Inorg. Chem. **2006**, *45*, 7004–7009

Inorganic Chemistry
Article

Observation of Internal Electron Transfer in Bulky Allyl Ytterbium Complexes with Substituted Terpyridine Ligands

Rosemary E. White,[†] Christin N. Carlson,[‡] Jacqueline M. Veauthier,[‡] Cheslan K. Simpson,[‡] J. D. Thompson,[§] Brian L. Scott,[‡] Timothy P. Hanusa,*,[†] and Kevin D. John*,[‡]

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and Chemistry and Materials Science and Technology Divisions, Los Alamos National Laboratory (LANL), Los Alamos, New Mexico 87545

Received April 10, 2006

A series of new bulky allyl terpyridyl–ytterbium complexes have been synthesized to determine the effect of allyl ligands on the internal charge-transfer process that exists in these materials. Compared to the pentamethylcyclopentadienyl–ytterbocene compound $Cp^*_2Yb(tpyCN)$ ($\nu_{C\equiv N} = 2172$ cm^{-1}), the symmetrically substituted allyl complex $[1,3\text{-}(SiMe_3)_2C_3H_3]_2Yb(tpyCN)$ possesses a markedly lowered C≡N frequency of 2130 cm^{-1}. Furthermore, the electronic nature of these bulky allyl complexes can be tuned, as demonstrated by the C≡N frequency of the asymmetric derivatives $[1\text{-}(SiMe_3)C_3H_4]_2Yb(tpyCN)$ and $[1\text{-}(SiPh_3)\text{-}3\text{-}(SiMe_3)C_3H_3]_2Yb(tpyCN)$ (2171 and 2164 cm^{-1}, respectively). The differences in these frequencies can be attributed to differences in the ligands' steric and electronic character. Single-crystal X-ray characterization of $[1,3\text{-}(SiMe_3)_2C_3H_3]_2Yb(tpy)$ reveals that the allyl moiety possesses shorter Yb–C and Yb–N bond distances than the Cp* analogue. The magnetic susceptibility data for $[1,3\text{-}(SiMe_3)_2C_3H_3]_2Yb(tpy)$ departs dramatically from the Curie law, with a room-temperature magnetic moment of 2.95 μ_B.

Introduction

The charge-transfer behavior of cyclopentadienyl sandwich compounds of the divalent lanthanides has been of interest for some time.[1,2] In particular, a variety of ytterbocene N-heterocyclic adducts (e.g., $Cp^*_2Yb(L)$, where $Cp^* = C_5Me_5$ and L = 2,2′-bipyridine (bpy),[1] 10-phenanthroline (phen),[1] 2,2′:6′,2″-terpyridine (tpy),[2] and 4′-cyano-2,2′:6′,2″-terpyridine (tpyCN)[2]) have been reported to display a stable charge-transfer electronic configuration derived from a spontaneous electron transfer from a diamagnetic Yb^{II} f^{14} metal center to the lowest unoccupied molecular orbital (LUMO) on the N-heterocyclic ligand, ($f^{14}\,\pi^{*0} \rightarrow f^{13}\,\pi^{*1}$). This spontaneous electron transfer has been examined extensively with electrochemical and spectroscopic methods.[2–4] Although the nature of the magnetic coupling between the Yb^{III} f^{13} metal center and the ligand radical anion is not the same for the aforementioned Cp* adducts, the room-temperature magnetic moments (μ_{eff}) are lower than that predicted for a Yb^{III} f^{13} metal center with a π^{*1} ligand.

In addition to the ytterbocene–polypyridyl complexes, we have studied the structures and catalytic activity of a series of bulky allyl lanthanide complexes including $[1,3\text{-}(SiMe_3)_2C_3H_3]_2Yb(THF)_2$ (**1**; THF = tetrahydrofuran).[5] The use of trimethylsilyl-substituted allyl ligands has become a common way to synthesize thermally stable allyl complexes throughout the periodic table. Indeed, the symmetrically substituted allyl ligand $[1,3\text{-}(SiMe_3)_2C_3H_3]^-$ has been incorporated into complexes with early-main-group metals,[5–8] transition metals,[9–11] lanthanides,[5,12–15] and actinides.[16] We report here the application of bulky allyl ytterbium synthons

---

* To whom correspondence should be addressed. E-mail: t.hanusa@vanderbilt.edu (T.P.H.), kjohn@lanl.gov (K.D.J.).

[†] Vanderbilt University.

[‡] Chemistry Division, Los Alamos National Laboratory.

[§] Materials Science and Technology Division, Los Alamos National Laboratory.

(1) Schultz, M.; Boncella, J. M.; Berg, D. J.; Tilley, T. D.; Andersen, R. A. *Organometallics* **2002**, *21*, 460–472.

(2) Veauthier, J. M.; Schelter, E. J.; Kuehl, C. J.; Clark, A. E.; Scott, B. L.; Morris, D. E.; Martin, R. L.; Thompson, J. D.; Kiplinger, J. L.; John, K. D. *Inorg. Chem.* **2005**, *44*, 5911–5920.

(3) Kuehl, C. J.; Da Re, R. E.; Scott, B. L.; Morris, D. E.; John, K. D. *Chem. Commun.* **2003**, 2336–2337.

