bp 80–81 °C (20 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 0.39 (s) (lit.[17] δ 0.29).

Desilylation of 4 with Tetra-*n*-butylammonium Fluoride (TBAF). To a solution of **4** (554 mg, 2.0 mmol) in THF (10 mL) was added dropwise a solution of TBAF (0.2 M in THF, dried over molecular sieves 4A, 10 mL, 2.0 mmol) at −78 °C. After 5 s, the reaction mixture was mixed with chilled ether (50 mL). The mixture was washed with 5% HCl, water, and saturated aqueous NaCl. Concentration of the organic layer on a rotary evaporator, after drying over anhydrous $MgSO_4$, gave 342 mg of a mixture of **2** (74%) and **5** (6%). Identification of the products was accomplished by the comparison with authentic samples on GLC and NMR. Yield of each compound was calculated from the mole ratio based on the proton ratios in ^{1}H NMR of the mixture.

Ethyl Cinnamate (14a). To a mixture of benzaldehyde (212 mg, 2.0 mmol) and TBAF (0.2 M in THF, 5 mL, 1.0 mmol) was added dropwise a solution of **4** (277 mg, 1.0 mmol) in THF (3 mL) at 0 °C. After 1 h of stirring, the reaction mixture was mixed with ether (50 mL). The mixture was washed with saturated aqueous NaCl, dried over $MgSO_4$, concentrated, and distilled to give 102 mg (58%) of **14a**.

Ethyl 4,4-Dimethyl-2-pentenoate (14d).[18] To a solution of **4** (554 mg, 2.0 mmol) and trimethylacetaldehyde (345 mg, 4.0 mmol) in THF (5 mL) was added dropwise TBAF (0.2 M in THF, 2 mL, 0.4 mmol) at −78 °C with continuous stirring for 1 h. After the addition of ether (50 mL), the mixture was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. Silica gel column chromatography (hexane/ether) of the residue gave **14d** (188 mg, 60%).

Ethyl 2-(Trimethylgermyl)propionate (19). To a solution of **4** (554 mg, 2.0 mmol) and methyl iodide (568 mg, 4.0 mmol) in THF (5 mL) was added dropwise TBAF (0.2 M in THF, 5 mL, 1.0 mmol) at −78 °C with continuous stirring for 1 h. After the addition of ether (50 mL), precipitated tetra-*n*-butylammonium iodide was filtered. The filtrate was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on a silica gel column (hexane/ether, 40:1) to give **2** (181 mg, 45%) and **19** (55 mg, 13%): bp 65 °C (13 mmHg, Kugelrohr); IR (film) 1715 (CO), 830, 610, 575 cm^{-1} (Me_3Ge); ^{1}H NMR ($CDCl_3$) δ 0.22 (9 H, s, Me_3Ge), 1.20 (3 H, d, J = 6.4 Hz, CH_3CH), 1.23 (3 H, t, J = 7.2 Hz, CH_3), 2.16 (1 H, q, J = 6.4 Hz, CH), 4.10 (2 H, q, J = 7.2 Hz, CH_2). Anal. Calcd for $C_8H_{18}GeO_2$: C, 43.91; H, 8.29. Found: C, 43.70; H, 8.18.

Registry No. **1**, 4071-88-9; **2**, 32583-34-9; **4**, 111999-58-7; **5**, 111999-59-8; **6**, 111999-60-1; **7**, 111999-61-2; **8**, 7428-06-0; **9**, 111999-62-3; **11**, 27394-64-5; **12**, 38860-13-8; (*E*)-**14a**, 4192-77-2; (*Z*)-**14a**, 4610-69-9; (*E*)-**14b**, 51577-37-8; (*Z*)-**14b**, 51577-38-9; **14d**, 87995-20-8; (*E*)-**15a**, 111999-64-5; (*Z*)-**15a**, 111999-65-6; (*E*)-**15b**, 111999-66-7; (*Z*)-**15b**, 111999-67-8; (*E*)-**15c**, 111999-68-9; (*Z*)-**15c**, 111999-69-0; **16**, 38860-05-8; **17**, 32329-69-4; **19**, 111999-63-4; ethyl acetate, 141-78-6; ethyl bromoacetate, 105-36-2; benzaldehyde, 100-52-7; trimethylacetaldehyde, 630-19-3; nonanal, 124-19-6; 2-ethylhexanal, 123-05-7.

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Lanthanoid–Olefin Complex Formation: A Matrix-Isolation Ultraviolet–Visible and Infrared Study of the Direct Synthesis of $(C_2H_4)_nEu$ Using Europium Atoms[†]

