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Chemistry of Weakly Solvated Lanthanide-Metal Cations. Synthesis, Characterization, and Catalytic Chemistry of $[Eu(CH_3CN)_3(BF_4)_3]_x$

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Abstract: The title compound, $[Eu(CH_3CN)_3(BF_4)_3]_x$, **1**, was synthesized by the $NOBF_4$ oxidation of metallic Eu in CH_3CN. The interaction of the BF_4^- ions with the Eu(III) center was established by molecular weight, conductivity, and ^{11}B and ^{19}F NMR spectral measurements. **1** was found to exist as a dimer in CH_3CN. In addition, it behaved as a 1:2 electrolyte, indicating the coordination of two of the BF_4^- ions per Eu(III) ion. However, the conductivity increased when chelating amines were added due to the partial displacement of the coordinated BF_4^- ions. The ^{11}B and ^{19}F NMR spectra of **1** in CH_3CN indicated the presence of two different types of BF_4^- anions, one of which was isotropically shifted due to interaction with the paramagnetic Eu(III) center. The coordinated BF_4^- anions could be displaced quantitatively by the addition of 2 equiv of NO_3^- ions per Eu(III) ion. A degenerate metathesis of the fluorine between the BF_3 and the coordinated BF_4^- ions was observed when BF_3 was added to a CH_3CN solution of **1**. **1** formed a charge-transfer complex with tetra-*p*-anisylethylene in CH_3NO_2 but not in CH_3CN. In addition, **1** initiated the oligomerization and the polymerization of styrene, α-methylstyrene, and 1,3-cyclohexadiene in CH_3NO_2. The molecular weights of the polymers obtained increased markedly on lowering the reaction temperature. At room temperature, indan derivatives were obtained from α-methyl- and α-phenylstyrene. The rate of polymerization of styrene was markedly attenuated when CH_3CN was used instead of CH_3NO_2. **1** also initiated the isomerization of quadricyclane and the ring-opening polymerization of 2(10)-pinene and cyclopropylbenzene in CH_3NO_2.

A property shared by a large number of transition-metal compounds is their ability to catalyze selective transformations of organic substrates in homogeneous solutions under mild conditions.[2] In contrast, examples of homogeneous catalytic activity by lanthanide-metal compounds are rare,[3] and this can be attributed to the general lack of lanthanide-metal compounds incorporating easily dissociable ligands. The ability to interact with the substrate by the dissociation of weakly held ligands is, of course, a necessary condition for homogeneous catalysis. However, most lanthanide-metal compounds incorporate strong donor ligands which do not exhibit dissociative behavior, and this prevents any significant interaction of weakly donating nonfunctionalized organic substrates with the metal center ("back-bonding", which often significantly strengthens the interaction of organic substrates such as olefins with transition metals, is not possible in the case of d^0 lanthanide-metal ions). We note, however, that organic substrates with oxygen-, nitrogen-, and other heteroatom-donor functionalities do interact with lanthanide-metal ions as evidenced by the use of β-diketonate derivatives of certain lanthanide-metal ions as NMR shift reagents for such compounds.[4] However, these shift reagents do not exhibit any appreciable interaction with non-heteroatom-substituted organic substrates.[5]

Our previous studies on CH_3CN-coordinated transition-metal cations revealed that by virtue of the presence of weakly coordinating acetonitrile ligands, these compounds are versatile homogeneous catalysts for a variety of transformations involving olefins and strained ring compounds.[6] As an extension of this study, we report the synthesis, characterization, and homogeneous catalytic chemistry of the corresponding CH_3CN-coordinated lanthanide-metal compound, $[Eu(CH_3CN)_3(BF_4)_3]_x$, **1**.

Results and Discussion

A. Synthesis and Characterization of $Eu(CH_3CN)_3(BF_4)_3$, 1. **1** was prepared in good yield by the oxidation of metallic Eu by $NOBF_4$ in CH_3CN (eq 1). Visible evolution of NO gas was noted

$$\mathrm{Eu} + 3\mathrm{NOBF_4} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{CH_3CN}} [\mathrm{Eu(CH_3CN)_3(BF_4)_3}]_x + 3\mathrm{NO} \qquad (1)$$

from the metal surface during the course of the reaction. The characteristic brown color of NO_2 was observed upon air oxidation of evolved NO. **1** was isolated as an orange, oxygen stable, but moisture sensitive solid. It was exceedingly soluble in polar organic solvents such as CH_3CN and CH_3NO_2 but practically insoluble in less polar solvents like $CHCl_3$ and C_6H_6 (THF was polymerized by **1**). The presence of bound CH_3CN molecules in **1** was indicated in the IR spectrum which exhibited $\bar{\nu}$(CN) at 2310 and 2280 cm^{-1}, typically shifted to higher wavenumbers due to coordination ($\bar{\nu}$(CN) for free CH_3CN = 2287 and 2251 cm^{-1}). In addition, there was a broad absorption corresponding to $\bar{\nu}(BF_4^-)$ at 1200–1000 cm^{-1}. The presence of coordinated CH_3CN molecules in **1** was further confirmed by the reaction of **1** with H_2O,

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(1) Alfred P. Sloan Research Fellow, 1984–1986.

(2) (a) Parshall, G. W. *Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley: New York, 1980. (b) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (c) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978.

(3) For recent reports, see: (a) Mauermann, H.; Swepston, P. N.; Marks, T. J. *Organometallics* **1985**, *4*, 200. (b) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (c) Evans, W. J.; Bloom, I.; Engerer, S. C. *J. Catal.* **1983**, *84*, 468. (d) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. In *Fundamentals of Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum: New York, 1979; Vol. 3, p 941. (e) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007. (f) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (g) Mazzei, A. *Makromol. Chem., Suppl.* **1981**, *4*, 61. (h) Zhiquan, S.; Jun, O.; Fusong, W.; Zhenya, H.; Fusheng, Y.; Baogong, Q. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3345. (i) Ballard, D. G. H.; Courtis, A.; Holton, J.; McMeeking, J.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1978**, 994. (j) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 480. (k) Forsberg, J. H.; Balasubramanian, T. M.; Spaziano, V. T. *J. Chem. Soc., Chem. Commun.* **1976**, 1060.

(4) (a) Horrocks, W. DeW. In *NMR of Paramagnetic Molecules*; LaMar, G. N., Horrocks, W. DeW., Holm, R. H., Eds.; Academic: New York, 1973; Chapter 12. (b) *Nuclear Magnetic Resonance Shift Reagents*, Sievers, R. E., Ed. Academic: New York, 1973.

(5) However, shift reagents that are effective for aromatics and olefins have been developed. These consist of solution mixtures of β-diketonate derivatives of lanthanide(III) and silver(I), the latter presumably binding to the organic molecules. For details, see: (a) Wenzel, T. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 382. (b) Wenzel, T. J.; Sievers, R. E. *Anal. Chem.* **1981**, *53*, 393. (c) Wenzel, T. J.; Bettes, T. C.; Sadlowski, J. E.; Sievers, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 5903.

(6) (a) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1984**, *23*, 3257. (b) Sen, A.; Lai, T.-W. *Organometallics* **1983**, *2*, 1059. (c) Sen, A.; Thomas, R. R. *Organometallics* **1982**, *1*, 1251. (d) Sen, A.; Lai, T.-W. In *Transition Metal Catalyzed Polymerizations*; Quirk, R. P., Ed.; Harwood Academic: New York, 1983; Part A, p 341. (e) Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415. (f) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627.