(4) Da Re, R. E.; Kuehl, C. J.; Brown, M. G.; Rocha, R. C.; Bauer, E. D.; John, K. D.; Morris, D. E.; Shreve, A. P.; Sarrao, J. L. *Inorg. Chem.* **2003**, *42*, 5551–5559.

(5) Simpson, C. K.; White, R. E.; Carlson, C. N.; Wrobleski, D. A.; Kuehl, C. J.; Croce, T. A.; Steele, I. M.; Scott, B. L.; Hanusa, T. P.; Sattelberger, A. P.; John, K. D. *Organometallics* **2005**, *24*, 3685–3691.

10.1021/ic060603x CCC: $33.50

in the development of new magnetic materials with two key objectives: (1) to determine the difference in the magnetic behavior between terpyridyl−ytterbium complexes with Cp* and bulky allyl ligands so as to understand the nature of the internal charge transfer and its impact on the magnetism of these molecular species and (2) to tune the electronic/magnetic behavior of these complexes through allyl substitution. To facilitate the latter, we have synthesized an asymmetrically substituted allyl ligand, $[1\text{-}(SiPh_3)\text{-}3\text{-}(SiMe_3)\text{-}C_3H_3]^-$, through a preparation similar to that of the symmetric trimethylsilylated allyl ligand.[5,17] In addition to these two allyl ligands, the previously reported,[17] less bulky asymmetric allyl ligand, $[1\text{-}(SiMe_3)C_3H_4]^-$, has also been used for comparison.

Experimental Section

General Considerations. All manipulations were performed with the rigorous exclusion of air and moisture using Schlenk or glovebox techniques. ^{1}H NMR spectra were obtained on a Bruker DPX 300-MHz or an Avance 400-MHz spectrometer and were referenced to the residual resonances of C_6D_6 (δ 7.16), THF-d_8 (δ 3.58), or toluene-d_8 (δ 2.09). IR spectra were recorded on a Thermo-Nicolet FT-IR module instrument Magna 760 spectrometer at 4 cm^{-1} resolution as mineral oil mulls. Elemental analysis (C and H) was performed by Desert Analytics (Tucson, AZ); complexometric methods were used for the analysis of Yb.[18]

Materials. $[1,3\text{-}(SiMe_3)_2C_3H_3]_2Yb(THF)_2$ (**1**) and $Yb(OTf)_2(THF)_3$ were prepared as previously described.[5] $K[1\text{-}(SiMe_3)C_3H_4]$ was prepared as a lithium salt according to the literature procedure[17] and transmetalated with potassium *t*-butoxide (KO-*t*-Bu). Allyltrimethylsilane was purchased from Gelest and degassed prior to use. Chlorotriphenylsilane (Gelest), *n*-butyllithium (*n*-BuLi; 2.5 M in hexane, Acros), KO-*t*-Bu (Strem), anhydrous YbI_2 (Aldrich), and 2,2′-6′,2″-terpyridine (tpy, Aldrich) were used as received. 4′-Cyano-2,2′:6′,2″-terpyridine (tpyCN) and 6,6″-dicyano-2,2′:6′,2″-terpyridine (tpy(CN)$_2$) were prepared according to literature procedures.[19] Potassium 6,6″-dicyano-2,2′:6′,2″-terpyridine ($K^+[tpy(CN)_2]^-$) was prepared by adding 1 equiv of freshly cut K metal to 1 equiv of tpy(CN)$_2$ in THF and stirring overnight at room temperature. Anhydrous solvents, tetrahydrofuran (THF), toluene, and methylene chloride were purchased from Aldrich or Acros and stored in the glovebox over activated 4 Å molecular sieves overnight and passed the ketyl test before use. Deuterated solvents (C_6D_6, THF-d_8, and toluene-d_8) were sparged with Ar and stirred over a Na/K (1:2) alloy, from which they were transferred under vacuum; $CDCl_3$ (Acros) was used as received.

Preparation of $1\text{-}(SiPh_3)\text{-}3\text{-}(SiMe_3)C_3H_4$. Allyltrimethylsilane (3.55 g, 31.07 mmol) and hexanes (100 mL) were added to a 250-mL Schlenk flask equipped with a stirring bar. After the solution was cooled to 0 °C, *n*-BuLi (12.4 mL, 31.10 mmol) was added dropwise over 20 min. After the solution was allowed to warm to room temperature overnight, it was brought into the glovebox. Chlorotriphenylsilane (9.16 g, 31.07 mmol) was added slowly over 10 min. Chlorotriphenylsilane was not soluble in the reaction mixture; therefore, THF (40 mL) was added to the solution, which immediately turned light orange and cloudy. The reaction was allowed to stir for 8 h. The solution was extracted with ∼25 mL of deionized water and ∼10 mL of diethyl ether three times each. The organic layers were combined, dried with magnesium sulfate, and filtered. Solvent was removed under vacuum, yielding 7.58 g of a white powder (20.3 mmol, 65% yield). ^{1}H NMR (25 °C, 300 MHz, $CDCl_3$): δ 7.51 (m, Si*Ph*$_3$, 6H), 7.38 (m, Si*Ph*$_3$, 9H), 6.07 (dt, $J_1 = 18.5$ Hz, $J_2 = 7.7$ Hz, CHC*H*CH$_2$, 1H), 5.48 (d, $J = 18.5$ Hz, C*H*CHCH$_2$, 1H), 2.48 (d, $J = 7.7$ Hz, CHCHC*H*$_2$, 2H), −0.08 (s, Si*Me*$_3$, 9H). MS: *m*/*e* 372 (M$^+$), 259 (SiPh$_3^+$), 105 (SiPh$^+$).