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$Eu(C_2H_4)_n$ complexes have been synthesized at 12 K by codepositing Eu atoms with ethylene, neat or doped in Ar or Xe. UV–visible absorption spectroscopy of the highest stoichiometry product revealed a broad, intense visible transition centered at 537 nm. The complex is unstable above 50 K, consistent with the absence of any evidence for reaction in 77 K metal vapor reactions. Optical spectroscopy of the products formed in dilute matrices indicated the formation of a lower stoichiometry $Eu{-}C_2H_4$ complex. This was confirmed by infrared studies of absorptions in the coupled $\nu(C{=}C)/\delta(CH_2)$ region. Under high dilution conditions, a matrix split 1198/1182 cm^{-1} doublet is assigned to a monoethylene europium π complex. Matrix-annealing experiments combined with Eu/C_2H_4 reactions in C_2H_4/rare-gas matrices of increasing C_2H_4 concentration trace the conversion of $Eu(C_2H_4)$ to the highest stoichiometry species absorbing at 1233 cm^{-1}. In general, the $Eu(C_2H_4)_n$ IR spectra are similar to those of matrix-isolated group VIII (8–10) and IB (11) ethylene π complexes. The optical spectra of the odd-electron lanthanoid–olefin molecules, however, most closely resemble those of the coinage metals. The latter show intense visible metal-to-ligand charge-transfer transitions. Similarly, the green absorption of the europium olefin complexes may be associated with excitations of the Eu f electrons into the olefin. The comparatively low thermal stability of the Eu and group IB (11) olefin complexes is rationalized with the Dewar–Chatt–Duncanson bonding description. Molecular orbital calculations indicate that a model C_{2v} $Eu(C_2H_4)$ species is only weakly bonded by donation from a europium f orbital into the π^* system of ethylene, with little "forward" donation from the olefin σ or π orbitals.

Introduction

Although common in organotransition-metal chemistry, isolable, formally zerovalent complexes are extremely rare in organolanthanoid chemistry.[1] This dichotomy in chemical stability is undoubtedly linked to several factors, chief among them being (1) the electropositive character of the lanthanoid metals which favors di- and trivalent oxidation states of these metals and (2) the relative inability of the corelike lanthanoid metal valence electrons

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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 13-18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

[1] The first well-characterized examples of formally zerovalent, thermally stable, isolable species of these metals, the lanthanoid diazadiene complexes, have only recently been reported. See Cloke, F. G. N.; de Lemas, H. C.; Sameh, A. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1344.

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to participate in the synergistic back-bonding interactions which stabilize zerovalent complexes of the transition metals.[2-4]

Attempted preparative syntheses of this elusive compound class have focused on macroscale metal vapor reactions.[1,5-8] Such techniques have been used to good effect in organotransition-metal chemistry for the synthesis of arene and olefin complexes[9] which have proven inaccessible using more traditional methods. Unfortunately, the macroscale metal vapor methodology has not resulted in well-characterized isolable species when applied to organolanthanoid–olefin reaction systems. Evans and coworkers[6] find that complicated, generally insoluble reaction mixtures result when lanthanoid metals are reacted with small olefin substrates at 77 K (products isolated by warming the reaction matrix to ambient temperature with concomitant removal of unreacted olefin). In cases where acidic hydrocarbon substrates are used (terminal alkynes),[7] di- and trivalent reaction products are isolated rather than the desired zerovalent species. These results indicate that although such reaction systems may yield zerovalent intermediates at low temperature, these complexes will not survive intact upon warming to ambient temperature. Unfortunately, macroscale metal vapor methodology is not designed for the meaningful spectroscopic characterization of zerovalent intermediates at low temperature. However, the procedural difficulties inherent in metal vapor synthesis can be surmounted if *microscale matrix-isolation* synthetic and spectroscopic studies are employed to investigate these demanding reaction systems. Such studies, which provide for careful control of such important parameters as metal atom and matrix gas deposition rate as well as reaction zone temperature (12 K and higher) and which allow for *direct* spectroscopic observation of the reaction zone (both upon deposition and during subsequent annealing studies), are sensitive and informative probes of the ability of metal atoms to self-associate (to form dimers, trimers, etc.) and to interact with unsaturated substrates to form characterizable (if not isolable) binary complexes.[10] Furthermore, these studies are exceptionally useful in cases (as with the lanthanoids) where the desired products are expected to be both thermally unstable and extremely air and moisture sensitive. Thus, using matrix-isolation synthesis and spectroscopy, Slater and Sheline[11] were able to convincingly demonstrate the existence of a variety of lanthanoid carbonyl complexes, $Ln(CO)_n$ (Ln = Pr, Eu, Gd, Ho, Nd, Yb; n = 1–6) via infrared spectroscopy and to confirm their extreme thermal instability through careful annealing studies.

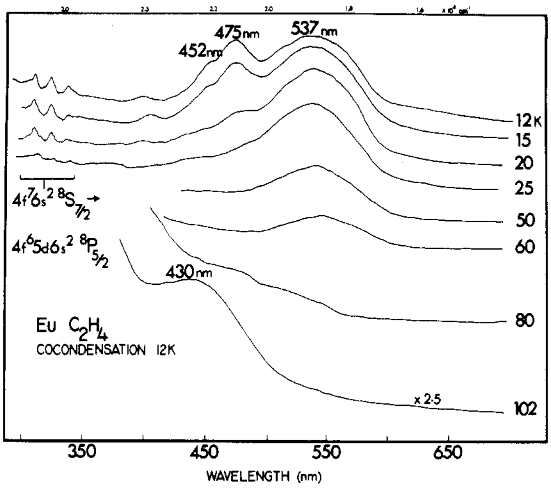

Figure 1. UV–visible absorption spectra resulting from the 12 K cocondensation of atomic Eu with ethylene ($Eu:C_2H_4 \simeq$ 1:10000), and matrix warmup through 102 K. The triplet of absorptions at 300–350 nm is due to d ← f transitions while those at 452 and 475 nm are due to p ← s transitions assigned to unreacted, metastable Eu atoms. The 537-nm absorption is produced by $Eu(C_2H_4)_n$.

