and 122.0 as singlets. Only the first signal at δ 152.2 was assigned to 6′-C by referring to 2-ethylpyridine (6-C, δ 149.1).[26] The methylene carbon of the piph moiety was observed at δ 48.9 as a singlet. Five carbons of the acac ligand appeared as singlets at δ 187.9 (C=O), 186.8 (C=O), 100.2 (CH), 28.2 (CH_3), and 27.7 (CH_3).

Reactions of 4 with Vinyl Compounds. The reactions of **4** with styrene and methyl vinyl ketone were examined in the presence of triethylamine.[2,27,28] Complex **4** reacted with styrene in refluxing *m*-xylene to yield *trans*-2-(2-picolyl)stilbene (**7**) in 44% yield. The IR, ^{1}H NMR, and mass spectra of **7** were in accord with the proposed formula.

Methyl vinyl ketone also reacted with **4** under milder conditions (in refluxing benzene) to afford a reddish brown oil. Its ^{1}H NMR spectrum indicated that the oil contained about 81% of *trans*-1-(2-(2-picolyl)benzylidene)acetone (**9**), about 8% of methyl 2-(2-picolyl)phenethyl ketone (**8**), and an unknown product and that the yield of **9** corresponded to nearly 80%. The ^{1}H NMR spectrum of **9** exhibited typical trans-vinylene protons as an AB quartet at δ 7.16 [$\Delta\delta = 1.42$, $^{3}J(HH) = 16$ Hz], whereas that of **8** showed an $AA'BB'$ pattern assignable to the ethylene group in the range of δ 2.5–3.0 (4 H) in place of the trans-vinylene protons. Even after the repeated column chromatographic treatments on alumina, **9** could not be isolated in a pure state owing to the contamination with a small amount of **8**. The formations of **7** and **9** strongly confirm the cyclopalladated structure of the piph moiety. The mechanism to form **8** is not clear at the present time, but the detail will be reported in a following paper.

Concluding Remarks.

The novel six-membered piph cyclopalladated structure in **3–6** was unambiguously confirmed on the basis of their elemental analyses, the aromatic proton resonances in the ^{1}H NMR spectra of **5**, the three quaternary carbons in the ^{13}C{^{1}H} NMR spectrum of **6**, and the formation of 2-(2-vinylated benzyl)pyridines. It is noteworthy that 2-benzylpyridine reacted smoothly with palladium(II) acetate to give the novel six-membered cyclopalladated complex **3**, in sharp contrast with the reaction with palladium(II) chloride leading to the formation of the addition product **1**. It has been already reported that palladium(II) acetate reacts to give five-membered cyclopalladation products with aryl-substituted nitrogen bases[15,17,22,23] and benzyl sulfide,[16] which afforded no cyclopalladated complex by the reactions with pallaldium(II) chloride or tetrachloropalladate(II) ion.

Acknowledgment. We thank Mrs. Hisako Mazume and Miss Yumi Kojima, Nagasaki University, for their technical assistance.

Registry No. **1**, 79272-87-0; **2**, 79272-88-1; **3**, 79272-89-2; **4**, 79299-89-1; **5**, 79272-90-5; **6**, 79272-91-6; **7**, 79272-71-2; **8**, 79272-72-3; **9**, 79272-73-4; methyl vinyl ketone, 78-94-4; styrene, 100-42-5.

---

(27) Kamiyama, S.; Kimura, T.; Kasahara, A.; Izumi, T.; Maemura, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 142.

(28) Kasahara, A.; Izumi, T.; Watabe, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 957.

Contribution from the Department of Chemistry,
University of Chicago, Chicago, Illinois 60637

Reactivity of Lanthanide Metal Vapor with Unsaturated Hydrocarbons. Reactions with Ethene, Propene, and 1,2-Propadiene[1]

WILLIAM J. EVANS,*[2] KRAIG M. COLESON, and STEVEN C. ENGERER

Received April 28, 1981

The reactions of ytterbium, samarium, and erbium metal vapor with ethene, propene, and 1,2-propadiene have been investigated by cocondensation of the metals with these hydrocarbons at 77 K followed by isolation and physical and chemical characterization of the organolanthanide products at room temperature. A variety of reaction pathways are traversed in these systems. Evidence for lanthanide metal insertion into C–H bonds, cleavage of carbon–carbon multiple bonds, homologation, oligomerization, and dehydrogenation is observed with these small hydrocarbon substrates. Cyclopropane is similarly highly reactive with erbium metal vapor.