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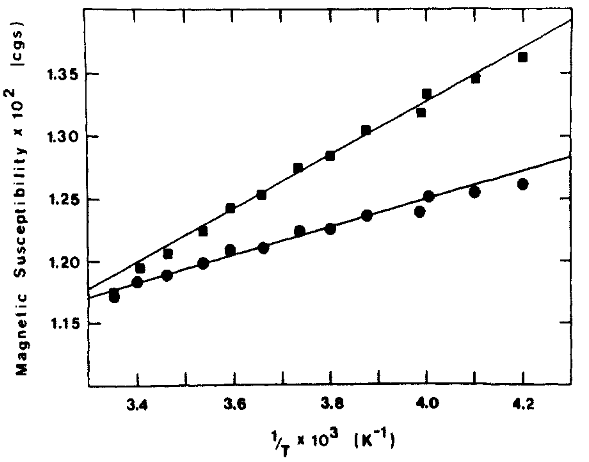

Figure 1. Curie law plot for $[Eu(CH_3CN)_3(BF_4)_3]_x$ in CD_3CN. Corrected for solvent contraction (●), uncorrected for solvent contraction (■).

which liberated ca. 2.2 mol of CH_3CN/mol of Eu(III). The magnetic susceptibility of **1** in CD_3CN was measured by the Evans NMR method.[7] As is evident from Figure 1, the molar magnetic susceptibility of **1** obeyed Curie law, at least over the limited temperature range studied. The effective magnetic moment, μ_{eff}, decreased from 5.29 μ_B at 298 K to 4.89 μ_B at 238 K. The electronic spectra of **1** were obtained by using the technique of time-resolved europium excitation spectroscopy (TREES).[8] The Eu(III) ion is rare in the fact that the ground ($^7F_0$) and the lowest emitting electronic states ($^5D_0$) both have $J = 0$. Therefore, only one $^7F_0 \rightarrow {}^5D_0$ transition is expected unless the symmetry of the ion is cubic or hexagonal when none is predicted.[9] The TREES spectrum for the $^7F_0 \rightarrow {}^5D_0$ transition in **1** in the solid state consisted of a single broad peak ($\nu_{1/2} = 1.35$ nm) centered at 578.3 nm. A long excited-state lifetime of $\tau = 2$ ms was measured. A broader peak ($\nu_{1/2} = 2.25$ nm) at the same position was observed when **1** was dissolved in CH_3CN. The long excited-state lifetime was expected since in contrast to the commonly observed aquo and amine complexes, no O–H or N–H oscillators were present on the Eu(III) to provide an efficient pathway for radiationless deexcitation.[8] The large width of the observed peak was presumably due to the presence of a number of energetically similar conformations and may be an indication of the weakness of the metal–ligand bonds in **1**.

An interesting problem involves the unusual formulation of **1**, which apparently contained only three CH_3CN ligands based on elemental analysis. This was unusual since the lanthanide elements generally have coordination numbers greater than 6 and at times as high as 12.[10] Anions of oxyacids such as ClO_4^- and NO_3^-, which normally exhibit little coordination ability, are known to bind to lanthanide-metal cations. Spectroscopic, conductivity, and X-ray crystallographic studies clearly demonstrate this type of cation/anion interaction both in solution and in the solid state.[11,16] However, to our knowledge, there are no prior studies concerning the possible interaction of BF_4^- with lanthanide-metal cations.

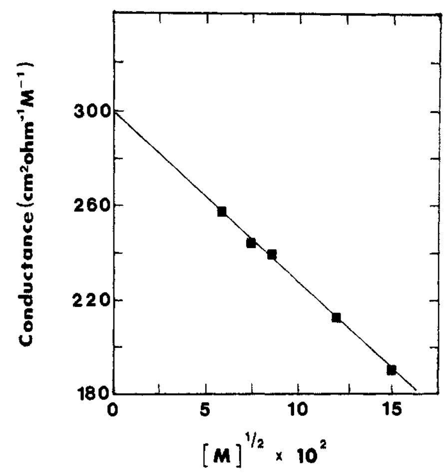

Figure 2. Conductivity plot for $[Eu(CH_3CN)_3(BF_4)_3]_x$ in CH_3CN.

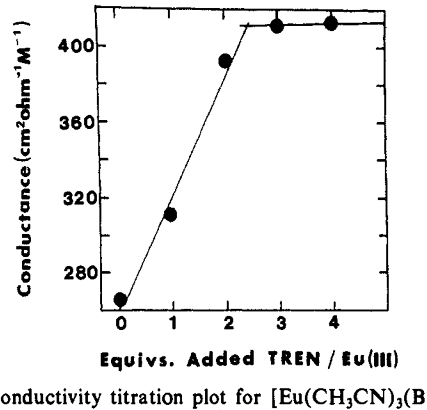

Figure 3. Conductivity titration plot for $[Eu(CH_3CN)_3(BF_4)_3]_x$ with added TREN. $[Eu(III)] = 8 \times 10^{-3}$ M.

Although BF_4^- is generally assumed to be noncoordinating, there are a few examples in transition-metal and actinide chemistry which involve the loose coordination of the BF_4^- anion to the metal.[12] In addition, in several instances the abstraction of a fluoride from BF_4^- has been demonstrated.[13] The above precedents, along with the relatively high Eu–F bond energy (ca. 126 kcal/mol),[14] have prompted us to look for possible interactions between Eu(III) and BF_4^- in complex **1**. Such interactions could well account for the apparent paucity of ligands around the Eu(III) center.

1 was found to exist as a dimer in CH_3CN, as revealed by a molecular weight measurement. This indicated the presence of bridging BF_4^- ions, perhaps in the structural mode Eu–F–BF_2–F–Eu. The presence of an analogous structural mode in a U(IV) compound has been recently reported.[12a] Extrapolated to infinite dilution, **1** in CH_3CN exhibited a conductivity of 298 cm² mol⁻¹ Ω⁻¹ (Figure 2), a value that fell within the observed range for 1:2 electrolytes.[15] For comparison, a similar conductivity experiment with $[Ni(CH_3CN)_6](BF_4)_2$ revealed a conductivity of 284 cm²

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(7) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(8) (a) Horrocks, W. DeW.; Sudnick, D. R. *Acc. Chem. Res.* **1981**, *14*, 384. (b) Horrocks, W. DeW.; Sudnick, D. R. *Science (Washington, D. C.)* **1979**, *206*, 1194. (c) For a review of lanthanide ion luminescence, see: Horrocks, W. DeW.; Albin, M. *Prog. Inorg. Chem.* **1984**, *31*, 1.

(9) Runciman, W. A. *Philos. Mag.* **1956**, *1*, 1075.

(10) (a) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. (b) Sinha, S. P. *Struct. Bonding (Berlin)* **1976**, *25*, 69.

(11) For recent reports, see: (a) Bunzli, J.-C. G.; Vuckovic, M. M. *Inorg. Chim. Acta* **1984**, *95*, 105. (b) Bunzli, J.-C. G.; Yersin, J.-R. *Inorg. Chim. Acta* **1984**, *94*, 301. (c) Bunzli, J.-C. G.; Vuckovic, M. M. *Inorg. Chim. Acta* **1983**, *73*, 53. (d) Bunzli, J.-C. G.; Klein, B.; Pradervand, G.-O.; Porcher, P. *Inorg. Chem.* **1983**, *22*, 3763. (e) Bunzli, J.-C. G.; Mabillard, C.; Yersin, J.-R. *Inorg. Chem.* **1982**, *21*, 4214. (f) Bunzli, J.-C. G.; Yersin, J.-R.; Mabillard, C. *Inorg. Chem.* **1982**, *21*, 1471. (g) Bunzli, J.-C. G.; Yersin, J.-R. *Inorg. Chem.* **1979**, *18*, 605. (h) Bunzli, J.-C. G. *Coord. Chem. Rev.* **1984**, *60*, 191 and references therein. (i) Ciampolini, M.; Mealli, C.; Nardi, N. *J. Chem. Soc., Dalton Trans.* **1980**, *376*. (j) Thomas, J. F.; Palenik, R. C.; Palenik, G. J. *Inorg. Chim. Acta* **1979**, *37*, L459. (k) Harman, M. E.; Hart, F. A.; Hursthouse, M. B.; Moss, G. P.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1976**, 396.

(12) (a) Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1082. (b) Nakai, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1637. (c) Raab, K.; Olgemoller, B.; Schloter, K.; Beck, W. *J. Organomet. Chem.* **1981**, *214*, 81. (d) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186. (e) Beck, W.; Schloter, K. *Z. Naturforsch., B* **1978**, *33B*, 1214. (f) Richter, K.; Fischer, E. O.; Kreiter, C. G. *J. Organomet. Chem.* **1976**, *122*, 187. (g) Gaughan, A. P.; Dori, Z.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1657. (h) Tomlinson, A. A. G.; Bonamico, M.; Dessy, G.; Fares, V.; Scaramuzza, L. *J. Chem. Soc., Dalton Trans.* **1972**, 1671.

(13) For example, (a) ref 12a. (b) Holt, E. M.; Hlatky, G. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 7302.

(14) *CRC Handbook of Chemistry and Physics*, 61st ed.; Weast, R. C., Ed. CRC Press: Boca Raton, FL, 1980; p F-222.