As a complement to our investigations of the adduct chemistry of trivalent lanthanoid complexes with unsaturated substrates,[12] we have initiated a matrix-isolation synthetic and spectroscopic program to probe zerovalent lanthanoid metal self-associative and ligand-interactive behavior. The ultimate goal of our work is to assay the strength and nature of lanthanoid metal/unsaturated substrate interactions through detailed UV–Vis and IR spectroscopic studies and to use those results to elucidate why isolable zerovalent lanthanoid complexes are rare (or to define stability criteria whereby such species can be obtained on a macroscopic, synthetically useful scale).

The system chosen for initial investigation is the reaction of europium atoms with ethylene, both neat and dilute in rare-gas matrices. This particular metal/substrate combination was chosen based upon the ease of vaporization of europium metal and upon the spectroscopic simplicity of the ethylene infrared vibrational spectrum. In addition, the large body of matrix-isolation work available on alkali and transition metal/ethylene systems[10,13-18] provides ready qualitative comparison of our results with other spectroscopically characterized systems.

Results and Discussion

UV–Visible Experiments. Condensation of europium (Eu) with neat ethylene at 12 K (under low Eu atom concentration conditions to eliminate complications due to metal aggregate formation)[19] produced an intensely colored purple matrix. The UV–vis absorption spectrum obtained at 12 K is shown in the top trace in Figure 1.

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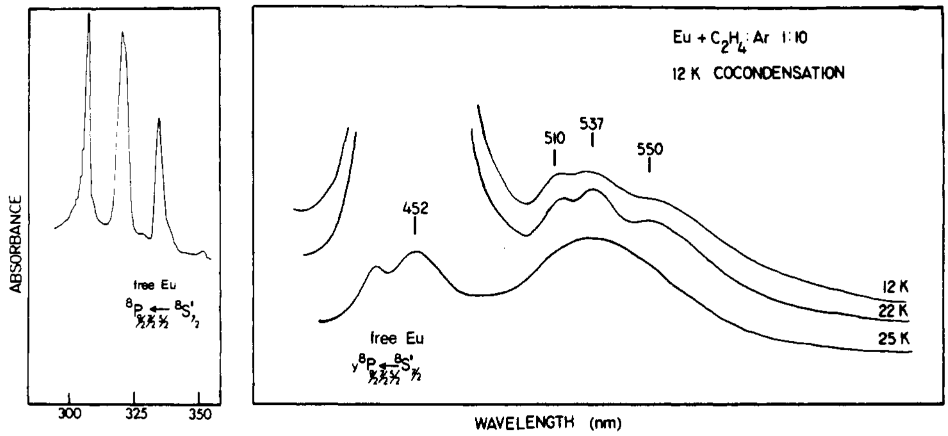

Figure 2. UV–visible absorption spectra observed on depositing Eu atoms with 1:10 C_2H_4:Ar at 12 K with annealing to 25 K.

The absorptions in the regions 300–350 and 450–500 nm are assigned to unreacted Eu atoms trapped in metastable sites.[19] Annealing the cocondensate at 20 K converted these atoms to a product (some of which is produced upon initial deposition) with a wavelength maximum at 537 nm. This purple compound was unstable above 50 K as shown in the thermal evolution of the absorption spectra in Figure 1. With careful annealing in the region 80–90 K, unreacted ethylene was removed in vacuo, leaving behind a species absorbing at 430 nm and possibly at higher energy, although the second absorption may be due to scattering by the slightly opaque matrix.

A related experiment, the cocondensation of Eu with neat ethylene at higher temperature (77 K), corroborates the thermal annealing studies; no detectable compounds are formed in the spectral region of interest. This latter experiment also indicates that simple Eu–olefin products are unlikely to be formed using 77 K (and above) cocondensation synthetic metal vapor techniques.

Ethylene was also diluted 1:10 and 1:25 in argon and cocondensed with Eu using Eu atom concentrations similar to those described above. Figure 2 documents these experiments. In comparing these results to the neat ethylene/Eu cocondensation, we observe that the d ← f transitions of unreacted Eu retain their position relative to those in neat ethylene. In contrast, the structured p ← s band in the visible range (420–470 nm) blue-shifts relative to that observed in the undiluted matrix. This effect is explained by noting that these latter orbitals are more susceptible to matrix-induced perturbations than the core-based d and f orbitals.

$Eu(C_2H_4)_n$ product formation is observed in both dilutions (as indicated by the emergence of at least three overlapping bands with maxima at 510, 537, and 550 nm in the visible spectra). Annealing these C_2H_4/Ar/Eu matrices at 22 K reduced the intensity of the 510- and 550-nm bands and those of uncomplexed Eu. The absorption at 537 nm, however, increased relative to the remaining bands. This behavior on annealing is consistent with conversion of one species to another associated with a change (an increase) in ligand ethylene stoichiometry as observed in speciating matrix-isolation studies of $M(C_2H_4)_n$ complexes where n varies from 1 to 3 and where M is a transition metal.[10] Support for this interpretation comes from matrix-isolation infrared spectroscopic studies (vide infra).