Preparation of $K[1\text{-}(SiPh_3)\text{-}3\text{-}(SiMe_3)C_3H_3]$. Hexanes (75 mL) was added to a 125-mL Schlenk flask containing vacuum-dried $1\text{-}(SiPh_3)\text{-}3\text{-}(SiMe_3)C_3H_4$ (5.00 g, 13.41 mmol) and a stirring bar. After the solution was cooled to 0 °C, *n*-BuLi (5.4 mL, 13.50 mmol) was added dropwise over 10 min. After the solution was stirred overnight while warming to room temperature, KO-*t*-Bu (1.52 g, 13.51 mmol) was added slowly. The solution became sticky and dark orange, and THF (25 mL) was added to increase the solubility of the product. The solution was stirred for 10 h. THF was removed under vacuum, and additional hexanes was added. The yellow solid that remained was filtered over a medium-porosity glass frit. The solid was washed with hexanes and dried under vacuum, yielding 2.08 g of yellow powder (6.14 mmol, 46% yield). ^{1}H NMR (25 °C, 300 MHz, C_6D_6): δ 7.66 (m, Si*Ph*$_3$, 6 H), 7.20 (m, Si*Ph*$_3$, 9H), 6.90 (t, $J = 16.1$ Hz, CHC*H*CH, 1H), 3.39 (d, $J = 16.1$ Hz, C*H*CHCH, 1H), 3.17 (d, $J = 16.1$ Hz, CHCHC*H*, 1H), 0.15 (s, Si*Me*$_3$, 9H).

Preparation of $[1\text{-}(SiMe_3)C_3H_4]_2Yb(THF)_2$ (2). In a scintillation vial, $Yb(OTf)_2(THF)_3$ (0.55 g, 0.80 mmol) was suspended in 10 mL of THF and cooled to −30 °C. In a separate vial, $K[1\text{-}(SiMe_3)\text{-}C_3H_4]$ (0.27 g, 1.77 mmol) in 5 mL of THF was also cooled to −30 °C. The latter solution was added to the stirring $Yb(OTf)_2(THF)_3$ suspension dropwise over 10 min. The resulting solution turned red-brown immediately and was allowed to stir overnight while warming to room temperature. The solvent was removed under vacuum, hexanes (30 mL) was added, and the resulting solution was filtered through a fine-porosity glass frit. The filtrate was dried under vacuum, yielding 0.35 g of a red-brown solid powder (0.61 mmol, 76% yield). ^{1}H NMR (25 °C, 300 MHz, toluene-d_8): δ 0.25 (s, Si*Me*$_3$). Other allylic peaks either were not observed or were obscured by solvent peaks. Anal. Calcd for $C_{20}H_{42}O_2Si_2Yb$: Yb, 31.82. Found: Yb, 31.79.

Preparation of $[1\text{-}(SiPh_3)\text{-}3\text{-}(SiMe_3)C_3H_3]_2Yb(THF)$ (3). In a scintillation vial, $Yb(OTf)_2(THF)_3$ (0.21 g, 0.31 mmol) was suspended in 10 mL of THF and cooled to −30 °C. In a separate vial, $K[1\text{-}(SiPh_3)\text{-}3\text{-}(SiMe_3)C_3H_3]$ (0.26 g, 0.63 mmol) in 5 mL of THF was cooled to −30 °C. The latter solution was added to the

---

(6) Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *Angew. Chem., Int. Ed.* **1999**, *38*, 217−219.

(7) Quisenberry, K. T. Ph.D. Dissertation, Vanderbilt University, Nashville, TN, 2005.

(8) Gren, C. K.; Hanusa, T. P.; Brennessel, W. W. *Polyhedron* **2006**, *25*, 286−292.

(9) Quisenberry, K. T.; Smith, J. D.; Voehler, M.; Stec, D. F.; Hanusa, T. P.; Brennessel, W. W. *J. Am. Chem. Soc*. **2005**, *127*, 4376−4387.

(10) Carlson, C. N.; Smith, J. D.; Hanusa, T. P.; Brennessel, W. W.; Young, V. G., Jr. *J. Organomet. Chem.* **2003**, *683*, 191−199.

(11) Smith, J. D.; Quisenberry, K. T.; Hanusa, T. P.; Brennessel, W. W. *Acta Crystallogr., Sect. C.* **2004**, *60*, m507−m508.

(12) Kuehl, C. J.; Simpson, C. K.; John, K. D.; Sattelberger, A. P.; Carlson, C. N.; Hanusa, T. P. *J. Organomet. Chem.* **2003**, *683*, 149−154.

(13) Woodman, T. J.; Schormann, M.; Bochmann, M. *Isr. J. Chem.* **2003**, *42*, 283−293.

(14) Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2003**, *22*, 3028−3030.

(15) Ihara, E.; Koyama, K.; Yasuda, H.; Kanehisa, N.; Kai, Y. *J. Organomet. Chem.* **1999**, *574*, 40−49.

(16) Carlson, C. N.; Hanusa, T. P.; Brennessel, W. W. *J. Am. Chem. Soc.* **2004**, *126*, 10550−10551.

(17) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 1382−1386.

(18) Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*, 2nd ed.; Methuen: London, 1969.