(15) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(16) Forsberg, J. H.; Kubik, T. M.; Moeller, T.; Gucwa, K. *Inorg. Chem.* **1971**, *10*, 2650.

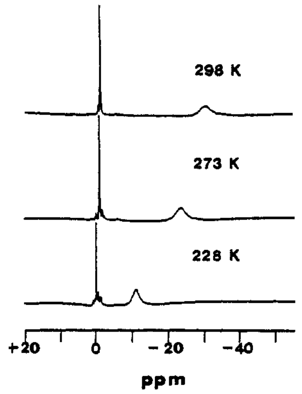

Figure 4. Variable-temperature ^{19}F NMR spectra of $[Eu(CH_3CN)_3(BF_4)_3]_x$ in CD_3CN. [Eu(III)] = 6.4×10^{-2} M.

mol^{-1} Ω^{-1} at infinite dilution. Conductivity measurements on trivalent lanthanide-metal compounds containing oxyacid anions generally reveal low conductivity values, and in particular, $Ln(NO_3)_3$ behaves as a nonelectrolyte in CH_3CN.[16] Since it has been shown that there is substantial cation–anion interactions in these latter complexes, a similar type of interaction may be involved for **1** (eq 2).

$$[Eu(CH_3CN)_3(BF_4)_3]_2 \xrightarrow{CH_3CN} [Eu(CH_3CN)_n(BF_4)_2]_2 + 2BF_4^- \quad (2)$$

If the BF_4^- anions were bound to Eu(III), then they could be displaced by other ligands. Accordingly, we measured the conductivity of **1** in CH_3CN in the presence of added amounts of two neutral donor ligands: triethylenetetramine (TREN) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The conductivities at infinite dilution for solutions of **1** containing 4 equiv of TREN and TMEDA were 524 and 496 cm^2 mol^{-1} Ω^{-1}, respectively. It is not clear what these high values correspond to;[15] however, if one assumed that **1** was no longer a dimer in the presence of excess TREN and TMEDA, then the conductivities at infinite dilution were 261 and 254 cm^2 mol^{-1} Ω^{-1}, respectively. These values were now in the range expected for 1:2 electrolytes[15] and indicated the displacement of a second coordinated BF_4^- anion on each Eu(III) ion by the incoming amine. Conductivity titrations of **1** in CH_3CN with TREN (Figure 3) and TMEDA indicated that after initial increases in conductivity, limiting values were reached which corresponded to the additions of 2.2 and 2.6 equiv of TREN and TMEDA per Eu(III) ion, respectively. The significance of these numbers remains unclear. We note here that no cation–anion interactions have been observed for $[Ln(TREN)_2](NO_3)_3$[16] (Ln = Sm through Yb) and $[Ln(TREN)_2](ClO_4)_3$[17] in the solid state. In CH_3CN, the two series of complexes behave as 1:1 and 1:3 electrolytes, respectively.

The ability of certain lanthanide-metal complexes to function as NMR shift reagents resides in the fact that due to the interaction of the substrate with the paramagnetic metal center, there is a shift in the resonance frequencies of the various nuclei in the former.[4] This isotropic shift is markedly dependent on the distance between the observed nucleus and the paramagnetic center. Since the BF_4^- anions of **1** contain two NMR-active nuclei, the ^{11}B and ^{19}F NMR spectral properties of this compound were examined.

The ^{11}B NMR spectrum of **1** at 25 °C, as a 6.35×10^{-2} M (in Eu(III)) solution in CH_3CN, was characterized by a sharp resonance at 4.7 ppm (vs. ethereal BF_3) and a broad resonance at 12.0 ppm. A very similar pattern was observed in the ^{19}F NMR spectrum taken under the same conditions, and it consisted of a sharp resonance at 0 ppm (vs. ethereal HBF_4) and a broad resonance at −26.47 ppm. As the solution was made more dilute in **1**, the broad resonance moved to a lower magnetic field, while the sharp resonance (presumably due to uncomplexed BF_4^- anion) was unaffected. Clearly, these observations indicated that two magnetically inequivalent ^{11}B and ^{19}F nuclei were present in CH_3CN solutions of **1**.

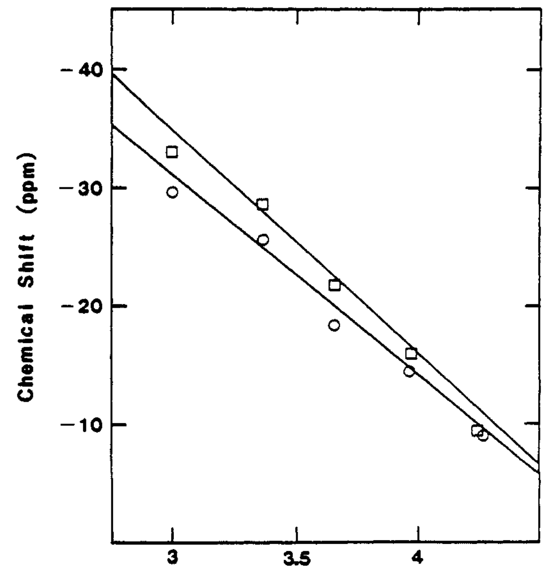

Figure 5. ^{19}F NMR chemical shift plot for the broad resonance of $[Eu(CH_3CN)_3(BF_4)_3]_x$ in CD_3CN. [Eu(III)] = 6.4×10^{-2} M (○), 12.7×10^{-2} M (□).

The theory of paramagnetic NMR spectra predicts a linear relationship between an isotropic shift and the reciprocal of absolute temperature.[4a] Figure 4 shows typical ^{19}F NMR spectra obtained for CH_3CN solutions of **1** as the temperature was lowered. The broad resonance moved progressively to lower magnetic fields as the solution temperature was decreased. The linear nature of the plot of the isotropic shift of this resonance vs. $1/T$ (Figure 5) clearly indicated the interaction of the fluorine atoms with the paramagnetic Eu^{3+} center. In an analogous observation, when the solution temperature was lowered, the broad resonance in the ^{11}B NMR spectrum of **1** moved to higher magnetic field while the sharp resonance was unaffected. However, the shift of the broad resonance was much smaller in magnitude in comparison with that observed in the ^{19}F NMR spectra. This seems reasonable since the boron nucleus was further away from the paramagnetic center and hence the isotropic shift was expected to be significantly smaller in magnitude.

Nitrate anions are known to bind lanthanide-metal cations. Hence, we have examined the possible competition between the NO_3^- and BF_4^- anions for the Eu^{3+} centers in **1**. The broad resonance present in the ^{19}F NMR spectra of **1** was found to move progressively to lower magnetic fields upon the addition of $NMe_4^+NO_3^-$. Plots of added NO_3^- ion vs. chemical shift of the broad resonance indicated that ca. 2 equiv of added NO_3^- ions per Eu(III) ion were required to remove all of the BF_4^- ions from an isotropic chemical shift, Figure 6. This was consistent with the results of the conductivity measurements which showed **1**, in CH_3CN, to be a 1:2 electrolyte or that two of the BF_4^- ions per Eu(III) ion were involved in ion pairing. The experiment also indicated that the NO_3^- anion had a much greater affinity for Eu^{3+} than did the BF_4^- anion.

There is precedent for the abstraction of fluoride from the BF_4^- anion,[13] and such a possibility existed in the present case since **1** was an effective Lewis acid as was evident from its catalysis of a variety of organic transformations (vide infra). The abstraction of fluoride from BF_4^- by **1** would produce BF_3 (eq 3). This appeared to be unlikely since the addition of BF_3 to a suspension of EuF_3 in CH_3CN did not result in the formation of **1**.

$$[Eu(CH_3CN)_3(BF_4)_3]_2 \xrightarrow{CH_3CN} [Eu(CH_3CN)_n(F)(BF_4)_2]_2 + 2BF_3 \quad (3)$$

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[17] (a) Johnson, M. F.; Forsberg, J. H. *Inorg. Chem.* **1976**, *15*, 734. (b) For the crystal structure of the related compound, $[Nd(TREN)_2(CH_3CN)](ClO_4)_3$, see: Eigenbrot, C. W.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2867.