Introduction

During the past few years, we have been investigating[3-7] the low-valent chemistry of the lanthanide elements in efforts to demonstrate experimentally that these metals have a more extensive chemistry than is found in their traditional, ionic, trivalent complexes and to provide a basis for seeking unusual catalytic transformations which involve the 4f elements. One approach which we have used in this study is the metal vaporization technique[8-13] in which metal vapor and a substrate are cocondensed at low temperature. This method has allowed us to examine the reactivity of zerovalent lanthanide metals

---

(1) "Abstracts of Papers", Second Chemical Congress of the North American Continent, Las Vegas, Nevada, Aug 1980; American Chemical Society: Washington, DC, 1980; INOR 297.

(2) Camille and Henry Dreyfus Teacher-Scholar.

(3) Evans, W. J.; Engerer, S. C.; Neville, A. C. *J. Am. Chem. Soc.* **1978**, *100*, 331.

(4) Evans, W. J.; Wayda, A. L.; Chang, C. W.; Cwirla, W. M. *J. Am. Chem. Soc.* **1978**, *100*, 333.

(5) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007.

(6) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, pp 941–952.

(7) Zinnen, H. A.; Pluth, J. J.; Evans, W. J. *J. Chem. Soc., Chem. Commun.* **1980**, 810.

(8) Skell, P. S.; McGlinchey, M. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 195.

(9) Timms, P. L.; Turney, T. W. *Adv. Organomet. Chem.* **1977**, *15*, 53.

(10) Klabunde, K. J. "Chemistry of Free Atoms and Particles"; Academic Press: New York, 1980.

(11) Blackborow, J. R.; Young, D. "Metal Vapor Synthesis in Organometallic Chemistry"; Springer-Verlag: Berlin, Germany, 1979.

(12) Moskovits, M.; Ozin, G. A. "Cryochemistry"; Wiley: New York, 1976.

(13) Preparative scale lanthanide metal vapor studies of cyclooctatetraenyl[14] and acetylacetonate[15] complexes have also been reported.

(14) DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625.

(15) Blackborow, J. R.; Eady, C. R.; Koerner Von Gustorf, E. a.; Scrivanti, A.; Wolfbeis, O. *J. Organomet. Chem.* **1976**, *108*, C32.

0020-1669/81/1320-4320$01.25/0

and to investigate how these metals interact with neutral unsaturated hydrocarbons. Our initial investigations with dienes[3] and internal alkynes[5,6] have demonstrated that the lanthanide metals react with these unsaturated hydrocarbons to form preparative-scale quantities of new classes of isolable, organolanthanide complexes.[13] These complexes were the first f element complexes known to catalytically activate molecular hydrogen in homogeneous systems.[5,6] More recent studies of lanthanide metal vapor cocondensation reactions involving terminal alkynes have demonstrated that the multiple bond is not the only possible point of reactivity in unsaturated hydrocarbons under these reaction conditions. For example, ytterbium, samarium, and erbium insert into the terminal C–H bond of 1-hexyne to form alkynide hydride complexes.[16]

In the present study, we have extended our general investigation of the interaction of the lanthanide metals with unsaturated hydrocarbons to organic substrates which are not as acidic as terminal alkynes and which lack substituent groups which have the potential of being alternative sites of reactivity. Ethene and 1,2-propadiene were studied for these reasons. Although the products of these small hydrocarbons cocondensation reactions are insoluble in common solvents, they do allow us to demonstrate that zerovalent lanthanide metals can effect a variety of transformations on unsaturated hydrocarbon substrates. Reactions involving metal insertion into C–H bonds, cleavage of carbon–carbon multiple bonds, homologation, oligomerization, and isomerization occur with these substrates. Extension of this metal vapor investigation to propene and cyclopropane further demonstrates a high degree of reactivity for the lanthanide metals and provides a soluble reaction product in the erbium propene case.