(19) Veauthier, J. M.; Carlson, C. N.; Collis, G. E.; Kiplinger, J. L.; John, K. D. *Synthesis* **2005**, 2683−2686.

stirring $Yb(OTf)_2(THF)_3$ suspension dropwise over 10 min. The resulting solution turned red-brown immediately and was allowed to stir overnight while warming to room temperature. The solvent was removed under vacuum, hexanes (30 mL) was added, and the resulting solution was filtered through a fine-porosity glass frit. The filtrate was dried under vacuum, yielding 0.24 g of a red-brown solid powder (0.23 mmol, 75% yield). Dissolution of the product in a small amount of hexanes and cooling to −30 °C allowed for the growth of X-ray-quality crystals. ^1H NMR evidence and elemental analysis both indicate the coordination of two THF molecules in **3**, while crystallographic data of **3** indicate the presence of one THF molecule. This disagreement may result from differences in solution and solid-state environments. ^1H NMR (25 °C, 300 MHz, THF-d_8): δ 7.61 (m, Si*Ph*$_3$, 10H), 7.28 (m, Si*Ph*$_3$ and CHC*H*CH, 22H), 4.00 (br s, THF, 8H), 3.56 (d, $J = 14.6$ Hz, $SiPh_3C$*H*CHCHSiMe$_3$, 2H), 3.50 (d, $J = 14.6$ Hz, $SiPh_3CH$-CHC*H*SiMe$_3$, 2H), 2.4 (br s, THF, 8H), 0.15 (s, Si*Me*$_3$, 18H). Anal. Calcd for $C_{56}H_{70}O_2Si_4Yb$: Yb, 16.32. Found: Yb, 16.87.

Preparation of [1,3-$(SiMe_3)_2C_3H_3]_2Yb$(tpy) (1·tpy). In a scintillation vial, **1** (0.10 g, 0.15 mmol) was suspended in 15 mL of toluene. This solution was added dropwise to a second vial containing tpy (0.04 g, 0.19 mmol). The reaction mixture immediately turned dark green and was allowed to stir overnight (16 h). The solvent was then removed under vacuum, approximately 15 mL of hexanes was added to the dark-green residue, and the solution was filtered through Celite and glass microfiber filter paper. The solvent was removed under vacuum, resulting in a dark-green powder (0.09 g, 75% yield). X-ray-quality crystals were grown from a concentrated solution of hexanes. ^1H NMR (25 °C, 400 MHz, THF-d_8): δ −0.13 (s, Si*Me*$_3$). ^1H NMR spectra at room temperature and −20 °C were identical; terpyridyl and C_3 allyl resonances were not observed. Anal. Calcd for $C_{33}H_{52}N_3Si_4Yb$: Yb, 22.27. Found: Yb, 21.97. λ_{max} (nm): 404, 610, 951.

Preparation of [1,3-$(SiMe_3)_2C_3H_3]_2Yb$(tpyCN) (1·tpyCN). Complex **1**·tpyCN was prepared using the same method as that for **1**·tpy, using 0.09 g (0.14 mmol) of **1** and 0.05 g (0.18 mmol) of tpyCN. The reaction mixture turned dark blue upon the addition of **1** in solution, and the isolated product was a dark-blue powder (0.09 g, 80% yield). ^1H NMR (25 °C, 400 MHz, THF-d_8): δ 0.01 (br s, Si*Me*$_3$), −0.02 (br s, Si*Me*$_3$). Terpyridyl and C_3 allyl resonances were not observed. Anal. Calcd for $C_{34}H_{52}N_4Si_4Yb$: Yb, 21.57. Found: Yb, 21.16. IR (mineral oil): 2130 cm^{-1} ($\nu_{C\equiv N}$). λ_{max} (nm): 356, 573, 923.

Preparation of [1,3-$(SiMe_3)_2C_3H_3]_2Yb(tpy(CN)_2)$ [1·tpy(CN)$_2$]. Complex **1**·tpy(CN)$_2$ was prepared using the same method as that for **1**·tpy, using 0.10 g (0.15 mmol) of **1** and 0.06 g (0.20 mmol) of tpy(CN)$_2$. The reaction mixture turned dark red-brown upon the addition of **1** in solution, and a dark-red-brown powder (0.11 g) was isolated in 86% yield. ^1H NMR (25 °C, 400 MHz, THF-d_8): δ −0.02 (br s, Si*Me*$_3$), −0.04 (br s, Si*Me*$_3$). Terpyridyl and C_3 allyl resonances were not observed. IR (mineral oil): 2125 cm^{-1} ($\nu_{C\equiv N}$). λ_{max} (nm): 411, 577.

Preparation of [1-$(SiMe_3)C_3H_4]_2Yb$(tpyCN) (2·tpyCN). Complex **2**·tpyCN was prepared using the same method as that for **1**·tpy, using 0.88 g (1.62 mmol) of **2** and 0.42 g (1.64 mmol) of tpyCN. The reaction mixture turned dark blue upon the addition of **2** in solution, and a dark-blue powder (0.86 g) was isolated in 80% yield. ^1H NMR (25 °C, 400 MHz, THF-d_8): δ −0.02 (br s, Si*Me*$_3$). Terpyridyl and C_3 allyl resonances were not observed. Anal. Calcd for $C_{28}H_{36}N_4Si_2Yb$: Yb, 26.30. Found: Yb, 26.40. IR (mineral oil): 2171 cm^{-1} ($\nu_{C\equiv N}$).