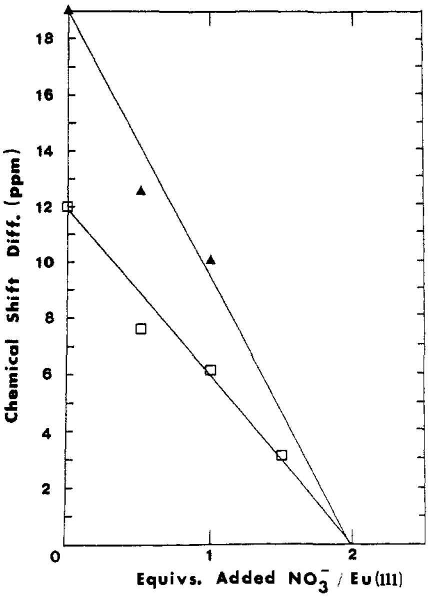
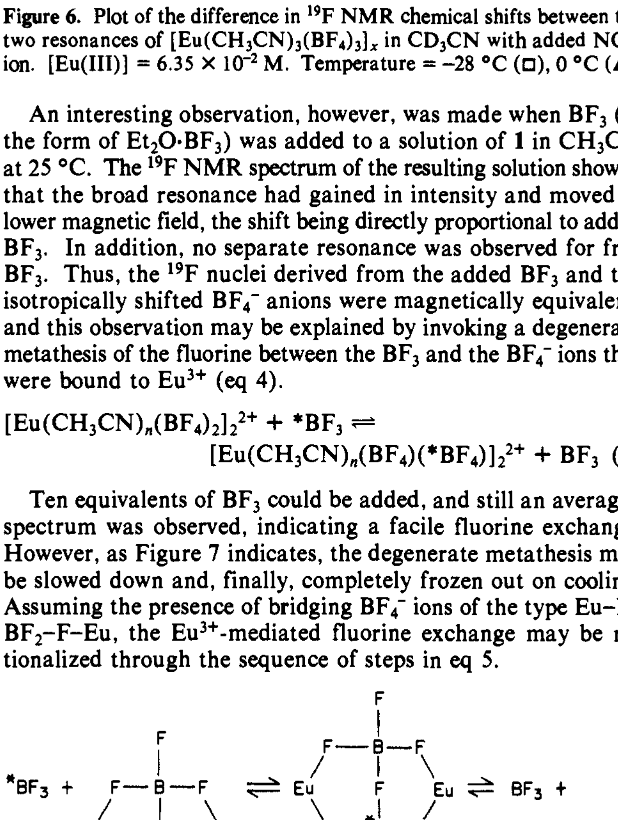


Figure 6. Plot of the difference in ^{19}F NMR chemical shifts between the two resonances of $[Eu(CH_3CN)_3(BF_4)_3]_x$ in CD_3CN with added NO_3^- ion. [Eu(III)] = 6.35 × 10^{-2} M. Temperature = −28 °C (□), 0 °C (▲).

An interesting observation, however, was made when BF_3 (in the form of $Et_2O{\cdot}BF_3$) was added to a solution of **1** in CH_3CN at 25 °C. The ^{19}F NMR spectrum of the resulting solution showed that the broad resonance had gained in intensity and moved to lower magnetic field, the shift being directly proportional to added BF_3. In addition, no separate resonance was observed for free BF_3. Thus, the ^{19}F nuclei derived from the added BF_3 and the isotropically shifted BF_4^- anions were magnetically equivalent, and this observation may be explained by invoking a degenerate metathesis of the fluorine between the BF_3 and the BF_4^- ions that were bound to Eu^{3+} (eq 4).

$$[Eu(CH_3CN)_n(BF_4)_2]_2^{2+} + {}^*BF_3 \rightleftharpoons [Eu(CH_3CN)_n(BF_4)({}^*BF_4)]_2^{2+} + BF_3 \quad (4)$$

Ten equivalents of BF_3 could be added, and still an averaged spectrum was observed, indicating a facile fluorine exchange. However, as Figure 7 indicates, the degenerate metathesis may be slowed down and, finally, completely frozen out on cooling. Assuming the presence of bridging BF_4^- ions of the type Eu–F–BF_2–F–Eu, the Eu^{3+}-mediated fluorine exchange may be rationalized through the sequence of steps in eq 5.



(5)

The Eu^{3+}-mediated metathesis of fluorine between BF_3 and BF_4^- anions has an analogy in organic chemistry. The Finkelstein reaction[18] involves halide exchange between an inorganic halide and an organic halide and is promoted by Lewis acids such as $FeCl_3$ and $ZnCl_2$. An interesting and related reaction was reported by San Filippo et al.[19] who observed that certain lanthanide-metal β-diketonate derivatives were able to induce substantial shifts in the ^1H and ^{19}F NMR spectra of simple alkyl fluorides. Furthermore, they reported that *tert*-butyl fluoride was rapidly polymerized by $Yb(fod)_3$.[20] A plausible mechanism for this reaction is shown in eq 6.

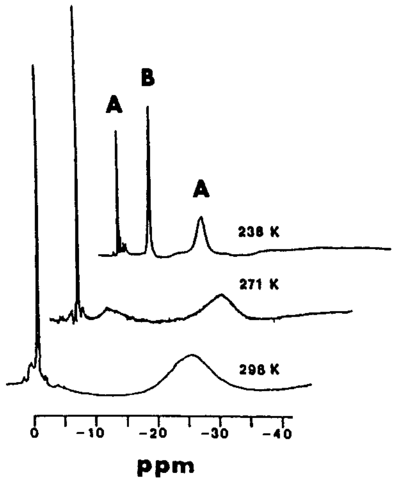


Figure 7. Variable-temperature ^{19}F NMR spectra of $[Eu(CH_3CN)_3(BF_4)_3]_x$ in CD_3CN with added BF_3. [Eu(III)] = 8.8 × 10^{-2} M, [BF_3] = 26.4 × 10^{-2} M. $Eu(CH_3CN)_3(BF_4)_3$, A; BF_3, B.

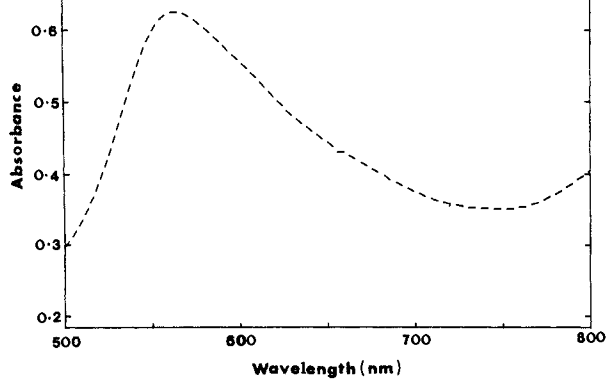
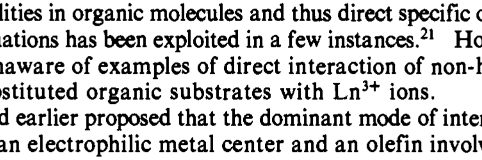


Figure 8. Spectrum obtained after 1 equiv of TAE was added to 5.1 × 10^{-3} M (in Eu(III)) solution of $[Eu(CH_3CN)_3(BF_4)_3]_x$ in CH_3NO_2.



(6)

B. Catalytic Chemistry of $[Eu(CH_3CN)_3(BF_4)_3]_x$, 1. As the experimental results described in the preceding section clearly demonstrated, the Eu^{3+} center in **1** was a strong Lewis acid. Indeed, the ability of Ln^{3+} ions to coordinate to the heteroatom functionalities in organic molecules and thus direct specific organic transformations has been exploited in a few instances.[21] However, we are unaware of examples of direct interaction of non-heteroatom-substituted organic substrates with Ln^{3+} ions.

We had earlier proposed that the dominant mode of interaction between an electrophilic metal center and an olefin involves the transfer of a significant amount of charge density from the olefin to the metal, concomitant with formation of an incipient carbo-

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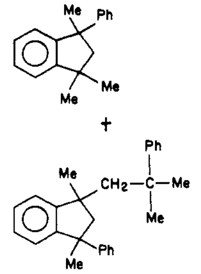
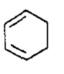
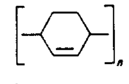
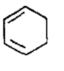
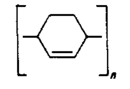
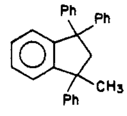
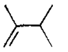
(18) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; p 381.