The interaction of ethene and propene with metal atom vapor has been studied previously by matrix isolation and hydrolytic decomposition methods for a variety of metals. These studies provide valuable background information for evaluating our results and are briefly described in the following paragraphs. Metal vapor reactions of allene and cyclopropane have not previously been described to our knowledge.

Ethene cocondensation reactions with Co, Rh, Ni, Pd, Pt, Co, Ag, Au, and Al have been studied by infrared[17] and EPR[18,19] spectroscopy under matrix isolation conditions at <10 K. In every case, these metals were observed spectroscopically to form π complexes with ethene.

Propene cocondensation reactions with 27 different metals at 77 K have been examined in one of the first general surveys of the potential of metal vapor chemistry.[20-23] In that study, characterization was accomplished by condensing D_2O onto the matrix in the reactor and identifying the hydrolytic decomposition products. In these propene reactions, the hydrolysis products varied considerably depending on the metal. Reactions involving a late transition metal such as nickel[20] liberated propene and propane (4:1) which were 75–85% deuterium free. This was interpreted to indicate that a π complex was formed with this metal, a conclusion also supported by separate spectroscopic studies.[9,17] Scrambling experiments with C_3H_6 and C_3D_6 did indicate that a chemically significant amount of a π-allyl hydride complex was in equilibrium with the more favored π complex, however.[8] Aluminum propene matrices formed primarily dideuteriopropane and dideuteriohexanes upon deuterolysis, a result consistent with addition of aluminum to the double bond to form 1,2-dialuminopropane and aluminopropyl radicals.[21] No evidence for either π complexation or substantial Al–H formation was observed in this case. The earlier transition metals, exemplified in this study by chromium,[22] were observed to exhibit intermediate behavior compared to nickel and aluminum. Propane, propene, and hexanes (5:2:1) were observed, but the deuterium incorporation pattern was found to be too complex to explain mechanistically. In general, it was postulated that the early transition metals had a greater tendency to form σ bonds and metallacyclopropane rings in alkene reactions than to form zerovalent π complexes. This general propene survey also included the first lanthanide metal alkene studies. Hydrolyses of erbium, dysprosium, and terbium propene matrices were briefly described as giving good yields of propanes and hexanes with high deuterium incorporation.[23]

There are three other metal vapor reaction systems which are relevant to our present study in that hydrolysis of their reaction products generates a variety of decomposition products (vide infra). In one case, nickel clusters formed from a nickel vapor/pentane cocondensate were reported to react with pentane at 143 K to generate a variety of organometallic products, as determined by hydrolysis of the matrix.[27] The insoluble nickel/pentane product, which was 80–90% nickel, reacted with H_2O to form ethane, propane, butane, and pentane. In another case, zirconium vapor was found to insert into C–H and C–C bonds of 2-methylpropane and 2,2-dimethylpropane to form insoluble organometallic products which generated C_1–C_4 and C_1–C_5 hydrocarbons, respectively, upon hydrolysis.[28] Reactions of 2-methylpropane with V, Ti, Cr, Mn, Fe, Ni, Co, Cu, Mo, and W were also surveyed. Zirconium was found to be the most active metal by far. A third system, in which an extensive range of hydrocarbons is formed upon hydrolysis, is the cocondensation of dimethyl and diethyl ether with calcium,[29] barium, and strontium.[30] C_1–C_8 hydrocarbons were formed from hydrolyses of these reaction products.