Preparation of [1-$(SiPh_3)$-3-$(SiMe_3)C_3H_3]_2Yb$(tpyCN) (3·tpyCN). Complex **3**·tpyCN was prepared using the same method as that for **1**·tpy, using 0.26 g (0.24 mmol) of **3** and 0.06 g (0.24 mmol) of tpyCN. The reaction mixture turned dark blue upon the addition of **3** in solution, and a dark-blue powder (0.23 g) was isolated in 81% yield. Terpyridyl and C_3 allyl NMR resonances were not observed. Anal. Calcd for $C_{64}H_{64}N_4Si_4Yb$: Yb, 14.73. Found: Yb, 14.59. IR (mineral oil): 2164 cm^{-1} ($\nu_{C\equiv N}$).

Magnetic Measurements. Magnetic measurements over the temperature range 2−300 K were made using a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer. The microcrystalline samples were sealed in borosilicate NMR tubes along with a small amount of quartz wool, which held the sample near the tube center. Contributions to the magnetization from quartz wool and the tube were measured independently and subtracted from the total measured signal. The magnetic susceptibility, defined as the sample magnetization M divided by the applied magnetic field H, was measured for **1**·tpy as a function of the temperature at an applied field of 0.1 T. Diamagnetic corrections were made using Pascal's constants.

X-ray Crystallography of 1·tpy. Single-crystal X-ray diffraction experiments for **1**·tpy were performed on a Bruker P4/CCD/PC diffractometer. Diffraction data were refined using *SHELXTL*.[20] Crystals were coated in mineral oil and mounted on a glass fiber at 203 K. Data collection and initial indexing and cell refinement were performed using *SMART*[21] software. Frame integration and final cell parameter calculation were carried out using *SAINT*[22] software. The data were corrected for absorption using the *SADABS*[23] program. Decay of the reflection intensity was not observed. The structures were solved using difference Fourier techniques. The initial solutions revealed the metal center and the majority of all other non-H positions. The remaining atomic positions were determined from subsequent Fourier syntheses. All H atoms were placed in ideal positions and refined using a riding model. The crystal and refinement parameters for **1**·tpy are listed in Table 1. Selected bond distances and angles are listed in Table 2.

Results and Discussion

Synthesis and Structural Characterization. The lithium salt of the asymmetric allyl ligand $[1\text{-}(SiMe_3)C_3H_4]^-$ was synthesized as described by Fraenkel;[17] subsequent transmetalation with KO-*t*-Bu yielded the potassium salt. The K complex of the symmetric allyl $[1,3\text{-}(SiMe_3)_2C_3H_3]^-$ was prepared as described in the literature,[5,17] and the trimethylsilyl- and triphenylsilyl-substituted ligand $[1\text{-}(SiPh_3)\text{-}3\text{-}(SiMe_3)C_3H_3]^-$ was prepared through a similar method.

Diallyl ytterbium complexes with each of these three allyl ligands were synthesized by treatment of 2 equiv of the corresponding potassium allyl complex with YbI_2 or $Yb(OTf)_2(THF)_3$ in THF at −30 °C (Scheme 1, reaction I). The resulting Yb complexes consist of two η^3-bound allyl ligands and one (**3**) or two (**1** and **2**) THF molecules, as indicated by the crystal structures (**1** and **3**) and ^1H NMR data. Crystallographic data for **1** have been reported previously.[5] X-ray-quality crystals of **3** were grown from a concentrated

---

[20] *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems: Madison, WI, 1997.

[21] *SMART*, version 4.210; Bruker Analytical X-ray Systems: Madison, WI, 1996.

[22] *SAINT*, version 4.05; Bruker Analytical X-ray Systems: Madison, WI, 1996.

[23] Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

Table 1. Crystal Data and Summary of X-ray Data Collection for **1**·tpy

empirical formula	$C_{33}H_{49}N_3Si_4Yb$
fw	773.15
space group	$P\bar{1}$
a, Å	10.202(4)
b, Å	12.018(4)
c, Å	17.226(6)
α, deg	71.618(5)
β, deg	77.715(5)
γ, deg	71.934(5)
V, Å^3	1889.8(12)
ρ_{calcd}, g cm^{-3}	1.359
Z	2
μ, mm^{-1}	2.625
λ(Mo Kα), Å	0.710 73
T, K	203
GOF[a]	1.069
R1 [$I > 2\sigma(I)$][b]	0.1065
wR2 [$I > 2\sigma(I)$][c]	0.2859
R1 (all data)[b]	0.1278
wR2 (all data)[c]	0.2957
largest diff peak/hole, e Å^{-3}	8.844 and −2.044