(19) San Filippo, J.; Nuzzo, R. G.; Romano, L. J. *J. Am. Chem. Soc.* **1975**, *97*, 2546.

(20) San Filippo, J.; Nuzzo, R. G.; Romano, L. J. *J. Org. Chem.* **1976**, *41*, 392.

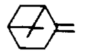
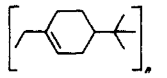
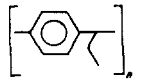
(21) (a) Bednarski, M.; Danishefski, S. *J. Am. Chem. Soc.* **1983**, *105*, 6968, 3716. (b) For a review of previous literature, see: Natale, N. R. *Org. Prep. Proced. Int.* **1983**, *15*, 387.

Table I. Catalytic Oligomerization, Polymerization, and Isomerization of Olefins Using $[Eu(CH_3CN)_3(BF_4)_3]_x$

olefin	olefin/Eu(III)	solvent	temp, °C	time	product	yield	M_w
$PhCH{=}CH_2$	100	CH_3NO_2	25	5 min	$(—PhCH—CH_2—)_n$	92	1 884
$PhCH{=}CH_2$	100	CH_3CN	25	1 day	$(—PhCH—CH_2—)_n$	32	13 000
$PhC(CH_3){=}CH_2$	100	CH_3NO_2	25	5 min		83	
$PhC(CH_3){=}CH_2$	70	CH_3NO_2	−23	4 h	$(—PhC(CH_3)—CH_2—)_n$	90	56 000
	70	CH_3NO_2	25	5 min		92	1 000
	70	CH_3NO_2	−23	4 h		89	34 000
$Ph_2C{=}CH_2$	3	CH_3NO_2	25	5 min		100	
	7	CH_3NO_2	25	15 min		88[a]	

[a] Thermodynamic equilibrium ratio ~12:88.

Table II. Catalytic Ring-Opening Reactions Using $[Eu(CH_3CN)_3(BF_4)_3]_x$[a]

substrate	substrate/ Eu(III)	product	yield	M_w
	7		100	
	100		95	1016
	70		95	590

[a] All reactions were performed at 25 °C in CH_3NO_2 as solvent.

cationic center at the olefin.[6] Such a transfer of charge should be particularly facile for olefins possessing strong electron-releasing substituents. An olefin that meets this requirement is tetra-*p*-anisylethylene (TAE) which has a low ionization potential of 6 eV[22] and which is known to form charge-transfer complexes with main-group electrophiles.[23] The addition of TAE to a solution of **1** in CH_3NO_2 caused an immediate development of intense blue color. The visible spectrum revealed an absorption maximum at 564 nm (Figure 8). We attempted to ascertain the stoichiometry of this reaction by carrying out a spectral titration while monitoring the absorbance at 564 nm. However, this was unsuccessful because successive additions of TAE to **1** caused a monotonic increase in absorbance without any leveling off, indicating the existence of an equilibrium. A similar blue solution with λ_{max} = 564 nm was formed when Br_2 was added to TAE, a reaction that is known to generate a TAE-Br_2 charge-transfer complex[22] and that eventually leads to the formation of TAE^{2+} cation.[24] Thus it is clear that there is a significant degree of charge transfer from the olefin to the metal when TAE interacted with **1**, and this represented the first clear example of the interaction of a lanthanide-metal center with an olefin. We also note here that no charge-transfer complex was formed when a similar reaction was carried out between TAE and BF_3.

Consistent with the formation of an olefin to metal charge-transfer complex when **1** reacted with TAE, **1** was found to cause the electrophilic activation of olefins and strained ring compounds. These reactions will be discussed subsequently; however, it is useful, at this point, to note the strong correlation between the formation of a complex with TAE and the ability of the metal to cause electrophilic activation of olefins. **1** did not form a complex with TAE when CH_3CN was used in place of CH_3NO_2 as the solvent. This was not surprising in view of the greater coordinating ability of CH_3CN since the complex formation would require the close approach of TAE to the Eu^{3+} center in **1**. Consistent with this, we observed that the reactivity of **1** vis-à-vis olefins was significantly attenuated in CH_3CN when compared to CH_3NO_2 as the solvent. For example, the polymerization of styrene by **1** was significantly faster in CH_3NO_2. In a similar vein, $[W(NO)_2(CH_3CN)_4](BF_4)_2$[6c] catalyzed the polymerization of styrene and the isomerization of 2,3-dimethyl-1-butene to the corresponding 2-butene in CH_3NO_2; however, in CH_3CN, the former reaction did not occur, and the isomerization reaction was significantly slowed down. Of note was the fact that this tungsten compound formed a TAE complex in CH_3NO_2 but not in CH_3CN. On the other hand, $[Pd(CH_3CN)_4](BF_4)_2$[6a,d-f] was an effective catalyst for the above polymerization and isomerization reactions in CH_3CN and also formed a TAE complex in this solvent. Clearly, therefore, for a given metal electrophile, the formation of a charge-transfer complex with TAE was a good qualitative measure of the strength of its interaction with olefins.

We have examined the catalytic chemistry of **1** vis-à-vis a number of olefins and strained-ring compounds, and our results are summarized in Tables I and II.

We had earlier demonstrated[6a] that the mechanism of C=C bond isomerization in olefins, catalyzed by electrophilic transition metals, involved an electrophilic cleavage of an allylic C—H bond rather than an oxidative addition of this C—H bond to the metal as is usually observed for electron-rich transition metals. The former mechanism must also operate for the catalytic isomerization

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[22] Buckles, R. E.; Womer, D. E. *J. Am. Chem. Soc.* **1958**, *80*, 5055.

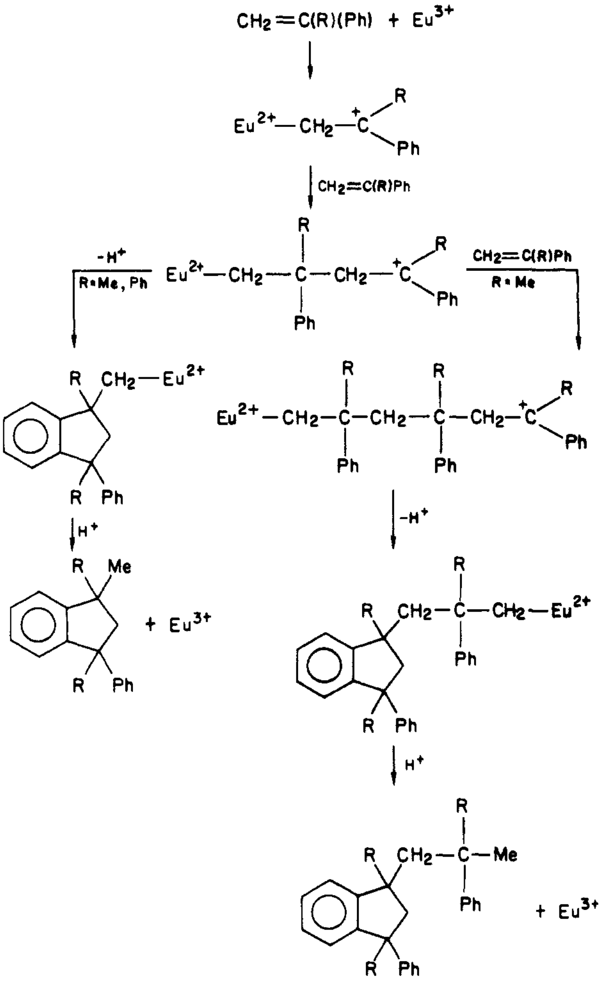
[23] Buckles, R. E.; Erickson, R. E.; Snyder, J. D.; Person, W. E. *J. Am. Chem. Soc.* **1960**, *82*, 2444.

[24] (a) Olah, G. A.; Grant, J. L.; Spear, R. J.; Bollinger, J. M.; Seriantz, A.; Sipos, G. *J. Am. Chem. Soc.* **1976**, *98*, 2501. (b) Baenziger, N. C.; Buckles, R. E.; Simpson, T. D. *J. Am. Chem. Soc.* **1967**, *89*, 3405.

of 2,3-dimethyl-1-butene by **1**, since the latter mechanism would have to involve an Eu(V) species, an oxidation state that is unknown for the lanthanide metals.

