (6) Å. This is consistent with the relative sizes of yttrium and erbium ions. Literature values for the radius of Y^{3+} range from being nearly equal[7] to that of Er^{3+} to being 0.013 Å larger[8] than Er^{3+}. The average cyclopentadienyl carbon to metal distances show a similar trend: 1, 2.68 Å; **4A**, 2.644 (7) Å; **4B**, 2.623 (9) Å. The Ln–C(1) and Ln–C(1)′ distances compare well with the Ln–C distances found in three-center, two-electron methyl-bridged organolanthanides. For example, $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$[13] has Y–C distances of 2.553 (10) and 2.561 (5) Å that are very close to the values found for Y–C(1) and Y–C(1)′ in 1. The Ln–Ln distances, 3.607 (1) Å for 1, 3.607 (1) Å for **4A**, and 3.582 (4) Å for **4B**, are also comparable to the Y–Y distance in $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$, 3.599 (8) Å.

All of the above-mentioned data are compatible with bonding scheme A in Figure 3. In this scheme, Ln–H has added to RNC to form the nitrogen analogue of a formyl ligand, a result consistent with observed similarities between CO and CNR ligands.[62] The formimidoyl ligand in this structure is unusual in that it is part of an electron-deficient bridge as is found in the $[(C_5H_5)_2Ln(\mu\text{-}CH_3)]_2$[13] and related complexes. In this scheme, nitrogen coordination to the metal would be explained via a lone pair donor bond in this structure i.e., =N:→Ln.

However, the Ln–N distances in these complexes, 2.325 (4) Å in 1, 2.312 (5) Å in **4A**, and 2.296 (5) Å in **4B**, are much shorter than those observed previously for dative =N:→Ln bonds to Y or Er involving neutral nitrogen donor ligands. Examination of seven lanthanide structures containing R_3N:→Ln donor bonds[63] shows a range of expected N:→Y distances from 2.47 to 2.63 Å (after the differences in radii are taken into account). By this comparison, the Ln–N distances in 1, **4A**, and **4B** are more reasonable for a Ln–N single bond involving an anionic NR_2 unit, Ln–NR_2, rather than a Ln←:NR_3 bond formed from a neutral NR_3 ligand. Note that these Ln–N distances are about 0.2 Å shorter than the Ln–C distances in these molecules and are the closest connection between the metal and the formimidoyl ligand.[64] Obviously, both the carbon and nitrogen atoms of the $(HCNCMe_3)^-$ ligand are interacting strongly with the yttrium and erbium metals, and bonding schemes such as B or C must be considered. In these cases, the formimidoyl carbon still participates in a three-center, two-electron bridge, but it has more carbene than anionic character. Structure B is the nitrogen analogue of η^2-formyl[32,65] and η^2-acyl complexes.[62,66]

The relative contributions of structures A–C to the bonding in 1 and 4 are uncertain. However, the virtual coplanarity of Ln, N(1), C(1), C(2), and H(1) and the short C–N distances suggest that B contributes least. The short

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Ln–N distance favors C over A as being the most important contributor. A similar structure is favored for $(C_5H_5)_3U[\eta^2\text{-}C(Me){=}N(C_6H_{11})]$.[35]

Conclusion

To the extent that CO and isocyanides are similar, these formimidoyl complexes can be viewed as model complexes for the unstable formyl intermediates formed in reductions of CO by metal hydrides.[32,65] The special μ,η^2 nature of the formimidoyl ligands in these complexes precludes assignment of the reaction as a 1,1- or 1,2-metal hydride addition to the C–N bond in $CNCMe_3$. However, the structures demonstrate yet another type of coordination mode for reduced ligands of this type.

The coordination geometry found in these μ,η^2-*N*-alkylformimidoyl complexes demonstrates that multiply bonded oxygen-free organic units can η^2-coordinate to lanthanide metals as well as to yttrium. These complexes provide yet another example of the close parallel between the chemistry of yttrium and that of the late lanthanide elements of similar radial size. Moreover, this similarity was demonstrated in a system which had considerable potential to show differences. Finally, the presence of both staggered and nearly eclipsed arrangements of cyclopentadienyl rings in **4A** and **4B** indicates that minor crystal packing effects can influence the relative orientations of cyclopentadienyl rings in complexes of this type.

