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Divalent Lanthanoid Synthesis in Liquid Ammonia. 1. The Synthesis and X-ray Crystal Structure of $(C_5Me_5)_2Yb(NH_3)(THF)$

Andrea L. Wayda* and James L. Dye†

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Robin D. Rogers

Department of Chemistry, Northern Illinois University, De Kalb, Illinois 60115

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By the use of new vacuum line technology and rigorous handling techniques, exclusively divalent europium and ytterbium pentamethylcyclopentadienides can be prepared in high yield via the reaction of the respective metals in liquid ammonia with pentamethylcyclopentadiene (C_5Me_5H). With use of this synthetic scheme, the unusual ammoniate $(\eta^5\text{-}C_5Me_5)_2Yb(NH_3)(OC_4H_8)$ has been isolated and crystallographically characterized. $(\eta^5\text{-}C_5Me_5)_2Yb(NH_3)(OC_4H_8)$ crystallizes in the orthorhombic space group $Pca2_1$ with unit-cell dimensions $a = 22.877$ (5) Å, $b = 15.489$ (3) Å, $c = 15.018$ (3) Å, and $D_{calcd} = 1.33$ g cm^{-3} for $Z = 8$. Least-squares refinement resulted in a final R value of 0.069 based on 3350 independent observed reflections. There are two molecules in the asymmetric unit. One molecule exhibits disorder between the NH_3 and THF sites resulting in an overlap of the N and O positions, while the other shows disorder only of the THF ring. In the second molecule, ammonia is coordinated to the metal center via a Yb(2)–N bond length of 2.55 (3) Å. The Yb(2)–O distances and average Yb(2)–C(π) bond lengths are 2.46 (3) and 2.77 (4) Å, respectively.

Introduction

Synthetically useful routes to divalent lanthanoid complexes of europium and ytterbium have been confined to five basic reaction types: 1, metathesis reactions between the divalent halides and appropriate substrates;[1,2] 2, reduction of a suitable trivalent organolanthanoid precursor,[3] 3, transmetalation between bulk metal and organomercurials,[4,5] 4, oxidative addition of alkyl halides to bulk metal,[6ab] 5, dissolution of the metals in liquid ammonia to yield divalent metal-ammonia solutions followed by reaction with an acidic substrate.[3,7-9]

Of the five methods, reaction type 5 is, in principle, the easiest to execute. The purest available starting materials are used (bulk metal powders and organic substrates) without need of derivative preparation (such as $YbCl_2$, LiC_5Me_5, NaOR, etc.), and the reaction solvent (NH_3) is relatively inert and easy to remove (bp –34 °C). In addition, product isolation and purification is simple since no difficult-to-remove alkali halide salts are generated in the reaction. Furthermore, reactions between metal solutions and unsaturated hydrocarbon substrates for which no suitable alkali-metal derivative exists can be readily investigated.

Unfortunately, this conceptually simple synthetic route is the least exploited of the five reaction types. This neglect stems from the mistaken assumption that solutions of these metals are unstable with respect to oxidation to the trivalent state. While it is certainly true that lan-

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† On sabbatical leave from Michigan State University, East Lansing, MI 48824.

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thanoid metal–ammonia solutions are thermodynamically unstable with respect to the formation of metal amides and hydrogen, decomposition at low temperatures under rigorously clean conditions is kinetically disfavored.[10] Hence, with careful handling techniques and the avoidance of substrates, which themselves promote oxidation to the trivalent state, high-yield syntheses of divalent lanthanoid complexes can be realized. To illustrate this point, we report the synthesis of $(C_5Me_5)_2Eu(THF)$ and the unusual crystallographically characterized ammoniate $(C_5Me_5)_2Yb(NH_3)(THF)$ via the reaction of lanthanoid metal–ammonia solutions and C_5Me_5H. Extension of this synthetic methodology to syntheses of divalent alkoxides and other compound classes will be reported at a later date.

Experimental Section

General Data. The extremely air and moisture sensitive compounds are handled in the recirculated argon atmosphere of a Vacuum Atmospheres HE-43 dri-lab. All glassware in contact with metal–ammonia solutions must be washed with HF cleaner (60% H_2O, 30% HNO_3, 5% HF, Alconox) to eliminate surface contaminants capable of catalyzing decomposition.

Materials. Ytterbium metal powder was obtained from Research Chemicals, Phoenix, AZ. Europium metal powder was obtained from Aesar, a division of Johnson and Mathey, Inc. Electronic grade ammonia was obtained from Matheson and was predried over a freshly distilled mirror of high purity sodium or potassium (Alfa) immediately before use. THF and toluene (Aldrich Sure-Seal grade) were distilled from sodium benzophenone ketyl under argon. Pentane (Aldrich Sure-Seal grade) was distilled from $LiAlH_4$ under argon. Pentamethylcyclopentadiene (C_5Me_5H, Aldrich) was dried over calcium hydride and distilled under vacuum immediately before use. Benzene-d_6 and THF-d_8 (Stohler Isotope Chemicals) were dried over sodium benzophenone ketyl.