The catalytic polymerization of styrene illustrated the remarkable effect of changing solvents. Lower yield of polystyrene possessing a significantly higher molecular weight was obtained on substituting CH_3CN for CH_3NO_2 as the reaction solvent. We had earlier demonstrated[6c] that the CH_3CN ligands in $[M(NO)_2(CH_3CN)_4](BF_4)_2$, (M = W, Mo) exchanged with the solvent CH_3CN molecules but not with the solvent CH_3NO_2 molecules, clearly indicating that CH_3CN was superior to CH_3NO_2 as a ligand for these systems. Therefore, the rate of initiation of styrene polymerization would be expected to be slower in CH_3CN. Also, since fewer initiations occurred in CH_3CN, the monomer/initiator ratio was higher in this solvent leading to the formation of higher molecular weight polystyrene.

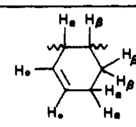
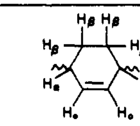
A characteristic feature of cationic polymerizations is that the molecular weight of the polymer obtained tends to increase with lower reaction temperatures.[25] This was observed for the polymerization of α-methylstyrene and 1,3-cyclohexadiene by **1** and was consistent with a carbocationic mechanism. The formation of head-to-tail cyclic dimer and trimer from α-methylstyrene at 25 °C may be rationalized by eq 7. The head-to-tail arrangement was a result of the greater stabilization of the carbocation when located on the α-carbon.



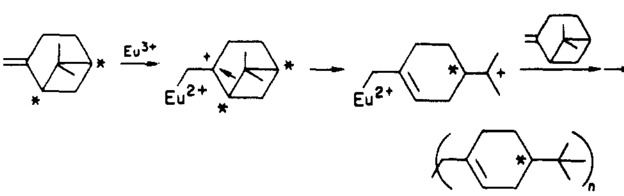
(7)

The structure of the poly(1,3-cyclohexadiene) obtained at 25 °C was examined by NMR spectroscopy. The ^1H NMR spectrum exhibited three broad resonances at 5.9 (H_0), 2.0 (H_α), and 1.6 ppm (H_β), the first two representing, respectively, the vinylic and allylic protons present in the polymer. Two types of polymer (1,2 and 1,4) may arise through the cationic polymerization of 1,3-cyclohexadiene.[26] The expected ^1H NMR data for these are given in Table III.[26b] The ratio H_α/H_β that we had obtained was 0.5, thus indicating that it was predominantly 1,4-poly(1,3-cyclohexadiene). The ratio $H_0/(H_\alpha + H_\beta)$ is a measure of the degree of branching or cross-linking in the polymer ($H_0/(H_\alpha + H_\beta)$ = 0.33 for unbranched polymer and 0 for completely cross-linked polymer). In the present case a value of 0.3 was obtained indicating the presence of at best a very modest degree of cross-linking.

Table III. Expected ^1H NMR Data for Poly(1,3-cyclohexadiene)

		
$H_0/(H_\alpha + H_\beta)$	1/3	1/3
H_α/H_β	1/1	1/2

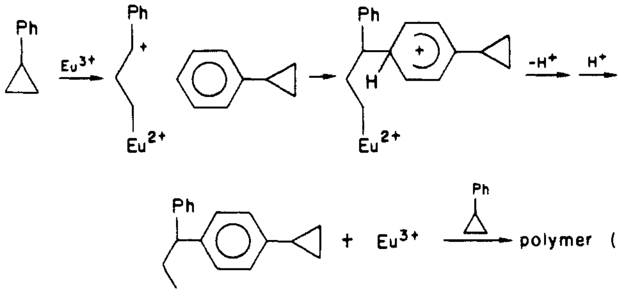
The catalytic polymerization of 2(10)-pinene by **1** was an example of carbocation-induced rearrangement[27] (eq 8). C-1 and C-5 constitute the chiral centers in the pinene. While the chirality



(8)

was lost at C-1 during polymerization, the mechanism as outlined in eq 8 predicts complete retention at C-5 and, indeed, the polymer was optically active. While 2(10)-pinene has been polymerized before,[28] to our knowledge there are no previous reports of optical activity of the resultant polymer.

The remarkable ring-opening polymerization of cyclopropylbenzene was evidently initiated by a heterolytic C–C bond cleavage of the cyclopropane ring followed by the alkylation of the phenyl group of a second monomer by the resultant carbocation, the whole process then being repeated (eq 9).



(9)

The NMR spectra of the polymer were in accord with the postulated structure. The ^{13}C NMR spectra were particularly informative: the pendant $-CHCH_2CH_3$ group was clearly evident from the ^1H-coupled spectrum which exhibited a doublet for the methine carbon, a 1:2:1 triplet for the methylene carbon, and a 1:3:3:1 quartet for the methyl group. Although the mechanism, as outlined in eq 9, indicates a para-substitution pattern for the phenyl groups, both ortho and para substitutions were to be expected and were observed. This was reflected not only in the number of ^{13}C NMR resonances for the ipso carbon of the phenyl groups but also in the two closely spaced peaks for the methine (52.91 and 52.53 ppm) and the methylene (28.87 and 28.71 ppm) carbons. As expected the spacing decreased with increasing distance from the phenyl group with only one peak being observed for the methyl group.

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(25) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1981; Chapter 4.

(26) (a) Kennedy, J. P. *Cationic Polymerization of Olefins: A Critical Inventory*; Wiley-Interscience: New York, 1975; p 192. (b) Imanishi, Y.; Matsuzaki, K.; Yamane, T.; Kohjiya, S.; Okamura, S. *Macromol. Sci., Chem.* **1969**, *A3*, 249.

(27) 2(10)-Pinene does not undergo anionic or free-radical-initiated polymerization; see: Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley: New York, 1982; Chapter 1.

(28) Reference 26a, p 215.

Conclusion

We have synthesized a novel Eu(III) complex which, by virtue of the presence of only weakly coordinating CH_3CN ligands, readily interacted with substrates that have low natural affinities toward Ln(III)-metal centers. Thus, using this complex, we have demonstrated (a) the interaction of the BF_4^- anion with a Ln^{3+} ion, (b) the direct interaction of an olefin with a Ln(III) center, an interaction that has been implicated but not previously observed in reactions involving olefins that are catalyzed by Ln(III) compounds,[3a-j] and (c) several catalytic transformations of non-heteroatom-substituted organic substrates. In addition, because of the presence of the labile CH_3CN ligands, this complex should serve as a useful precursor to other Eu(III) compounds. Such a possibility is currently under study.

Experimental Section

Analytical Instrumentation. IR spectra were recorded on a Perkin-Elmer Model 580 spectrometer. ^1H NMR spectra were recorded on either a Varian EM360 spectrometer or on Bruker WM360 and WP200 FT-NMR spectrometers. ^{13}C NMR spectra were recorded on Bruker WM360 and WP200 FT-NMR spectrometers. ^{19}F NMR spectra were recorded on a JEOL PS-100 spectrometer. ^{11}B NMR spectra were recorded at the University of California at Los Angeles at 126.6 MHz. UV–Vis spectra were recorded on a Hewlett-Packard Model 8450A spectrometer. TREES data were obtained by using a procedure described elsewhere.[8a] Gas chromatography was performed on a Varian 3700 gas chromatograph equipped with a flame ionization detector. GC/MS data were obtained on a Finnigan 3200 computerized GC/MS equipment. The molecular weights of polymers were obtained by either osmometry (performed by Schwartzkopf Microanalytical Laboratory, New York) or gel permeation chromatography using a Waters Associates equipment with a refractive index detector. μ-Styragel columns were used and polystyrene standards were used to calibrate the instrument. Specific rotation of polypinene was measured on a Perkin-Elmer 241MC polarimeter. Conductivity data were obtained on a Sybron/Barnstead PM-70CB conductivity bridge with a Yellow Springs Instrument Co. 3403 cell. Elemental analyses were performed by Dornis u. Kolbe Mikroanalytisches Lab., Mulheim, Germany.

General Procedure. Reagent-grade chemicals were used. CH_2Cl_2 and CH_3CN were dried by distillation from CaH_2. CH_3NO_2 was dried by fractional distillation from anhydrous $CaCl_2$ followed by storage over 4-Å molecular sieves. C_6H_6 and Et_2O were dried by distilling from CaH_2 followed by storage over sodium benzophenone. All solvents and liquid chemicals were deoxygenated by either vacuum distillation or by purging with N_2 prior to use. All reactions and physical measurements were carried out either under vacuum or in a N_2 atmosphere. All metal compounds were stored in a N_2-filled drybox.