Acknowledgment. For support of this research, we thank the Division of Basic Energy Sciences of the Department of Energy (W.J.E., J.H.M.) and the National Science Foundation (J.L.A., W.E.H.). We also thank the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (to W.J.E.), and the Alfred P. Sloan Foundation for a research fellowship (to W.J.E.). We thank Professor R. J. Doedens for help with the erbium structure.

Registry No. 1, 86528-30-5; 2, 86528-32-7; 3, 86528-31-6; 4, 105834-48-8; $[(C_5H_5)_2Y(\mu\text{-}H)(THF)]_2$, 80642-73-5; $[(C_5H_5)_2Y(\mu\text{-}D)(THF)]_2$, 80642-74-6; $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$, 80658-44-2; $[(C_5H_5)_2Er(\mu\text{-}H)(THF)]_2$, 80642-71-3; Me_3CNC, 7188-38-7.

Supplementary Material Available: Tables of thermal parameters for 1 and 4 (2 pages); listings of structure factor amplitudes for 1 and 4 (30 pages). Ordering information is given on any current masthead page.

Synthesis, Crystal Structure, and Stereoisomerism of the Alkylidene Complex $(\eta^5\text{-}C_5H_5)WOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ and Related Complexes

Yun Chi and John R. Shapley*

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Joseph W. Ziller and Melvyn Rowen Churchill*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214

Received June 3, 1986

The reaction of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (1) with HCl or BCl_3/H_2O at ambient temperatures generates the alkylidene complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ (**3**, isomer **b**) isolated in 65–90% yield. Complex **3b** crystallizes in the triclinic space groups $P\bar{1}$ with $a = 9.2724\ (32)$ Å, $b = 11.3130\ (43)$ Å, $c = 14.0040\ (62)$ Å, $\alpha = 69.790\ (31)°$, $\beta = 77.236\ (30)°$, $\gamma = 83.700\ (20)°$, $V = 1343.6\ (9)$ Å^3, and $Z = 2$. Convergence of the structure solution was reached with $R_F = 3.7\%$ for all 3526 unique data ($R_F = 3.1\%$ for those 3085 data with $|F_o| > 6\sigma(|F_o|)$. The metal atoms adopt the "butterfly" configuration typical of 62-electron clusters, with the chlorine atom bridging the wing-tip osmium atoms (Os(1)–Cl = 2.488 (3) Å, Os(3)–Cl = 2.463 (3) Å; Os(1)–Cl–Os(2) = 98.4 (1)°). Three carbonyl groups are bound to each Os atom, while the Cp ligand is bound to W. The oxygen atom is involved in a $W{=}O{:}\!\rightarrow\!Os$ bridge, with W=O(1) = 1.786(9) Å, Os(3)—O(1) = 2.126 (8) Å, and <W—O(1)—Os(3) = 99.2 (4)°. The μ-alkylidene moiety bridges W and Os(1), with W–C(1) = 2.064 (11) Å, Os(1)–C(1) = 2.196 (11) Å, and <W–C(1)–Os(1) = 85.0 (4)°; the $-CH_2Tol$ substituent is oriented anti to the triply edge-bridged W–Os(1)–Os(3) face. Pyrolysis of **3b** in refluxing toluene generates an isomeric alkylidene complex **3c** isolated in 71% yield and characterized spectroscopically. Treatment of 1 with HBr or HSPh generates analogous alkylidene compounds $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}X)(\mu\text{-}CHCH_2Tol)$ (X = Br (**4**) or SPh (**5**)); in these cases both stereoisomers are obtained directly. The substitution of a carbonyl ligand in **3b** by ^{13}CO or PPh_2Me is shown to be stereoselective; activation by both the bridging oxo and the bridging chloro ligands is proposed.

Introduction

Treatment of the oxo–alkylidyne complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (1) with hydrogen gas provides the oxo–alkylidene complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CHCH_2Tol)$ (2).[1,2] The crystal structure of one form of 2 (≡ **2a**) has been determined,[3] but in solution it coexists with a second isomer (≡ **2b**).[2] Pyrolysis of **2** in refluxing xylenes gives yet a third isomer (≡ **2c**).[4] As part of our further study of the reactivity of 1, we have examined its reactions with certain HX reagents (HCl, HBr, and HSPh) and have found that alkylidene complexes $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}X)(\mu\text{-}CHCH_2Tol)$ (X = Cl (**3**), Br (**4**), or SPh

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