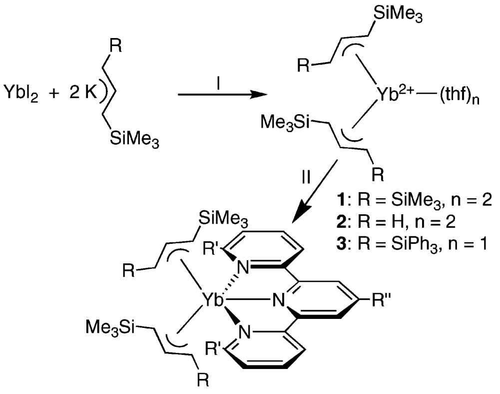
[a] GOF = $[\Sigma[w(F_o^2 - F_c^2)]^2/(n - p)]^{1/2}$; n = number of reflections, and p = total number of parameters refined. [b] R1 = $\Sigma|F_o| - |F_c|\Sigma|F_o|$. [c] wR2 = $[\Sigma[w(F_o^2 - F_c^2)]^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**·tpy

atoms	distance	atoms	angle
Yb−N1	2.39(2)	C−C−C(allyl, ave)	121.4(2)
Yb−N2	2.27(1)	N1−C−C−N2	−5.8
Yb−N3	2.38(1)	N3−C−C−N2	−3.4
Yb−C(ave)	2.60(4)	A_{cent}−Yb−A_{cent}[a]	135.9

[a] A_{cent} is defined as the centroid comprising three allyl C atoms.

Scheme 1. Reaction I: Synthesis of **1**−**3** (in THF at −30 °C) and Reaction II: Synthesis of **1**·tpy, **1**·tpyCN, **1**·tpy(CN)$_2$, **2**·tpyCN, and **3**·tpyCN (in Toluene at Room Temperature)



1•tpy: R = SiMe$_3$; R', R'' = H
1•tpyCN: R = SiMe$_3$; R' = H; R'' = CN
1•tpy(CN)$_2$: R = SiMe$_3$; R' = CN; R'' = H
2•tpyCN: R, R' = H; R'' = CN
3•tpyCN: R = SiPh$_3$; R' = H; R'' = CN

hexanes solution at −30 °C. The structure exhibited severe disorder, and only the atom connectivity could be established (see the Supporting Information).

Complexes **1**−**3** were treated with terpyridine derivatives tpy, tpyCN, and tpy(CN)$_2$ (Figure 1) in toluene at room temperature as shown in Scheme 1, reaction II. In each case, a color change from purple occurred immediately (to dark green for tpy, dark blue for tpyCN, and dark red-brown for tpy(CN)$_2$). Terpyridyl adducts of **1**−**3** are air- and moisture-sensitive and are thermally unstable above room temperature. Despite the use of large frequency windows, the C_3 allyl and terpyridyl resonances of these complexes were not evident in their ^{1}H NMR spectra. This is indicative of the expected paramagnetic $f^{13}\,\pi^{*1}$ configuration. In contrast, the SiMe$_3$ proton resonances are observed, presumably because of the fact that they are spatially isolated from the Yb^{III} center and the ligand radical anion. The absorption bands in the UV−vis−near-IR spectra of adducts of **1** are listed in the Experimental Section. They show $\pi-\pi^*$ and $\pi^*-\pi^*$ transitions that demonstrate electron transfer between the ytterbium (donor) and terpyridyl ligand (acceptor). Neither the parent allyl complexes (**1**−**3**) nor their terpyridyl derivatives display the reversible redox behavior exhibited by their Cp* analogues. Chemical isolation of cationic complexes was attempted using common oxidizing agents (e.g., AgOTf); however, these reactions provide intractable solids. We believe that this redox instability is due to the propensity of the allyl groups to reductively eliminate, providing hexadiene products.[9,24]

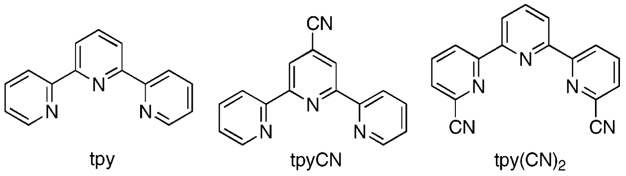


Figure 1. Terpyridine ligands: tpy, tpyCN, and tpy(CN)$_2$.

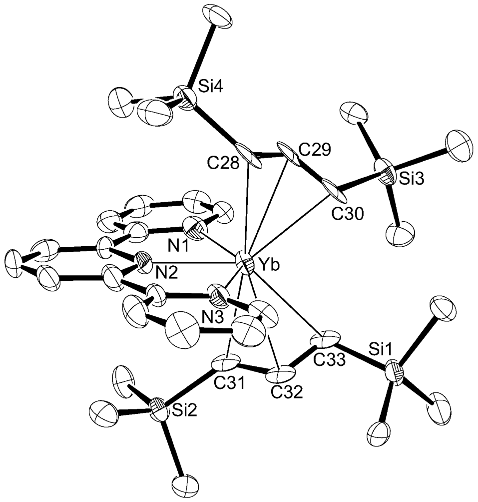


Figure 2. Thermal ellipsoid representation of **1**·tpy (50% probability ellipsoids). H atoms have been omitted for clarity.

X-ray-quality crystals of **1**·tpy were grown in a concentrated solution of hexanes at −30 °C overnight; the structure is shown in Figure 2. The two allyl ligands in **1**·tpy are in an anti configuration with an average C−C−C angle of 121.4(2)° (see Table 2). This value has contracted relative to that of **1** (128.9°), which suggests a slight rehybridization of the allyl moiety that is consistent with a greater extent of electron donation to the Yb center. The allyl ligands are π-bound to the Yb center, with Yb−C bond lengths ranging from 2.52(2) to 2.62(2) Å (Table 2). These distances are shorter than the analogous distances for **1** (Yb−C 2.741-(9)−2.754(9) Å).[5] This is to be expected given that the

---

(24) John, K. D.; Salazar, K. V.; Scott, B. L.; Baker, R. T.; Sattelberger, A. P. *Organometallics* **2001**, *20*, 296−304.