Measurements. Infrared spectra were recorded on solid samples that had been mulled with dry, degassed Nujol and sandwiched between 25 × 4 mm NaCl plates protected from the atmosphere in an O-ring sealed Barnes Presslok holder. Spectra were recorded with a Nicolet 5DX FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Chemical shifts are referenced to the residual protons contained in each solvent for ^{1}H NMR and to the chemical shift of the solvent for ^{13}C NMR. Complete elemental analyses were obtained from Analytische Laboratorien, Postfach 1249, D-5250, Engelskirchen, West Germany. Magnetic susceptibility measurements were conducted by using a Faraday balance.

Manipulations. Central to the success of this chemistry was the development of a greaseless double-manifold vacuum system and ancillary equipment that permit easy handling of the highly reactive metal–ammonia solutions.[11,12] A diagram of the system is included in the supplementary material. Specific features are as follows: (1) double-manifold design with *separate, isolated* pumping for *each* manifold. The medium vacuum/inert-gas manifold is used for rough pumping and volatile solvent manipulation while the high vacuum manifold is reserved for high vacuum manipulations ($P \leq 10^{-5}$ torr). Since no large volumes of gas are pumped through this manifold, pump-down times are fast. Grease-free construction utilizing Teflon valves, O-ring joints, flexible stainless steel tubing, and connecting stainless steel hardware (all equipped with ammonia-compatible elastomers) allows easy connections to the main manifold and is easy to dismantle and clean. (2) All apparatus for high vacuum manipulations (such as multiple trap-to-trap transfers) normally conducted using permanent static glass installations is connected to the line with Cajon flexible stainless steel tubing, Ultra-Torr unions, and modified glass apparatus. (3) Ammonia delivery into the lower manifold is conveniently monitored with a pressure regulator capable of delivering subatmospheric pressure. Overpressure problems are thus totally eliminated.

Control reactions in which europium and ytterbium were dissolved in liquid ammonia and subjected to washings, filtrations, and other routine manipulations were run in order to assess the stability of these solutions in the absence of substrate. Decomposition to metal amide and hydrogen was monitored by collection of evolved hydrogen with a Toepler pump.

Essentially no decomposition was observed just after preparation of the solutions at −78 °C. After four washes and 2.25 h at ~−15 °C, 13.9% of the europium metal solution had decomposed. An 8.7% decomposition was observed for the ytterbium metal solution. After storage overnight at −20 °C, an additional 4.3% of the europium metal solution had decomposed. No further decomposition of the ytterbium metal solution was observed.

When control reactions were conducted carefully (precooling of the H cell frit before filtration, total apparatus in contact with solutions never allowed to warm above −15 °C), solutions were prepared and manipulated and stored at −78 °C overnight with minimal decomposition (Eu, 8.2; Yb, 5.4).

$(C_5Me_5)_2Yb(NH_3)(THF)$. In an argon-filled drybox, 5.5 mmol of ytterbium metal powder was loaded into one arm of a modified Kontes H cell equipped with Teflon valves fitted with ethylene–propylene copolymer O-rings. A stoichiometric amount of C_5Me_5H (11 mmol) was placed in the other sidearm, and the apparatus was closed. The cell was removed from the drybox attached to the described vacuum line and evacuated to outgas the metal (assisted by gentle heating with a heat gun). During these manipulations, the C_5Me_5H was cooled to −78 °C to prevent evaporative losses. With the reaction cell pumping on the high vacuum manifold, the lower manifold was prepared for ammonia predrying and transfer. A 100-mL round-bottom flask equipped with a 15-mm O-ring joint was loaded with a small amount of high purity sodium or potassium and attached to the vacuum line with a 15-mm O-ring equipped fritted adapter (to prevent ammonia spray over into the system during transfer). Evacuation of the flask, followed by heating, produced a mirror of the alkali metal. Ammonia was condensed onto the metal mirror (T = −78 °C) at manifold pressures approximately equal to two-thirds of an atmosphere. The deep blue metal–ammonia solution was then frozen to −196 °C, and any hydrogen produced during dissolution was removed. (*Caution* The solution must be frozen slowly. Otherwise, severe bumping will occur). Coolant was removed from the metal–ammonia flask, the reaction cell was closed to the high vacuum manifold and opened to the lower manifold, and ammonia was transferred onto the ytterbium metal powder by cooling the cell sidearm to −78 °C. When sufficient ammonia had been distilled into the H cell, the apparatus was removed from the vacuum line and placed in a cooling bath maintained at ~−34 °C. After cooling the H cell surfaces to be contacted with metal–ammonia solution (including the frit), the ytterbium–ammonia solution was poured through the frit onto the C_5Me_5H.[13] To effect complete transfer of the ytterbium metal,[14] ammonia was back-distilled from the reaction sidearm to produce additional ytterbium–ammonia solution which was filtered over as above. This process was continued until no blue solution was produced in the sidearm originally containing ytterbium powder.[15] With all reactants now in one sidearm, the H cell was removed to the

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[12] This vacuum system and ancillary equipment and hardware is now commercially available from Crown Glass Co., 990 Evergreen Drive, Somerville, NJ 08876.