Infrared Experiments. An extensive literature concerning matrix-isolated transition-metal–olefin complexes exists.[10,13–18] In ethylene complexation studies, the position of the ν_{12} B_{3u} antisymmetric deformational mode of the uncoordinated olefin,[15] normally observed as a very strong transition at 1436–1438 cm^{-1} is predicted to decrease slightly, whereas the frequency of the symmetric $\delta_s(CH_2)\nu_3$ A_1 mode is expected to increase.[10,18,20] Moreover, it is known from these studies that, upon complex formation, an absorption of low intensity associated with the ν(C=C) stretching vibration is expected in the 1550–1450 cm^{-1} region. The magnitude of the decrease of this frequency is a sensitive probe of the extent of metal–olefin π-complexation.[10,20] However, the decrease in the ν(C=C) may draw the ν(C=C) and $\delta_s(CH_2)$ modes closer in frequency. As a result, the symmetric $\delta_s(CH_2)$ can couple strongly with the ν_2 A_1 C=C stretching vibration.[18,21] This effect makes it difficult to assign the lower frequencies (1550–1000 cm^{-1}) to specific modes. This point has been strongly emphasized by Manceron and Andrews[18] in a recent study of lithium atom–ethylene π-complexation. Thus, in matrix-isolated transition-metal–ethylene complexes, two bands are generally observed which are indicative of π-complex formation.[10,20] The strongest telltale absorption is detected between 1120 and 1250 cm^{-1}. In addition, and depending on the ligand stoichiometry about the metal atom, a weak band can sometimes be observed in the range 1400–1500

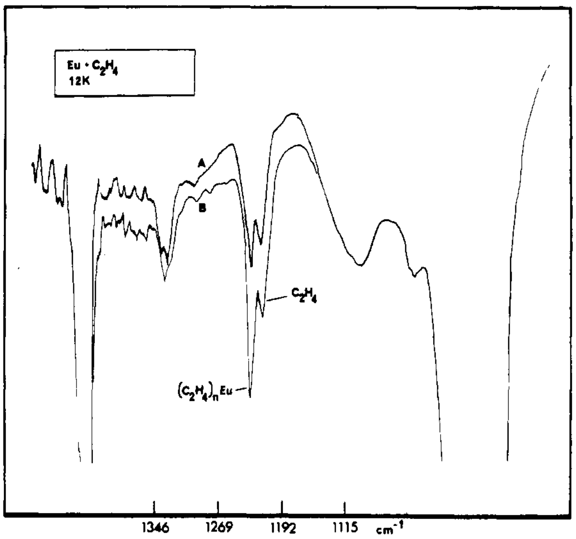

Figure 3. Infrared spectra in the region of the $\delta(CH_2)$ symmetric deformational mode, observed (A) on depositing Eu atoms with C_2H_4 (Eu:C_2H_4 ≃ 1:1000) at 12 K and (B) on annealing to 18 K. Product absorption occurs at 1233 cm^{-1}.

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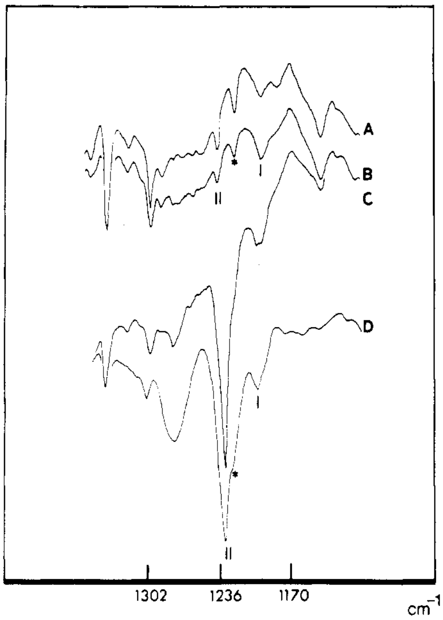

Figure 4. Infrared spectra (transmission) observed (A) on depositing Eu atoms with 1:100 C_2H_4:Xe at 12 K (Eu:Xe $\simeq$ 1:10000), showing absorptions of (C_2H_4)Eu and $(C_2H_4)_n$Eu, labeled I (1197/1182 cm^{-1}) and II (1233 cm^{-1}), respectively, (B) on annealing the matrix at 30 K and (C) 40 K, and (D) C_2H_4:Ar (1:25) codeposition with Eu at 12 K showing absorptions for $(C_2H_4)_n$Eu labeled I and II.

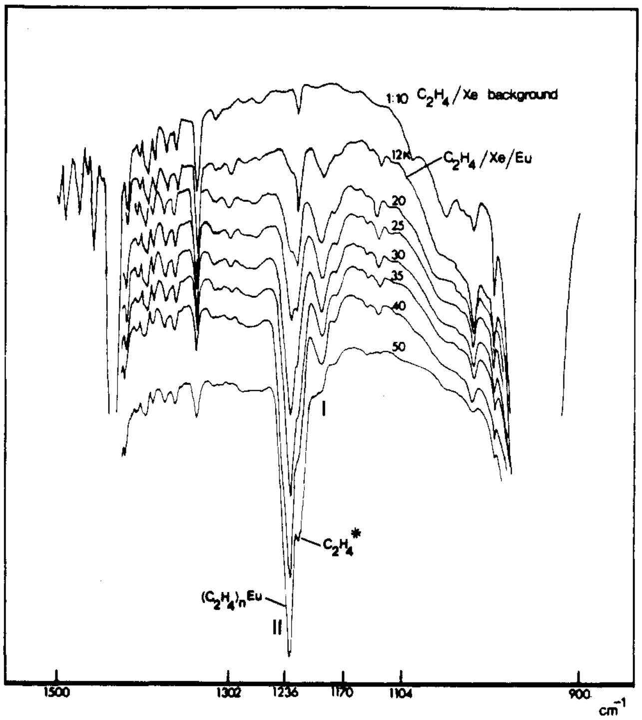

Figure 5. Infrared spectra (transmission) observed on codepositing Eu atoms with 1:10 C_2H_4:Xe at 12 K showing absorptions of (C_2H_4)Eu (I), $(C_2H_4)_n$Eu (II), and free C_2H_4 (*), followed by a warmup program inducing conversion of I to II.

cm^{-1}. In both regions, the modes giving rise to the absorptions are approximately described as mixed ν(C=C)/δ_s(CH_2).