Table 3. IR C≡N Stretching Frequencies[a]

compound	$\nu_{\mathrm{C\equiv N}}$ (cm^{-1})	compound	$\nu_{\mathrm{C\equiv N}}$ (cm^{-1})
tpyCN	2238[2]	Cp*$_2$Yb(tpyCN)	2172[2]
tpyCN$^-$	2149[2]	tpy(CN)$_2$	2238
1·tpyCN	2130	tpy(CN)$_2^-$	2130
2·tpyCN	2171	**1**·tpy(CN)$_2$	2125
3·tpyCN	2164		

[a] All spectra were obtained in mineral oil except that of Cp*$_2$Yb(tpyCN), which was measured in toluene.

lanthanide in **1** is divalent, whereas for **1**·tpy, the metal center is effectively trivalent. The tpy ligand is η^3-bound to the metal center with Yb−N bond lengths from 2.27(2) to 2.39(2) Å. The analogous distances in Cp*$_2$Yb(tpy) (Yb−C 2.41(1)−2.42(1) Å) are slightly longer.[3] Evidently, the more compact allyl ligand allows for closer Yb−C and Yb−tpy binding than is possible with the sterically bulky pentamethylcyclopentadienyl ligands.

IR Spectroscopy. The C≡N moieties of tpyCN and tpy(CN)$_2$ provide an excellent means to gauge the extent of charge transfer for the allyl derivatives. The C≡N stretching frequencies for **1**−**3**·tpyCN, **1**·tpy(CN)$_2$, and the neutral and anionic forms of the free ligands (tpyCN and tpy(CN)$_2$) are presented in Table 3.[2] The tpyCN adducts of the asymmetrically substituted allyl complexes (**2**·tpyCN and **3**·tpyCN) have stretching frequencies very close to that reported for Cp*$_2$Yb(tpyCN) (Table 3) with C≡N stretches between 2164 and 2172 cm^{-1}. This correspondence is not unexpected because allyls are believed to have electron-donating ability similar to that of cyclopentadienyl ligands.[6]

Surprisingly, however, the C≡N stretching frequency for the symmetric allyl complex **1**·tpyCN (2130 cm^{-1}) is ~40 cm^{-1} lower than that of the analogous Cp* derivative and is even lower than the C≡N stretching frequency for the anionic form of the free ligand (tpyCN$^-$; $\nu_{\mathrm{C\equiv N}} = 2149$ cm^{-1}). It seems that, compared to **2**·tpyCN (with 1 SiMe$_3$ per allyl), the additional trimethylsilyl group on the allyl ligand of **1**·tpyCN increases the electron-density donation to the metal center, which in turn increases electron transfer to the tpyCN ligand. A similar trend is observed for allylcarbonyl complexes of transition metals. For example, the bis(1,3-trimethylsilyl)-substituted allylmetal complexes (e.g., [1,3-(SiMe$_3$)$_2$C$_3$H$_3$]$_2$Fe(CO)$_2$) have lower CO stretching frequencies than their unsubstituted analogues.[7] The relatively high C≡N stretching frequency of **3**·tpyCN can be explained based on steric considerations, because the allyl groups are farther away from the Yb center, which should inhibit a stronger electron-donating interaction. Furthermore, the electron-withdrawing ability of SiPh$_3$ should also lead to a smaller degree of electron donation.[25]

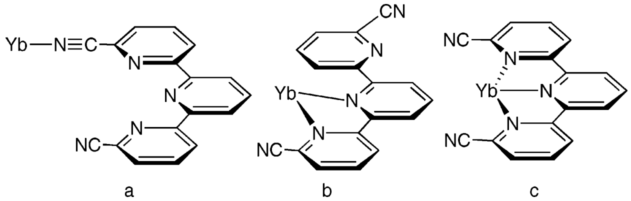


Figure 3. Possible binding modes for **1**·tpy(CN)$_2$.

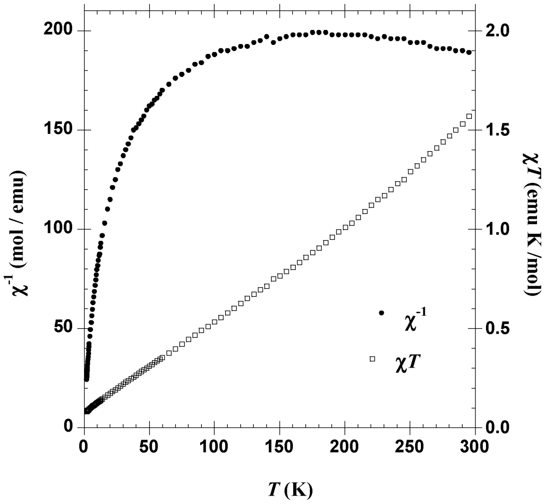


Figure 4. χ^{-1} vs T and χT vs T plots of **1**·tpy. The data were measured in an applied field of 0.1 T.