[13] Alternatively, the C_5Me_5H can be slowly transferred onto the ytterbium–ammonia solution. Gentle heating with a heat gun is necessary to expediently effect this transfer. We note that although both possible methods of reaction give identical products in *this* reaction, other lanthanoid metal–ammonia/substrate combinations may behave differently.

[14] Europium and ytterbium metal–ammonia solutions separate into two phases; a more dilute blue phase and a concentrated, difficult-to-filter gold/bronze phase (see ref 9). Therefore, this phenomenon necessitates successive washings with fresh back-distilled ammonia to effect complete transfers of the metal powders.

[15] In practice, a small amount of undissolved material (presumably metal oxide) is always left behind after complete dissolution of the bulk lanthanoid metal. Its presence does not appear to affect reactions in which the substrate is transferred *onto the metal–ammonia solution*. However, since dissolution of the lanthanoid metal in liquid ammonia followed by filtration *onto the substrate* effectively constitutes a purification of the bulk metal powder, we prefer this mode of addition in reactions where either addition procedure is acceptable.

freezer ($T = -20$ °C) where, with occasional manual shaking, the reaction was allowed to continue overnight. The reaction was judged to be complete when no blue color remained to the ammonia solution (24–36 h), and a large amount of precipitated deep red-brown material was observed. Connection of the apparatus to the Toepler pump manifold allowed evolved hydrogen to be removed and determined (70% theoretical yield). The product was then washed several times with ammonia by distillation of the solvent from the wash sidearm (originally the ytterbium sidearm) back onto the reaction product. When the washes were clear, the apparatus was reconnected to the vacuum line and the ammonia removed. The product in the H cell was pumped at medium and high vacuum until the last traces of unbound ammonia had been removed. The resulting deep brick red/purple powder was removed to the drybox for workup.

The crude product, formulated as $(C_5Me_5)_2Yb(NH_3)_x$, was sparingly soluble in toluene and ether to yield deep green solutions. Extraction with THF resulted in facile dissolution of the product to yield a deep green solution that rapidly turns deep red-purple as weakly bound ammonia was lost upon standing or rotary evaporation. Filtration of the solution and removal of THF by rotary evaporation allowed the isolation of analytically pure deep red-purple $(C_5Me_5)_2Yb(NH_3)(THF)$ in 75% yield. Crystals of the complex suitable for X-ray diffraction can be grown by slow diffusion of pentane onto a saturated THF/pentane solution of the compound at ambient temperature: IR (Nujol mull, cm^{-1}) 3344 (w), 3238 (w), 2721 (m), 1646 (w), 1337 (w), 1309 (w), 1293 (w), 1243 (w), 1178 (s), 1032 (s), 925 (w), 878 (s), 840 (m), 798 (w), 723 (m); ^1H NMR (benzene-d_6) δ 3.47 (m, α-THF), 2.27 (s, $(C_5(CH_3)_5)$, 1.46 (m, β-THF)]; ^{13}C NMR (THF-d_8) δ 108.89 ($C_5(CH_3)_5$), 10.16 ($C_5(CH_3)_5$)]; $\mu_{eff} = 0.00$ ($T = 298$ K). Anal. Calcd for $YbC_{24}H_{41}ON$: C,54.12; H,7.76; N,2.63; Yb,32.48; O,3.00. Found: C, 53.90; H, 7.55; N, 2.46; Yb, 32.30; O, 3.79 (by difference).

$(C_5Me_5)_2Eu(THF)$. Reaction of 0.3665 g (2.41 mmol) of europium powder with 0.643 g (4.72 mmol) of C_5Me_5H in liquid ammonia (C_5Me_5H transferred onto blue europium–ammonia solution) yielded a deep rust red powder (reaction time ~24 h, crude product washed several times with ammonia until washes were clear). Removal of the H cell to the drybox followed by dissolution of the crude product in THF produced an intense red-orange solution. Filtration followed by solvent removal yielded analytically pure $(C_5Me_5)_2Eu(THF)$ in 67% yield: IR (Nujol, cm^{-1}) 2721 (m), 1295 (w), 1283 (w), 1241 (m), 1210 (m), 1128 (w), 1035 (s) 955 (w), 932 (w), 899 (s), 798 (w), 725 (w); $\mu_{eff} = 7.99\ \mu_B$ ($T = 298$ K). Anal. Calcd for $EuC_{24}H_{38}O$: C,58.29; H,7.74; Eu,30.73; O,3.23. Found: C, 58.17; H, 7.76; Eu, 30.95; O, 3.12 (by difference).