When Eu atoms were cocondensed with neat $^{12}C_2H_4$ at 12 K (Eu:C_2H_4 $\simeq$ 1:1000), the infrared spectra (A, B) displayed in Figure 3 were obtained. Besides the bands due to unreacted ethylene, a new absorption was detected at 1233 cm^{-1}, adjacent to a 1221 cm^{-1} absorption of free ethylene. (The latter transition is assigned to a ν_6 B_{1g} CH rocking mode,[13] formally *gerade* (infrared forbidden) in D_{2h} symmetry or in the site symmetry of ethylene in the crystalline solid. Its presence here indicates that our solid matrix deposit of ethylene is disordered. Hence, in line with observations by Rytter and Gruen,[13] we find that the ν_6 mode is always weakly active for ethylene diluted in the rare-gas solids.) Controlled annealing of the neat ethylene/Eu matrix at 18 K resulted in growth of the 1233 cm^{-1} absorption. The formation of additional product upon warming, shown here by the enhancement of the 1233 cm^{-1} band, is consistent with the conversion of metastable Eu atoms to product and corroborates our analysis of the optical absorption experiments. Moreover, there is a complete loss of product giving rise to this transition when the matrix is warmed above 60 K, again consistent with the results described above and in Figure 1.

As previously discussed, UV–vis absorption studies of Eu reactions in dilute ethylene matrices resulted in the observation of new absorptions suggestive of Eu–olefin products of different stoichiometry. These optical absorption results are supported by a series of infrared/matrix-isolation dilution studies (Figures 4 and 5). Trace A in Figure 4 was collected after codepositing Eu with 1:100 C_2H_4:Xe at 12 K for 7 h. The salient features of this spectrum are labeled and discussed below. We propose that I is associated with a monoethylene europium complex absorbing at 1197 and 1182 cm^{-1}. The two bands most likely derive from the same species trapped in different substitutional sites.[14] Annealing the matrix at 30 K (trace B) favors conversion to the more stable site. Of particular interest in these spectra is the presence of a transition at 1233 cm^{-1} (labeled II) which is weaker in terms of integrated intensity than the 1197 cm^{-1} band. This absorption occurs at a frequency identical with that obtained in the neat C_2H_4/Eu experiment (and in trace D for Eu in 1:25 C_2H_4/Ar).

A program of annealing performed in the range 12–40 K demonstrated that the set of new absorptions can be attributed to two distinct species. Traces B and C record the effect of increasing temperature. (Selection of the more rigid Xe matrix allows one to work at elevated temperatures. In the lower melting Ar matrix the complex would normally decompose. This suggests that the Xe matrix imparts a greater kinetic stability to the product.) Spectrum B demonstrates that species I develops relative to II in the initial stages of annealing at 30 K. Such behavior is expected for Eu atoms diffusing and encountering dilute target ethylene molecules since as the Tammann[9] temperature is approached and exceeded, enhanced material transport favors formation of the higher stoichiometry compound (II) at the expense of species I (curve C).

We have also studied the matrix produced by codepositing 1:10 C_2H_4:Xe (Eu:gas $\simeq$ 1:1000). These infrared spectra and their thermal evolution under annealing are shown in Figure 5. On deposition at 12 K, the two major Eu–olefin transitions assigned to I and II are immediately apparent. The conversion to the higher stoichiometry species on warmups through 50 K is striking.

The results of a final experiment which probed the effect of changing the rare gas/dopant ratio, at fixed total Eu, with the purpose of indicating the presence of at least two distinct compounds are shown in Figure 6. As expected, the ratio of absorbances, ν_{1233}/ν_{1203}, changes from 3.8:1 (1/25 C_2H_4/Ar, Figure 6c) to 5.5:1 (1/10 C_2H_4/Ar, Figure 6b) in the direction expected for a concentration-dependent competitive formation of species II. Attempts to unambiguously assign the ligand stoichiometry of I and II based on mixed $^{12}C_2H_4$/$^{13}C_2H_4$ isotopic labeling studies were unsuccessful, owing to accidental overlaps and the

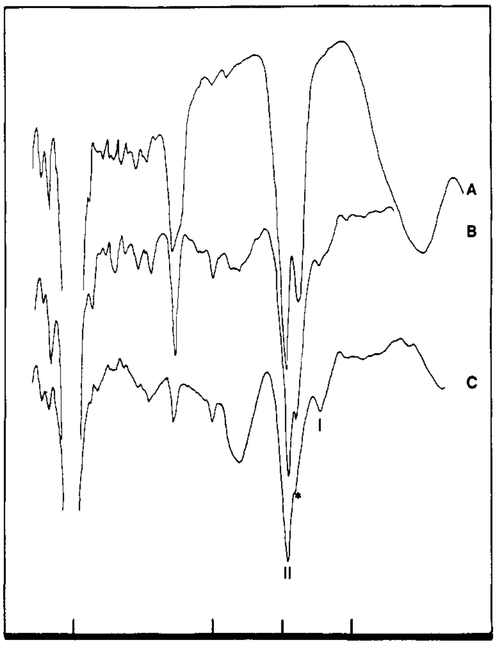

Figure 6. Effect of varying C_2H_4 dilution factor in Ar on Eu-$(C_2H_4)_n$ product distributions: (A) Eu in neat C_2H_4; (B) 1:10 C_2H_4:Ar; (C) 1:25 C_2H_4:Ar. At 1:25 C_2H_4:Ar, the ratio of (II) 1233 cm^{-1}/(I) 1203 cm^1 is 3.8:1, at 1:10 C_2H_4:Ar the ratio is 5.5:1.