There are fewer complexes available for comparison in the case of tpy(CN)$_2$ because we have been unable to isolate the analogous Cp*Yb(tpy(CN)$_2$) complex, but the overall trend of the IR data is similar to that of the diallylytterbium adducts of tpyCN. Specifically, the C≡N stretching frequency of **1**·tpy(CN)$_2$ (2125 cm^{-1}) is slightly lower (~5 cm^{-1}) than that of a tpy(CN)$_2$ anion. This frequency can provide a great deal of information about the connectivity of the tpy(CN)$_2$ ligand, where three bonding modes are plausible for the ligand (Figure 3). Coordination in an η^1 fashion to the nitrile group (Figure 3a) is unlikely because we would anticipate an increase in the C≡N stretch, as has been observed for Cp*$_2$YbI(NCtpy) and other η^1-nitrile complexes.[2,26,27] Furthermore, asymmetric binding of the type shown in Figure 3a,b would provide two distinct C≡N stretches. Therefore, the motif in Figure 3c is the most reasonable binding mode for tpy(CN)$_2$ in **1**·tpy(CN)$_2$. To substantiate this binding motif, the geometry of a model of **1**·tpy(CN)$_2$ was optimized using density functional theory (B3PW91/SDD; see the Supporting Information). The resulting structure is similar to that of the crystal structure of **1**·tpy, where the tpy(CN)$_2$ ligand is η^3-bound to the Yb center (Figure 3c). In the optimized structure, the distance between the metal and nitrile groups (Yb−C(N)) averages to 3.575 Å, which indicates that steric crowding around the Yb does not prevent the terpyridyl ligand from being η^3-bound to the Yb center.

Magnetic Susceptibility. The magnetic susceptibility (χ) for compound **1**·tpy was measured as a function of temperature and is presented in Figure 4. The interpretation of the magnetic data is based on the premise that the neutral electronic configuration is f^{13} π^{*1}. The χ^{-1} vs T plot for **1**·tpy departs dramatically from the Curie law and exhibits a temperature-dependent profile reminiscent of previously examined species such as Cp*$_2$Yb(L) (L = bpy,[1] tpy,[2] and tpyCN[2]). Field-dependent χ vs T measurements of **1**·tpy (see

---

(25) Dilman, A. D.; Mayr, H. *Eur. J. Org. Chem.* **2005**, 1760−1764.

(26) Coerver, H. J.; Curran, C. *J. Am. Chem. Soc.* **1958**, *80*, 3522−3523.

(27) Kubota, M.; Schulze, S. R. *Inorg. Chem.* **1964**, *3*, 853−856.

the Supporting Information) at 0.1 and 5 T do not diverge above 10−15 K, suggesting that there is no ferromagnetic impurity in the material under study.

Unfortunately, the redox instability of the allyl complexes (as evidenced by the irreversible nature of the electrochemistry of **1**·tpy and our inability to isolate a chemically oxidized analogue) prevents us from determining the room-temperature magnetic moment of the monocationic complex. The room-temperature magnetic moment of **1**·tpy (2.95 μ_B) is lower than that reported for Cp*$_2$Yb(tpy) (3.77 μ_B); both room-temperature magnetic moments are significantly lower than the value expected for an uncoupled Yb^{III} ion and an organic radical (4.85 μ_B). We were unable to obtain magnetic data beyond 300 K because of the thermal instability of **1**·tpy. The nature of these low magnetic moments is currently being investigated using a variety of variable-temperature techniques (UV−vis−near-IR, magnetic circular dichroism, and NMR) to probe the nature of the magnetic coupling in this class of materials.

Summary and Conclusions

In summary, we have prepared a new series of Yb-based, internal charge-transfer complexes using a series of bulky allyl ligands to explore the direct comparison of the bulky allyl moiety with Cp*. The symmetrically substituted allyl ligand [1,3-$(SiMe_3)_2C_3H_3$] in **1**·tpy is less sterically demanding than Cp* because it allows for closer Yb−tpy binding (Yb−N(ave) 2.35 Å for **1**·tpy and 2.42 Å for Cp*$_2$Yb(tpy)). Neither the parent allyl complexes (**1**−**3**) nor their terpyridyl derivatives display the reversible redox behavior exhibited by their Cp* analogues. Chemical isolation of cationic complexes was attempted using common oxidizing agents; however, these reactions provide intractable solids, presumably as a result of reductive elimination of the allyl groups. The symmetric allyl complex, **1**·tpy, displays temperature-dependent magnetic behavior similar to that of Cp*$_2$Yb(tpy) with a room-temperature magnetic moment that is lower than that predicted for an uncoupled Yb^{III} center and a ligand radical anion. The C≡N stretching frequency of **1**·tpyCN (2130 cm^{-1}) is significantly lower than that of Cp*$_2$Yb(tpyCN) (2172 cm^{-1}), which appears to be a combination of the electronic effect of the two $SiMe_3$ groups and the aforementioned reduction in steric pressure. Furthermore, we have demonstrated that we can tune the electronic properties of these complexes via allyl substitution as evidenced by changes in the C≡N stretching frequencies of the associated terpyridylnitrile ligands.

Acknowledgment. We thank LANL's Laboratory Directed Research and Development (LDRD) ER program and the Petroleum Research Fund, administered by the American Chemical Society, for financial support. C.N.C., J.M.V., and R.E.W. thank the Seaborg Institute for postdoctoral and student fellowships. We thank Dr. David E. Morris for conducting electrochemistry experiments.

Supporting Information Available: X-ray crystallographic files in CIF format for **1**−**3**, coordinates for the optimized structure of **1**·tpy(CN)$_2$, and a plot of χ vs T for **1**·tpy. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060603X