X-ray Data Collection, Structure Determination, and Refinement for $(\eta^5\text{-}C_5Me_5)_2Yb(NH_3)(OC_4H_8)$. Single crystals of the air-sensitive compound were sealed under nitrogen in thin-walled glass capillaries. Data collection was carried out by Crystalytics Co.[16] Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 10°$) accurately centered on the diffractometer are given in Table I. The systematic absences indicated the space group to be either $Pca2_1$ or $Pcam$ (a nonstandard setting of $Pbcm$). Initially, statistical indicators employing normalized structure factors indicated the noncentrosymmetric $Pca2_1$ to be the correct choice. This choice of space group was confirmed by the successful solution and refinement of the structure.

Data were collected on a Nicolet P$\bar{1}$ autodiffractometer using 1.0° wide ω scans and graphite-monochromated Mo Kα radiation. Each of these 1.0° wide scans were divided into 17 equal time intervals, and those 13 contiguous intervals that had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for half the total time used for the net scan (13/17 of the total scan time) were measured at ω settings 1° above and below the calculated Kα doublet value for each reflection. A summary of data collection parameters is given in Table I. The entire data set was corrected empirically for absorption by using ψ scans for five reflections having 2θ between 8.4° and 25.4° and were then reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections. The range of relative transmission factors is 0.60–1.00.

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

compd	$(\eta^5\text{-}C_5Me_5)_2Yb(NH_3)(OC_4H_8)$
mol wt	532.6
space group	$Pca2_1$
cell const	
a, Å	22.877 (5)
b, Å	15.489 (3)
c, Å	15.018 (3)
cell vol, $Å^3$	5321 (2)
molecules/unit cell	8
ρ(calcd), g cm^{-3}	1.33
μ(calcd), cm^{-1}	37.1
radiatn	Mo Kα
cryst dimens, mm	0.95 × 0.52 × 0.28
scan speed, deg/min	
$3 < 2\theta < 43°$	6.0
$43 < 2\theta < 55°$	4.0
std reflctns	(0,6,9), (1,12,6), (2,29), (4,15,1), (6,11,0), (10,0,0)
decay of stds	±5%
reflctns measd ($+h,+k,+l$)	6342
2θ range, deg	$\leqslant 55$
reflctns collected [$I \geqslant 2.5\sigma(I)$]	3350
no. of parameters varied	252
GOF	8.0
R	0.069
R_w	0.080

Calculations were carried out with the SHELX system of computer programs.[17] Neutral atom scattering factors for Yb, O, N, and C were taken from Cromer and Waber,[18] and the scattering for ytterbium was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[19]

The positions of the two independent ytterbium atoms were located by using the direct methods program MULTAN.[20] Subsequent difference Fourier maps phased on the ytterbium atoms revealed the positions of the non-hydrogen atoms. It became apparent that in molecule 1 (Yb(1)) an orientational disorder between the NH_3 and THF groups was present, resulting in an overlap of the O and N positions. Two positions corresponding to O or N and eight half-height carbon atom positions corresponding to the THF ring were located. It was not possible to resolve the disorder between O and N. Attempted refinement of the occupancy factors starting at 0.5–0.5 resulted in no significant change. The O and N positions were refined with mixed scattering factors. The eight carbon atoms were refined with occupancy factors of 0.5.

Molecule 2 (Yb(2)) did not exhibit the same type of disorder. However, C(46) and C(47) of the THF group were found to be disordered. This type of disorder for THF moieties is not uncommon.[21] Least-squares refinement of the disordered model with isotropic temperature factors led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.125$. The hydrogen atoms could not be located and were not included in any of the refinement. Refinement of Yb(1), Yb(2), O(2), and N(2) anisotropically and the other non-hydrogen atoms isotropically led to final values of $R = 0.069$ and $R_w = 0.080$. For the inverse absolute configuration the values were $R_1 = 0.069$ and $R_2 = 0.081$. A final difference Fourier showed no feature greater than 1.7 e/$Å^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |_C|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.[22]

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(22) See paragraph at the end of paper regarding supplementary material.