Table I. Coupled $\nu(C{=}C)/\delta_s(CH_2)$ Infrared Spectral Transition Energy (cm^{-1}) for $(C_2H_4)_nM$ (Where M = Co, Ni, Pd, Cu, Ag, Au, or Eu and n = 1–3)

metal	$(C_2H_4)_3M$	$(C_2H_4)_2M$	$(C_2H_4)M$
Co	1225		
Ni	1245	1225	1223
Pd	1255	1242	1223
Cu	1252	1228	1156/1138^a
Ag			1152/1132^a
Au			1144/1135^a
Eu			1198/1182^a

^{a} Splitting due to multiple trapping site effect.

overall low intensities of the transitions in the region 1000–1300 cm^{-1}.

Comparison with Matrix-Isolation Spectroscopic Studies of Transition-Metal–Olefin Complexes. Table I lists the positions of the infrared transitions associated with the coupled $\nu(C{=}C)/\delta_s(^{12}CH_2)$ modes in a range of M–olefin species.[10,14-16,18,20,21,24-26] Similarities are readily apparent between the optical/infrared absorption and bonding properties of the coinage metal and europium–ethylene complexes. Unfortunately, although the presence of infrared transitions in the 1200 cm^{-1} region of the spectrum suggests Eu–ethylene π-complexation,[22] the extent of metal olefin interaction cannot be inferred from the data for the reasons given above. Further insight into the Eu–ethylene σ/π bonding interaction will require the determination of a realistic force field via a complete normal coordinate analysis for which a more extensive set of vibrational data is necessary. Nevertheless, several important qualitative comparisons can be made with transition-metal systems by using the available infrared spectroscopic and thermal stability data.

It is evident from Table I that in a series of complexes $(C_2H_4)_nM$, the infrared peaks shift little on increasing n or changing M. In contrast, electronic absorption shows that the metal-to-ligand charge-transfer transitions are quite sensitive to such variations. Hence, the group IB (11) metal–ethylene complexes are highly colored,[14] whereas those of the group VIII (8–10) metals have no visible absorptions.[15]

Unlike their group VIII (8–10) counterparts, the group IB (11) and europium–ethylene complexes are open-shell systems bearing at least a single unpaired electron in a predominantly metal-localized orbital having a small HOMO–LUMO gap. In each coinage metal case (n = 1, 2, M = Cu; n = 1, M = Ag, Au), the metal–ligand charge-transfer transition has been associated with excitation of the unpaired electron[15] into an ethylenic level having mainly π^* character. A similar process may occur in the odd-electron europium–ethylene compounds, i.e., excitations of f electrons into predominantly ligand-based orbitals. A further similarity is in the thermal stability of the complexes. Like the $Eu(C_2H_4)_n$ complexes, olefin complexes of the coinage metals decompose readily on warming toward 77 K. The comparatively low thermal stability of the coinage metal complexes can be rationalized with the Dewar–Chatt–Duncanson description of bonding in metal–olefin compounds,[23,24] the results of matrix-isolation EPR experiments by Kasai et al.[16,17] and Xα–SW[15] and ab initio[25] molecular orbital calculations of monoethylene complexes of the group IB (11) metals. All indications are that these are primarily σ-bonded molecules. The fully occupied d orbitals are essentially corelike and therefore unable to participate in donating charge density into the π^* level of ethylene, an effect which is known to increase the stability of the group VIII (8–10) congeners.

Table II. Structure Parameters and α Values for the Xα Calculation of $Eu(C_2H_4)^a$

atom	x	y	z	radius	α
outer sphere	0.00	0.00	0.00	5.9941	0.71696
Eu	0.00	0.00	0.00	2.7213	0.69549
C	0.00	1.2650	−3.8360	1.5506	0.75928
H	1.7554	2.3283	−3.8360	1.1757	0.77725
C	0.00	−1.2650	−3.8360	1.5506	0.75928
H	1.7554	−2.3283	−3.8360	1.1757	0.77725
H	−1.7554	−2.3283	−3.8360	1.1757	0.77725
H	−1.7554	2.3283	−3.8360	1.1757	0.77725

^{a} Positions and radii reported in multiples of the Bohr radius (a_0) of the hydrogen atom.

To explore the modes of bonding possible in these europium–olefin species and to compare them further with the coinage and transition metals, we have performed Xα–scattered wave molecular orbital calculations on a model $Eu(C_2H_4)$ molecule in C_{2v} symmetry. Table II gives the structural parameters for the spin-restricted computation. The energy level diagram of Figure 7 displays the ordering of the molecular orbitals obtained from the calculation converged to a state having five unpaired spins.