$[Pd(CH_3CN)_4](BF_4)_2$,[6a] $[W(NO)_2(CH_3CN)_4](BF_4)_2$,[6c] and $[Ni(CH_3CN)_6](BF_4)_2$[29] were prepared by literature methods.

Preparation of $[Eu(CH_3CN)_3(BF_4)_3]_x$, 1. Eu chips (0.30 g, 1.97 mmol) and $NOBF_4$ (0.68 g, 5.82 mmol) were stirred in 50 mL of CH_3CN under vacuum. The NO generated in the course of the reaction was removed periodically. After stirring for 1 day, the mixture was filtered to yield an orange filtrate. This was concentrated under vacuum to a viscous solution (5 mL). Benzene (30 mL) was added and the solution stirred vigorously. The solvent was then removed and the solid dried under vacuum (25 °C, 10^{-3} torr) to yield 0.67 g (63%) of orange crystalline material. IR (Nujol): $\bar{\nu}$(CN) 2310, 2280 cm^{-1}, $\bar{\nu}(BF_4^-)$ 1200–1000 cm^{-1}. Anal. Calcd for $C_6H_9N_3B_3F_{12}Eu$: C, 13.5; H, 1.7; N, 7.8; B, 6.1; Eu, 28.4. Found: C, 13.4; H, 1.7; N, 7.7; B, 6.3; Eu, 28.9. Molecular Weight (in CH_3CN) Calcd for Dimer of **1**: 1071. Found:[31] 1078.

Hydrolytic Decomposition of 1. **1** (0.053 g, 0.099 mmol in Eu(III)) was added to 1.0 mL of D_2O. After the solution stirred for 5 min, 0.005 mL of CH_3OH was added as an internal standard. The ^1H NMR of the solution exhibited resonances due to uncomplexed CH_3CN (2.08 ppm) and the methyl protons of methanol (3.36 ppm). An integration revealed that 2.2 equiv of CH_3CN/1 equiv of Eu(III) was formed.

Magnetic Susceptibility Measurements of 1. A solution was prepared by dissolving 0.1 mL of CH_2Cl_2 in 4.0 mL of CD_3CN. A 0.05-mL portion of this solution was sealed into a glass capillary. Another solution was prepared by dissolving 0.030 g of **1** (0.056 mmol in Eu(III)) in 2.0 mL of the CH_2Cl_2–CD_3CN mixture. This solution was placed in an NMR tube along with the solution sealed in the glass capillary. The NMR tube was then sealed, and the ^1H NMR spectra were recorded every 5 deg from 298 to 238 K. The magnetic susceptibility was then calculated from the data by the Evans procedure.[7]

Reactions with Tetra-*p*-anisylethylene (TAE).[22] These were typically carried out by adding a 0.25 M solution of TAE in CH_2Cl_2 to ca. 10^{-3} M solution of the appropriate metal compound in CH_3NO_2 or CH_3CN. The reaction of the TAE with Br_2 was performed analogously.

Catalytic Isomerization of 2,3-Dimethyl-1-butene. 2,3-Dimethyl-1-butene (0.079 mL, 0.054 g, 0.64 mmol) was added to a solution of 0.050 g of **1** (0.093 mmol in Eu(III)) in 0.50 mL of CD_3NO_2. The solution was allowed to stir at 25 °C for 15 min following which the organic layer was removed by vacuum distillation. The ^1H NMR spectrum of this solution showed a resonance at 1.62 ppm due to 2,3-dimethyl-2-butene. The product composition was verified by gas chromatography (Porapak N column) by coinjection with authentic samples. Similar procedures were used with other metal compounds.

Catalytic Polymerization of Styrene. Styrene (1.18 mL, 1.07 g, 10 mmol) was added slowly to a stirred solution of 0.055 g of **1** (0.10 mmol in Eu(III)) in 2.0 mL of CH_3NO_2 with the immediate precipitation of the polymer. The product was dissolved in a minimum amount of $CHCl_3$ and chromatographed through a silica gel column. Evaporation of the solvent under vacuum gave 0.98 g (92%) of pure white polymer of molecular weight 1900. When CH_3NO_2 was replaced by CH_3CN as the solvent, no immediate reaction with styrene was noted and the solution was allowed to stir for 1 day before any change in solution viscosity was observed. Workup similar to that described above gave 0.33 g (32%) of polymer with molecular weight 13 000. Similar experimental procedures were used when other metal compounds were used as initiators.

Catalytic Oligomerization of α-Methylstyrene at 25 °C. α-Methylstyrene (1.25 mL, 1.13 g, 9.59 mmol) was added dropwise to a stirred solution of 0.055 g of **1** (0.10 mmol in Eu(III)) in 1.0 mL of CH_3NO_2. An immediate increase in solution viscosity was observed. The reaction mixture was diluted with 30 mL of $CHCl_3$ and chromatographed through a silica gel column. Removal of the solvent in vacuum yielded 0.94 g (83%) of a viscous oil. Flash chromatography using hexane as the solvent was effective in separating the two components. The dimer and the trimer were formed in the ratio of 5:1. For dimer. ^1H NMR ($CDCl_3$): 7.4–7.0 (9 H, Ph), 2.45, 2.18 (2 H, ABq, J = 12.8 Hz, CH_2), 1.69, 1.32, 1.03 ppm (9 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 150.9–148.7, 127.9–122.5, 59.4, 50.8, 42.8, 30.8, 30.4 ppm. Mass spectrum, m/e: 236 (M^+), 221 ($M^+ - 15$). For trimer. ^1H NMR ($CDCl_3$): 7.4–7.0 (14 H, Ph), 2.59, 1.92 (2 H, ABq, J = 13.4 Hz, CH_2), 2.16, 1.70 (2 H, ABq, J = 14.6 Hz, CH_2), 1.61, 1.28, 1.14, 0.95 ppm (12 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 153.7–148.3, 127.9–122.9, 57.4, 54.9, 51.2, 47.6, 38.6, 33.4, 30.8, 29.2, 28.6 ppm. Mass spectrum m/e: 339 ($M^+ - 15$).

Catalytic Polymerization of α-Methylstyrene at −23 °C. **1** (0.05 g, 0.093 mmol in Eu(III)) was dissolved in 1.0 mL of CH_3NO_2 and the solution cooled to −23 °C. α-Methylstyrene (0.83 mL, 0.76 g, 6.39 mmol) was then added to the above solution with stirring. The reaction mixture was then maintained at −23 °C until it had nearly solidified (4 h). The polymer was then dissolved in a minimum volume of $CHCl_3$ and purified by silica gel chromatography. Evaporation of the solvent under vacuum left 0.68 g (90%) of pure poly(α-methylstyrene) having an average molecular weight of 56 000.

Catalytic Polymerization of 1,3-Cyclohexadiene. The polymerization at 25 °C and at −23 °C, using **1** as a catalyst, was carried in a manner analogous to that described for the polymerization of α-methylstyrene.

Dimerization of 1,1-Diphenylethylene. A catalyst solution was prepared by dissolving 0.071 g of **1** (0.13 mmol in Eu(III)) in 1.0 mL of CD_3NO_2. To this was added 0.08 mL (0.82 g, 0.45 mmol) of 1,1-diphenylethylene with stirring. A precipitate began forming immediately, and the solvent was removed under vacuum after 5 min. The organic product was extracted with $CDCl_3$ and a ^1H NMR spectrum of the solution showed essentially complete conversion to the indan derivative which was isolated by the evaporation of the solvent. ^1H NMR ($CDCl_3$): 7.4–7.0 (19 H, Ph), 3.45, 3.10 (2 H, ABq, J = 12 Hz, CH_2), 1.6 ppm (3 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 150.5–147.5, 128.8–125.0, 61.4, 60.9, 51.2, 28.9, ppm. Mass spectrum, m/e: 360 (M^+), 283 ($M^+ - 77$).

Catalytic Isomerization of Quadricyclane. Quadricyclane (0.065 mL, 0.06 g, 0.65 mmol) was slowly added to a solution of 0.05 g of **1** (0.093 mmol in Eu(III)) in 0.5 mL of CD_3NO_2. After the solution was stirred for a few minutes, the organic layer was removed by vacuum distillation. The ^1H NMR spectrum of this solution showed complete conversion to norbornadiene.