Table II. Final Fractional Coordinates for $(C_5Me_5)_2Yb(NH_3)\cdot OC_4H_8$

atom	*x/a*	*y/b*	*z/c*
Yb(1)	0.39318 (5)	0.43895 (8)	0.5000
Yb(2)	0.62487 (5)	0.03094 (8)	0.4550 (1)
X(1)[a]	0.360 (1)	0.470 (2)	0.342 (2)
X(2)	0.450 (1)	0.582 (2)	0.501 (3)
O(2)	0.643 (1)	0.103 (2)	0.598 (2)
N(2)	0.548 (1)	0.146 (2)	0.424 (2)
C(1)	0.441 (2)	0.280 (2)	0.533 (2)
C(2)	0.437 (2)	0.278 (2)	0.440 (2)
C(3)	0.477 (2)	0.344 (3)	0.404 (3)
C(4)	0.506 (1)	0.377 (2)	0.475 (2)
C(5)	0.481 (2)	0.334 (3)	0.560 (3)
C(6)	0.410 (2)	0.208 (3)	0.587 (3)
C(7)	0.396 (2)	0.219 (3)	0.380 (3)
C(8)	0.491 (2)	0.355 (3)	0.312 (3)
C(9)	0.558 (2)	0.428 (3)	0.467 (3)
C(10)	0.508 (3)	0.349 (4)	0.659 (4)
C(11)	0.276 (2)	0.466 (3)	0.531 (3)
C(12)	0.291 (2)	0.396 (3)	0.582 (3)
C(13)	0.325 (2)	0.415 (3)	0.653 (3)
C(14)	0.334 (2)	0.500 (3)	0.653 (3)
C(15)	0.311 (2)	0.540 (3)	0.590 (3)
C(16)	0.236 (4)	0.524 (6)	0.466 (8)
C(17)	0.258 (3)	0.307 (4)	0.529 (6)
C(18)	0.340 (3)	0.377 (5)	0.741 (6)
C(19)	0.360 (3)	0.553 (4)	0.731 (5)
C(20)	0.293 (4)	0.634 (6)	0.573 (7)
C(21)	0.339 (4)	0.415 (6)	0.284 (6)
C(22)	0.340 (3)	0.454 (4)	0.197 (5)
C(23)	0.328 (3)	0.545 (5)	0.219 (5)
C(24)	0.358 (3)	0.559 (5)	0.298 (5)
C(21)	0.479 (4)	0.613 (6)	0.413 (6)
C(22)	0.479 (4)	0.713 (7)	0.445 (8)
C(23)	0.509 (4)	0.681 (6)	0.551 (7)
C(24)	0.469 (3)	0.626 (5)	0.569 (5)
C(25)	0.603 (1)	0.121 (2)	0.544 (3)
C(26)	0.601 (1)	0.142 (2)	0.453 (3)
C(27)	0.551 (2)	0.107 (2)	0.409 (3)
C(28)	0.521 (1)	0.060 (2)	0.485 (3)
C(29)	0.550 (2)	0.071 (2)	0.563 (3)
C(30)	0.647 (2)	0.162 (3)	0.617 (4)
C(31)	0.640 (2)	0.207 (3)	0.401 (3)
C(32)	0.534 (2)	0.115 (3)	0.313 (4)
C(33)	0.461 (2)	0.019 (3)	0.446 (4)
C(34)	0.532 (2)	0.043 (3)	0.659 (3)
C(35)	0.673 (2)	0.097 (3)	0.296 (3)
C(36)	0.695 (2)	0.149 (3)	0.363 (3)
C(37)	0.733 (2)	0.102 (2)	0.417 (3)
C(38)	0.731 (2)	0.016 (3)	0.378 (3)
C(39)	0.692 (2)	0.018 (3)	0.300 (3)
C(40)	0.631 (2)	0.132 (4)	0.225 (4)
C(41)	0.685 (2)	0.250 (3)	0.381 (3)
C(42)	0.775 (2)	0.128 (3)	0.490 (4)
C(43)	0.779 (3)	0.058 (4)	0.392 (5)
C(44)	0.687 (2)	0.050 (3)	0.232 (4)
C(45)	0.614 (2)	0.185 (3)	0.631 (3)
C(46)	0.624 (4)	0.185 (5)	0.731 (6)
C(47)	0.653 (5)	0.108 (7)	0.762 (8)
C(48)	0.672 (2)	0.076 (4)	0.677 (4)
C(46)	0.649 (3)	0.216 (5)	0.701 (6)
C(47)	0.681 (4)	0.150 (6)	0.721 (6)

[a] X(1) and X(2) correspond to the two disordered O and N positions in molecule 1 (see Experimental Section).

Discussion and Results

The earliest use of rare-earth metal–ammonia solutions in organolanthanoid synthesis is the preparation of Ln(C_8H_8) (Ln = Eu, Yb) by Hayes and Thomas.[7] These materials were shown to contain exclusively divalent lanthanoids by magnetic susceptibility measurements. The insolubility of these materials in all common organic solvents has precluded the development of their reaction chemistry. Fischer and Fischer[8] and Calderazzo et al.[3] next independently reported preparations of $(C_5H_5)_2Yb$ and $(C_5H_5)_2Eu$. The former note in their experimental section that care must be taken to add the cyclopentadiene slowly to the ytterbium–ammonia solution in order to avoid the production of trivalent reaction products. The latter researchers report the presence of trivalent ytterbium byproducts in their isolated product but provide no experimental detail. Murphy and Toogood[9] prepared insoluble europium propynide by reaction of a solution of europium metal in liquid ammonia with propyne. They also report difficulty obtaining pure divalent products with ytterbium metal.