Reference to Figure 7 shows a series of levels, clustered between −0.17 and −0.27 Ry which, with the exception of the $3b_2$ level, are essentially europium f orbitals. These are nonbonding in character. The free ethylene levels $1b_{3g}$, $3a_g$, $1b_{2u}$, $2b_{1u}$, and $2a_g$[26] correlate with those in the Eu-(C_2H_4) complex as $1a_2$, $4a_1$, $2b_1$, $2b_2$, and $2a_1$, respectively. The order of these latter levels is the same as that found in other calculations of transition-metal–ethylene com-

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[22] No transitions were observed in the range 1550–1900 or 400–600 cm^{-1} expected for $\nu(M-H)$ or $\nu(M-C)$ stretching modes. Such transitions would have been expected if Eu atom insertion into the ethylene C–H bond had occurred.

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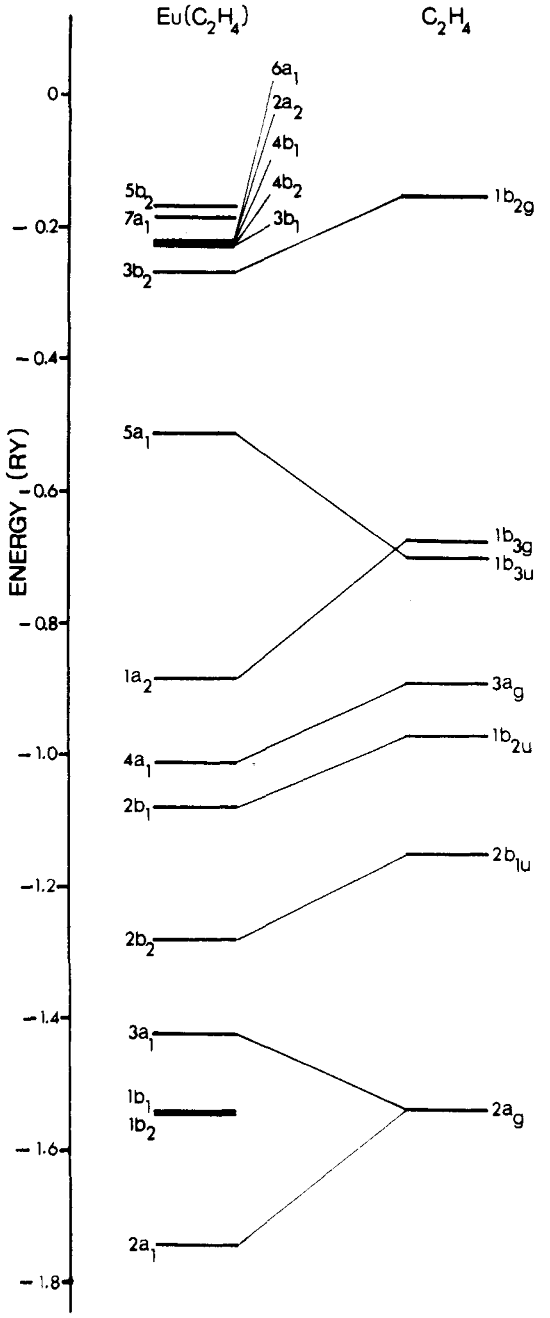

Figure 7. SCF–Xα–SW spin-restricted energy level diagram for model Eu(C_2H_4) of C_{2v} symmetry. The uppermost levels have the following occupation numbers in order of decreasing absolute value of the energy: $3b_1(2)$, $4b_2(1)$, $4b_1(1)$, $2a_2(1)$, $6a_1(1)$, $7a_1(1)$.

plexes.[15] The intraligand localized symmetry combinations of the C–H bonds are represented by the $1a_2$, $4a_1$, $2b_1$, and $2b_2$ molecular orbitals. The europium *p* orbitals derived from the free atom $5p^6$ valence set are bracketed by the ligand $2b_2$ and $2a_1$ levels.

We find that the europium p_x and p_y orbitals which transform as b_1 and b_2 do not interact with the ethylene molecule. Inspection of the wave functions and partial wave analyses reveals, however, significant mixing of the Eu and ethylene functions in the totally symmetric representations, $2a_1$ and $3a_1$. In the present parametrization, europium contributes about 40% p character to the $2a_1$ MO (C–C σ-bond (45% C, sp hybrid)). However, this bonding interaction is overbalanced by a strongly antibonding combination of Eu p (56%) and ligand sp (28%) wave functions in the $3a_1$ MO. Such mixing into the ligand framework orbitals is not unprecedented[27] and merely suggests the possibility of refinements to the Dewar–Chatt–Duncanson paradigm of synergic bonding in emphasizing the importance of σ-orbital participation. Within this paradigm, the critical Eu(C_2H_4) bonding interactions are those involving the $5a_1$ and $3b_2$ symmetry orbitals. These are represented in the wave function contour diagrams of Figure 8. These diagrams clearly show that the $5a_1$ level,[28] usually implicated in "forward-donation" (involving mixing of the occupied π HOMO of the ethylene molecule and the unoccupied level(s) of the metal center), is nonbonding. Thus, the complex appears to be held together by a small donation of charge density from the doubly occupied $f_{z(x^2-y^2)}$ orbital of Eu into the π^* system of ethylene. The theoretical analysis therefore strongly points to f-orbital participation in the bonding of this complex in the given geometry. In this context, the weakening of the olefin C=C bond correlates with the observed shift of the coupled ν(C=C) and $\delta(CH_2)$ modes to lower frequency. However, weakening of the σ-ethylene bond would lead to the same observed effect and cannot be ruled out as a factor.