Catalytic Polymerization of 2(10)-Pinene. To a solution of 0.050 g of **1** (0.093 mmol in Eu(III)) in 1.0 mL of CH_3NO_2 was slowly added 1.01 mL (0.756 g, 6.4 mmol) of (−)-2(10)-pinene with stirring, resulting in the immediate formation of the polymer. The product was dissolved in $CHCl_3$ and chromatographed through a silica gel column. Removal of the solvent under vacuum yielded 0.72 g (95%) of pure polypinene

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(29) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1960**, 3705.

(30) Kennedy, J. P.; Chou, T. *Adv. Polym. Sci.* **1976**, *21*, 1.

(31) Molecular weight determined by isothermal distillation using Singer method. See: (a) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820. (b) Singer, R. *Justus Liebigs Ann. Chem.* **1930**, *478*, 246.

J. Am. Chem. Soc. **1986**, *108*, 4103–4105

which had a molecular weight of 1000 and $[\alpha]_D$ −8.4° (c 0.0083, CHCl$_3$). ^{1}H NMR (CDCl$_3$): 5.3, 1.9, 1.6, 0.9 ppm (br). The ^{1}H NMR spectrum was found to match with that reported previously.[30]

Catalytic Polymerization of Phenylcyclopropane. Phenylcyclopropane (0.80 mL, 0.756 g, 6.4 mmol) was added to a solution of 0.050 g of **1** (0.093 mmol in Eu(III)) in 1.0 mL of CH_3NO_2. The solution was allowed to stir for 5 days after which time an oily white layer appeared above the catalyst solution. CHCl$_3$ (40 mL) was added, and the resulting mixture was chromatographed through a silica gel column. Removal of the solvent under vacuum yielded 0.71 g (95%) of a viscous oil of molecular weight 600. ^{1}H NMR (CDCl$_3$): 7.17 (4 H, br), 3.63 (1 H, br), 1.96 (2 H, br), 0.84 ppm (3 H, br). ^{13}C{^{1}H} NMR (CDCl$_3$): 145.3, 142.7, 128.8–125.9, 52.9, 52.5, 28.9, 28.7, 12.8 ppm. Selected ^{13}C NMR (^{1}H-coupled): 52.9 (d, J = 125 Hz, CH), 52.5 (d, J = 125 Hz, CH), 28.9 (t, J = 125 Hz, CH$_2$), 28.7 (t, J = 125 Hz, CH$_2$), 12.8 ppm (q, J = 125 Hz, CH$_3$).

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Registry No. 1, 102233-99-8; Eu, 7440-53-1; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; $CH_2{=}C(CH_3)CH(CH_3)_2$, 563-78-0; 1-PhCH-CH$_2$-)$_n$, 9003-53-6; $PhCH{=}CH_2$, 100-42-5; $PhC(CH_3){=}CH_2$, 98-83-9; 1-PhC-(CH$_3$)CH$_2$-)$_n$, 25014-31-7; $Ph_2C{=}CH_2$, 530-48-3; 1,3-cyclohexadiene, 592-57-4; poly(1,3-cyclohexadiene) (homopolymer), 27986-50-1; poly-(1,3-cyclohexadiene) (SRU), 102233-96-5; norbornadiene, 121-46-0; 1,3-dimethyl-1,3-diphenyl-2,3-dihydroindene, 102233-98-7; 1,3-dimethyl-1-(2-methyl-2-phenylpropyl)-3-phenyl-2,3-dihydroindene, 41906-71-2; 1-methyl-1,3,3-triphenyl-2,3-dihydroindene, 19303-32-3; 6,6′-dimethyl-2-methylenebicyclo[3.1.1]heptane, 127-91-3; poly(6,6′-dimethyl-2-methylenebicyclo[3.1.1]heptane) (homopolymer), 25719-60-2; poly(6,6′-dimethyl-2-methylenebicyclo[3.1.1]heptane) (SRU), 40022-48-8; cyclopropylbenzene, 873-49-4; polycyclopropylbenzene (homopolymer), 102233-95-4; polycyclopropylbenzene (SRU), 102233-97-6; tetracyclo[3.2.0^{2,7}.0^{4,6}]heptane, 278-06-8.

Group IIB (12[†]) Metal Alkyls: The Synthesis of Trifluorosilyl and Trifluoromethyl Alkyls of Cadmium and Zinc

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Abstract: Metal vapors of cadmium and zinc have been reacted with trifluorosilyl and trifluoromethyl radicals to produce several new metal alkyls. A low temperature radio frequency glow discharge or plasma of hexafluoroethane and hexafluorodisilane was used to generate the trifluoromethyl and trifluorosilyl radicals, respectively. The compounds bis(trifluorosilyl)cadmium, bis(trifluorosilyl)zinc, bis(trifluoromethyl)cadmium, and bis(trifluoromethyl)zinc were isolated at low temperatures. All compounds were unstable at room temperature with the exception of bis(trifluorosilyl)cadmium which was marginally stable at 20 °C. Addition of glyme (glyme = dimethoxyethane) to the cadmium compounds gave stable alkyl–cadmium–glyme complexes while the addition of pyridine to the zinc compounds yielded stable complexes. The synthesis and physical properties are reported.

Over the past 6 years, a novel synthesis for fully substituted metal alkyls has been developed in our laboratories. The technique involves the reaction of metal vapors with radicals that are produced in a radio frequency generated glow discharge or plasma. Although radicals can be produced by using a variety of techniques, we have found low pressure plasmas to be very clean and convenient source of radicals if plasma gases with very simple and symmetrical structures are used. For example, ethane, hexafluoroethane, and hexafluorodisilane have been used as a source for methyl, trifluoromethyl and trifluorosilyl radicals, respectively.[1]

In spite of the extensive study of fluorocarbon-substituted metal compounds in recent years, very few compounds exist in which the SiF_3 ligand is bonded to an element other than carbon. A general synthesis for trifluorosilyl organometallic compounds has been absent from the scene, and it is particularly significant that no organolithium reagent such as $LiSiF_3$ exists, for this potential reagent is unstable at temperatures above −80 °C.[2] The first metal trifluorosilyl complex, $F_3SiCo(CO)_4$, was prepared by using a method analogous to that used by Chalk and Harrod for preparing $R_3SiCo(CO)_4$ complexes (R = organic groups).[3] The reaction of trifluorosilane with the binuclear metal carbonyl $Co_2(CO)_8$ gave $F_3SiCo(CO)_4$ in 84% yield.[4] Similar reactions at 160 °C with $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$ yielded $F_3SiMn(CO)_5$, $F_3SiRe(CO)_5$, and $F_3SiFe(\pi C_5H_5)(CO)_2$.[4] It was later noticed that the compounds could be made equally well with iodotrifluorosilane in place of the trifluorosilane, but the products were more difficult to separate.[5] The scarcity of known trifluorosilyl compounds is not too surprising when one considers the forcing reaction conditions necessary (160 °C) with older synthetic methods. Recently Sharp has reported the synthesis of P $(SiF_3)_3$ using a novel approach.[6] The compound was prepared from $\cdot SiF_3$ radicals generated by mercury-sensitized photolysis of Si_2F_6 in the presence of PF_3.

In an earlier publication, we reported the successful preparation of the first fully substituted trifluorosilyl complexes.[1c] For example, $Hg(SiF_3)_2$, $Bi(SiF_3)_3$, $Te(SiF_3)_2$, and $Sb(SiF_3)_3$ can be prepared by using the metal vapor/plasma chemistry.

Experimental Section

Starting Materials. Cadmium shot was obtained from PCR and zinc mesh was purchased from MCB. Reagent grade pyridine and glyme were used after drying over 4Å molecular sieves. Ether, methylene

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[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) (a) Juhlke, T. J.; Bierschenk, T. R.; Lagow, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 3229. (b) Firsich, D. W.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* **1981**, 7344. (c) Bierschenk, T. R.; Juhlke, T. J.; Lagow, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 7340.

(2) Lagow, R. J., unpublished results.

(3) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 1133.

(4) Hagen, A. P.; MacDiarmid, A. G. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 345.

(5) Schrieke, R. R.; West, B. O. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 141.

(6) Sharp, K. G. *J. Chem. Soc., Chem. Commun.* **1977**, 564.

0002-7863/86/1508-4103$01.50/0