The paucity of detail in the Calderazzo et al. and Murphy and Toogood experimental sections makes it difficult to ascertain if the ytterbium–ammonia solutions are fundamentally unstable with respect to oxidation to the trivalent state under all reaction conditions and choice of reactant or if adventitious contaminants promote formation of trivalent ytterbium side products. We conducted control reactions to assess the stability of lanthanoid metal–ammonia solutions in the absence of substrate, using rigorously clean glassware and stringent vacuum line techniques (see Experimental Section). In both cases, we observed minimal decomposition of the metal–ammonia solutions (Eu, 8.2; Yb, 5.4) when performing routine manipulations. We therefore conclude that rare-earth metal–ammonia solutions are stable under our reaction conditions and handling techniques. Any trivalent reaction products arising from reactions performed utilizing our protocol must originate from substrate promoted oxidation. The utility of these methods is demonstrated by synthesis of the divalent pentamethylcyclopentadienides. C_5Me_5H was chosen as substrate since (1) it is easily handled and purified, (2) its steric bulk should preclude the formation of side product $(C_5Me_5)_3Yb$, and (3) the divalent organolanthanoid compounds derived from it are known crystalline materials[1,2a] that exhibit interesting chemistry in electron-transfer reactions.[23]

Slow distillation of C_5Me_5H onto a freshly prepared solution of lanthanoid metal in liquid ammonia (or alternately pouring a lanthanoid metal–ammonia solution onto C_5Me_5H) produces a reaction solution from which deeply colored products slowly precipitate. Complete reaction (as judged by the bleaching of the characteristic deep blue color of the metal–ammonia solutions) requires 1–2 days at −20 °C.[24] The finely divided powders of the crude pentamethylcyclopentadienides are intensely colored (deep red-purple for ytterbium; rust orange-brown for europium).

The crude materials are nonstoichiometric ammoniates. The infrared spectra are dominated by bands associated with coordinated ammonia[25] (3394, 3353, 3262, 1646, 1532, and 1154 cm^{-1}) and are identical for both metals. However, once dissolved in THF and crystallized, their chemical behavior deviates. The europium complex is isolated as the monotetrahydrofuranate and characterized by infrared spectroscopy, magnetic moment, and complete elemental analysis. This compound has been previously synthesized by Andersen and co-workers by the metathesis reaction

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[23] Andersen, R. A. 16th Rare Earth Research Conference, Tallahassee, FL, April 1983.

[24] The majority of lanthanoid metal–ammonia/substrate combinations that we have investigated (or reinvestigated), notably Yb–NH_3/C_8H_8 and Yb–NH_3/2ROH react instantaneously upon mixing. Hence, the relatively long reaction times observed here provide a good test of the long-term stability of these highly reactive solutions under actual reaction conditions. The high yields of pentamethylcyclopentadienides isolated confirm our studies with control reactions on the viability of these reactive solutions over the studied time span.

[25] Nakamoto, K. "The Infrared Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1978.

Table III. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Yb(NH_3)\cdot OC_4H_8$

	Bond Distances		
Yb(1)-X(1)[a]	2.54 (3)	Yb(1)-X(2)	2.56 (2)
Yb(1)-C(1)	2.74 (4)	Yb(1)-C(2)	2.83 (3)
Yb(1)-C(3)	2.82 (4)	Yb(1)-C(4)	2.78 (3)
Yb(1)-C(5)	2.74 (4)	Yb(1)-C(11)	2.75 (4)
Yb(1)-C(12)	2.72 (4)	Yb(1)-C(13)	2.80 (4)
Yb(1)-C(14)	2.84 (4)	Yb(1)-C(15)	2.80 (4)
Yb(2)-O(2)	2.46 (3)	Yb(2)-N(2)	2.55 (3)
Yb(2)-C(25)	2.75 (3)	Yb(2)-C(26)	2.74 (3)
Yb(2)-C(27)	2.81 (4)	Yb(2)-C(28)	2.80 (3)
Yb(2)-C(29)	2.83 (4)	Yb(2)-C(35)	2.82 (5)
Yb(2)-C(36)	2.80 (5)	Yb(2)-C(37)	2.76 (4)
Yb(2)-C(38)	2.70 (4)	Yb(2)-C(39)	2.80 (4)
Cent1[b]-Yb(1)	2.505	Cent2-Yb(1)	2.513
Cent3-Yb(2)	2.503	Cent4-Yb(2)	2.500
	Bond Angles		
X(1)-Yb(1)-X(2)	89 (1)	O(2)-Yb(2)-N(2)	87.5 (9)
Cent1-Yb(1)-Cent2	135.11	Cent1-Yb(1)-X(1)	104.03
Cent1-Yb(1)-X(2)	105.84	Cent2-Yb(1)-X(1)	107.91
Cent2-Yb(1)-X(2)	105.15	Cent3-Yb(2)-Cent4	139.31
Cent3-Yb(2)-O(2)	105.88	Cent3-Yb(2)-N(2)	103.55
Cent4-Yb(2)-O(2)	107.19	Cent4-Yb(2)-N(2)	100.93

[a] X(1) and X(2) correspond to the two disordered O and N positions in molecule 1 (see Experimental Section). [b] Cent1 is the centroid of the plane defined by atoms C(1)-C(5), Cent2 the centroid of the plane defined by atoms C(11)-C(15), Cent3 the centroid of the plane defined by the atoms C(25)-C(29), and Cent4 the centroid of the plane defined by atoms C(35)-C(39).