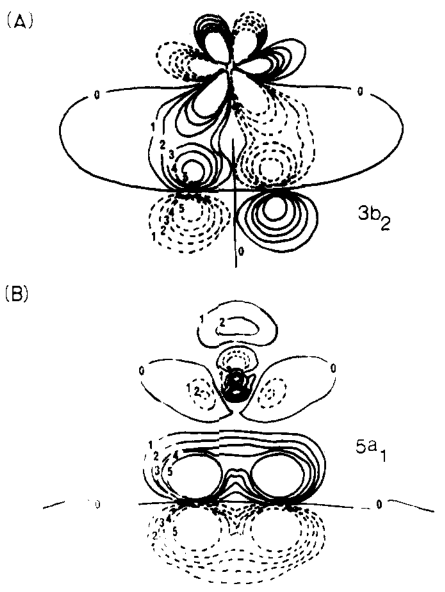

Figure 8. Wave function contour diagrams for (A) the $3b_2$ and (B) the $5a_1$ molecular orbitals. Positive wave function contours are indicated by solid lines and negative contours by dashed lines. Contour values: (0) 0.00, (1) 0.050, (2) 0.075, (3) 0.10, (4) 0.125, (5) 0.16 in units of (electrons/a^3)$^{1/2}$. Zero contours represent nodal surfaces.

In summary, the synergistic "forward–back" bonding interactions so critical to the stability of group VIII (8–10) and other transition-metal complexes[20,27] is absent in europium, as it is in the coinage metals. However, in detail, it would appear that ethylene is bonded to Eu in a manner different from that of Cu, Ag, or Au.

Conclusions

When cocondensed at 12 K, Eu atoms and ethylene react to form intensely colored purple Eu(C_2H_4)$_n$ complexes. When prepared in neat ethylene matrices, the products are unstable above 60 K. Consistent with this lack of thermal stability, no complexes are observed to form when reactants are cocondensed at 77 K. These results indicate that formally zerovalent europium–ethylene complexes are unlikely to be synthesized by using preparative scale metal

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[28] The europium atom contribution to this orbital consists of extensively hybridized s, p, d, and f functions that account for the complicated appearance of the contour plot.

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atom techniques which conventionally operate at 77 K.

The intense visible absorptions of these odd-electron lanthanoid complexes resemble the open-shell group IB (11) metal complexes (metal-to-ligand charge-transfer transitions) more closely than those of the group VIII (8–10) metals. UV–vis absorption spectroscopy of the reaction of Eu with ethylene diluted in argon gave evidence for products of different ligand stoichiometry. These results were confirmed by dopant gas dilution matrix-isolation infrared spectroscopic studies which gave evidence for π-complex formation, a highly coordinatively unsaturated monoethylene europium complex, and a species having higher ethylene coordination.

Molecular orbital calculations indicate that these molecules are weakly bonded by europium f orbital donation to the olefin π^* system, with forward donation from the occupied ethylene π orbital providing little enhancement of overall complex stability.

Experimental Methods

Materials. Research grade rare gases (Matheson) were used throughout these studies. Europium powder was obtained from Aesar.

Manipulations and Methods. Europium powder was transferred under argon in a Vacuum Atmospheres drybox to a boron nitride lined tantalum Knudsen cell. The cell was then mounted onto the water-cooled resistance electrodes of a plexiglass flanged furnace assembly and the entire unit sealed under argon in a plastic bag. Transfer of the furnace unit to the cryostat of the matrix-isolation unit was accomplished under a vigorous argon purge. A customized metal vapor cryogenic unit (Torromis, available from Torrovap Industries, Toronto, Canada) was employed in this work.

Metal and substrate vapors were cocondensed onto a sodium chloride (UV–vis) or cesium iodide (IR) window maintained at 12 K by an Air Products Displex CSW 202 variable-temperature He gas refrigerator. A quartz crystal microbalance strategically positioned in the furnace provided quantitative measure of the Eu atom deposition rate. The flow of gas was determined from measurements of the pressure drop per unit time in a reservoir of known volume. Matrix sample preparations typically required 1–2 h for UV–vis studies and 5–8 h for IR spectroscopic analyses. UV–vis spectra were obtained with a Cary 17 spectrometer. IR spectra were obtained by using a Nicolet 5DX-FTIR.

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Note Added in Proof. The synthesis of the first authentic Ln(0) species, the crystallographically characterized bis(η-1,3,5-tri-*tert*-butylbenzene) sandwich complexes of Y and Gd has recently been reported. (Brennan, J. G.; Cloke, F. G. N.; Sameh, A. A.; Zaikin, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1668.)

Registry No. Eu(C_2H_4), 111559-70-7; C_2H_4, 74-85-1; Eu, 7440-53-1.

Electrochemical Oxidative Induced Isomerization of Dicarbene Metal Carbonyl Complexes

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The one-electron oxidation of *trans*-(carbene)$_2$M(CO)$_4$ (M = Cr, Mo, W) complexes results in their rapid isomerization to the corresponding cis cations. Remarkably, the cis cations have an oxidation potential approximately 200 mV higher than the trans complexes. This apparent paradox is explicable by the large difference in thermodynamic stabilities of the cis and trans neutral complexes. Rates of isomerization as well as energies of activation were determined. A novel photoelectric cell was developed utilizing the dicarbene complexes.

Introduction

Electron-transfer chain catalyzed isomerizations of organometallic complexes represent an ever growing area of study. These studies not only are of theoretical interest but also can be highly useful synthetically.[1–15] Busch's original report is a classic example of how ETC-catalyzed reactions can be used synthetically.[11] In this paper, we would like to report some unusual observations regarding the electrochemical oxidation of some dicarbene carbonyl

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