of $EuCl_2$ and NaC_5Me_5.[2a] No ammonia remains bound to the metal as evidenced by the total absence of the strong band at 1178 cm^{-1} indicative of coordinated ammonia.[25] However, when Ln = Yb, the isolated complex retains one molecule of ammonia bound to the metal. The identification of this unusually stable ammoniate is based upon infrared, ^1H NMR, and ^{13}C NMR spectroscopy, magnetic moment, and complete elemental analysis. The infrared spectrum confirms the presence of coordinated ammonia (strong band observed at 1178 cm^{-1}). The ^1H NMR and ^{13}C NMR spectra are virtually identical with that observed by Andersen et al. for the closely related $(C_5Me_5)_2Yb(THF)$.[2a] No resonances assignable to coordinated ammonia are observed in the ^1H NMR spectrum. We attribute this effect to hyperfine coupling to nitrogen which would be expected to give three broad lines in the spectrum which could be lost in the base line. The observed difference in the ability of these divalent metals to strongly coordinate ammonia is most likely due to the enhanced Lewis acidity of the smaller divalent ytterbium. We emphasize that in neither case are trivalent byproducts observed in the synthesis supporting the suitability of metal–ammonia reactions for the synthesis of these compounds.

To determine if the Yb–N bond in $(C_5Me_5)_2Yb(NH_3)(THF)$ is unusually short and to establish standards for coordinated ammonia bond lengths in organolanthanoid complexes, we have undertaken a single-crystal X-ray structure determination of the complex. Satisfactory crystals of the complex were grown by slow diffusion of pentane into a saturated THF/pentane solution of the complex at ambient temperature. There are two molecules in the asymmetric unit of $(\eta^5\text{-}C_5Me_5)_2Yb(NH_3)(OC_4H_8)$. Molecule 1 exhibits disorder between the NH_3 and THF groups resulting in an overlap of the N and O positions that could not be resolved. The second molecule does not show this type of disorder, and the discussion of O and N distances will be confined to this molecule which is depicted in Figure 1.

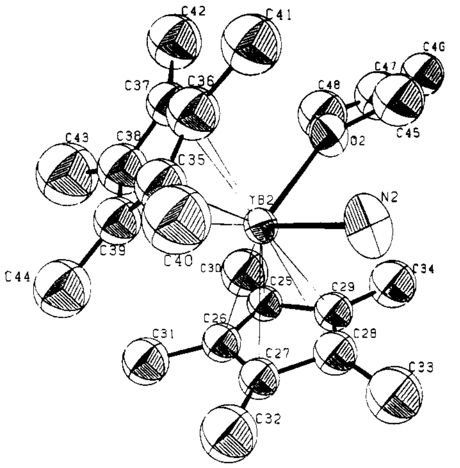

Figure 1. Molecular structure and atom labeling scheme for one of the two molecules in the asymmetric unit of $(\eta^5\text{-}C_5Me_5)_2Yb(NH_3)(OC_4H_8)$. The disorder of atoms C(46) and C(47) is not shown.

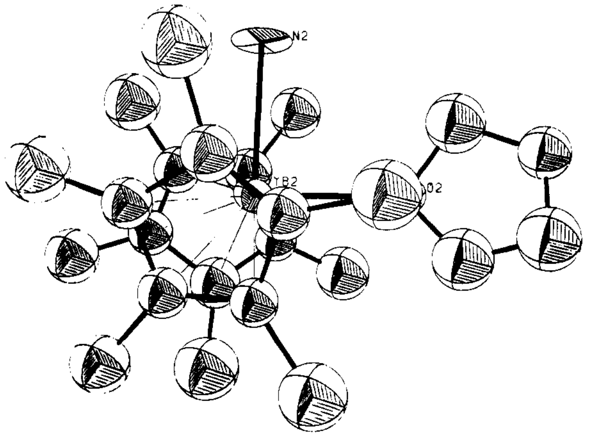

Figure 2. View of molecule 2 depicting the staggered C_5Me_5 rings.

The disorder and resulting high standard deviations preclude all but the most general description of the structure. The two pentamethylcyclopentadienyl ligands are staggered (Figure 2) with average Yb–C distances of 2.77 (4) Å for both molecules. As expected, this value is longer than that observed for the seven-coordinate Yb(II) species $(\eta^5\text{-}C_5Me_5)_2Yb(OC_4H_8)$[2a] and approximately the same as that found in the eight-coordinate Yb(II) complex

$(\eta^5\text{-}C_5Me_5)_2Yb(NC_5H_5)_2$.[26] The Yb(2)–O(2) separation of 2.46 (3) Å is slightly longer than the 2.41 Å found for $(\eta^5\text{-}C_5Me_5)_2Yb(OC_4H_8)$.[2a] Again, although the standard deviations are high, one would expect an increase of 0.06 Å in the ionic radius of eight-coordinate Yb(II) vs. seven-coordinate Yb(II).[27]

It is unfortunate that the disorder in molecule 1 obscures the Yb(1)–N(1) distance but this important aspect of the structure is observed in the second molecule. Here, the Yb(2)–N(2) separation is 2.55 (3) Å. This short distance shows that the ammonia molecule is held tightly enough by the ytterbium metal to resist displacement by other donor solvents. A similar Yb–N distance of 2.56 Å has been found in $(\eta^5\text{-}C_5Me_5)_2Yb(NC_5H_5)_2$.[26]

In conclusion, our results indicate that organolanthanoid synthesis in liquid ammonia is a viable alternate route to standard metathetical schemes when appropriate cautions are exercised as to choice of substrate and reaction conditions.

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Registry No. $(C_5Me_5)_2$ Yb(NH_3)(THF), 91443-87-7; $(C_5Me_5)_2$ Eu(THF), 91443-88-8; Yb, 7440-64-4; Eu, 7440-53-1.

Supplementary Material Available: Schematic diagram of vacuum line and ancillary equipment and tables of thermal parameters, bond distances and angles, best plane results, and observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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[26] Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A. *Inorg. Chem.* **1982**, *21*, 2647.

[27] Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

Photochemistry and Electronic Structure of the $(\eta^5\text{-}C_5H_5)_2MoS_2$ Complex

Alice E. Bruce, Mitchell R. M. Bruce, Anthony Sclafani, and David R. Tyler*

Department of Chemistry, Columbia University, New York, New York 10027

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The photochemistry of the Cp_2MoS_2 complex was studied in order to determine if d–d excited states gave different photochemistry than the S → Mo charge-transfer excited states. The various excited states were identified with the aid of a self-consistent field–Xα–scattered-wave molecular orbital calculation. No wavelength dependent photochemistry was found as irradiation of the Cp_2MoS_2 complex in inert solvents at all selected wavelengths led to Cp_2MoS_4. The mechanism of Cp_2MoS_4 formation was studied. Two pathways seemed likely: photochemical extrusion of either S_2 or S_2^{2-}. The formation of Cp_2MoS_4 does not necessarily imply the extrusion of S_2 rather than S_2^{2-} because the latter species can disproportionate: $2S_2^{2-} \rightarrow S_2 + 2S^{2-}$. In order to differentiate between homolytic and heterolytic Mo–S bond cleavage pathways, the Cp_2MoS_2 complex was irradiated in $CDCl_3$. The products in this solvent are Cp_2MoCl_2 and Cp_2MoS_4, at all wavelengths. Other unidentified minor products also formed in the photochemical reactions of the Cp_2MoS_2. Since the reaction of molybdenocene with $CHCl_3$ produces Cp_2MoCl_2 and because attempts to trap Cp_2Mo^{2+} failed, it is proposed that homolytic extrusion of S_2 follows irradiation of the Cp_2MoS_2 complex. Reasons for the wavelength independent photochemistry and for the homolytic extrusion of S_2, upon irradiation in either the $14a_1 \rightarrow 9b_1$ d–d band (490 nm) or the $6a_2 \rightarrow 9b_1$ S → Mo charge-transfer (420 nm) band, are discussed.

Introduction

In a recent paper we reported that S → Ti charge-transfer excitation of the Cp_2TiS_5 complex led to homolytic cleavage of a Ti–S bond.[1] This result led us to pose two questions. First, was homolytic cleavage typical of S → M CT excited states? And second, was this behavior characteristic only of S → M CT excited states or will d–d excited states also lead to homolytic cleavage of S–M bonds in organometallic sulfide complexes? To answer these questions we decided to study the photochemistry of the Cp_2MoS_2 complex, a molecule with a d^2 configuration. The presence of d–d transitions allowed us to compare the reactivity of d–d excited states with the reactivity of the S → M CT states.

In order to differentiate between the d–d and S → M CT bands in the absorption spectrum of the Cp_2MoS_2 complex, we used the SCF–Xα–SW molecular orbital method to calculate the electronic structure of the complex. With the aid of the MO calculation we were able to assign the bands in the electronic spectrum of the complex. This paper reports the results of our molecular orbital study of the Cp_2MoS_2 complex and also the results of some photochemical reactions.

Experimental Section

SCF–Xα–SW Procedure. Calculations were carried out by using the SCF–Xα–SW method.[2] Current versions of the programs were used,[3] and they were run on the chemistry department's DEC VAX 11/780 computer. Norman's procedure for interpolation of overlapping sphere sizes was used to optimize the virial coefficient at one.[4,5] The electronic transition energies

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[1] Bruce, A. E.; Bruce, M. R. M.; Tyler, D. R., *J. Am. Chem. Soc.*, in press.

[2] (a) Slater, J. C. "The Calculation of Molecular Orbitals"; New York, 1979 and references therein. (b) Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 143–185 and references therein. (c) Rosch, N.; Klemperer, W. G.; Johnson, K. H. *Chem. Phys. Lett.* **1973**, *23*, 149–154. (d) Johnson, K. H.; Smith, F. C. *Phys. Rev. B: Solid State* **1972**, *5*, 831–843.

[3] The programs were received from K. H. Johnson in 1981 and converted for use on a DEC VAX 11/780 by W. H. Klemperer and M. R. Bruce.

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