Results and Discussion

Ethene Reactions. Cocondensation of ytterbium, samarium, and erbium metal vapor with ethene at 77 K generates matrices which vary in color depending on the particular metal used and its concentration. The metals which are easiest to vaporize, ytterbium and samarium (vapor pressure = 10^{-2} torr at 555 and 742 °C, respectively[12]), generally form matrices which are dark brown or black. On the other hand, erbium (vapor pressure = 10^{-2} torr at 1175 °C) generally forms an orange matrix which contains brown areas where the metal is most concentrated. For each metal, after the reaction is warmed to room temperature and excess ethene is removed, a dark brown matrix remains which is insoluble in alkanes, arenes, and ethers. Complexometric metal analyses (Table I) indicate that the reaction products contain 70–80% metal.

---

(16) Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672.

(17) Power, W. J.; Ozin, G. A. *Adv. Inorg. Chem. Radiochem.* **1980**, *23*, 79 and references therein.

(18) Kasai, P. H.; McLeod, D., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 5609.

(19) Kasai, P. H.; McLeod, D., Jr.; Watanabe, T. *J. Am. Chem. Soc.* **1980**, *102*, 179.

(20) Ni: Skell, P. S.; Havel, J. J.; Williams-Smith, D. L.; McGlinchey, M. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1098.

(21) Al: Skell, P. S.; Wolf, L. R. *J. Am. Chem. Soc.* **1972**, *94*, 7919.

(22) Cr: Skell, P. S.; Williams-Smith, D. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 3337.

(23) The remaining 23 metals are briefly described in review articles,[11,24] an abstract,[25] and a government report.[26]

(24) McGlinchey, M. J.; Skell, P. S. In ref 12, p 167.

(25) Skell, P. S. *Proc. Int. Congr. Pure Appl. Chem.* **1971**, *23*, 215.

(26) Skell, P. S. Government Report No. AFOSR-75-0200; National Technical Information Service, U.S. Department of Commerce: Springfield, VA, 1975 (described in ref 11).

(27) Davis, S. C.; Klabunde, K. J. *J. Am. Chem. Soc.* **1978**, *100*, 5973.

(28) Remick, R. J.; Asunta, T. A.; Skell, P. S. *J. Am. Chem. Soc.* **1979**, *101*, 1320.

(29) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 3649.

(30) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Organomet. Chem.* **1980**, *194*, C22.

Table I. Stoichiometries, Yields, and Characterization Data

reactants	metal ingot size, g (mmol)	reaction time, min	product wt, g	% metal in product	prominent IR abs, cm^{-1}	product of reaction with $(CH_3)_3SiCl^c$
				$H_2C{=}CH_2{}^a$		
Yb	1.1 (6.4)	100	0.46	71	1865 w, 1740 w	Me_3SiH
Sm	2.3 (15.3)	60	1.05	76		
Er	2.5 (15.0)	60	0.16	70	1580 br	Me_3SiH
				$H_2C{=}C{=}CH_2{}^a$		
Yb	1.8 (10.4)	45	1.1	72	1870, 1650 br	no reaction
Sm	2.4 (16.0)	75	1.6	72	1865, 1655 br	no reaction
Er	2.0 (12.0)	35	0.8	55	1885, 1700 v br	no reaction
				$CH_3CH{=}CH_2{}^a$		
Yb	2.5 (14.4)	50	2.3	80	1860, 1650 s br, 1520	Me_3SiH $Me_3SiCH_2CH{=}CH_2$
Sm	2.3 (15.3)	70	1.6	80	1600 v br	Me_3SiH $Me_3SiCH_2CH{=}CH_2$
Er	2.9 (17.3)	60	0.62 insoluble	55	1730 w br, 1600 w br, 865	*b*
			0.10 soluble	57	1890 w, 1720 s br, 1535 w, 865 w	

[a] Approximate quantities of hydrocarbons: C_2H_4, 0.6 mol; C_3H_4, 1.8 mol; C_3H_6, 0.6 mol. [b] Trace amounts of $(CH_3)_3SiH$ and $(CH_3)_3SiCH_2CH{=}CH_2$. [c] All metal vapor products except the soluble Er/propene product (last entry of the table) reacted with CCl_4 to form $HCCl_3$.

The 20–30% of remaining organic material corresponds to a minimum of two C_2H_4 units per metal (cf. $Ln(C_2H_4)_2$ contains 73–76% Ln), if all the metal in the sample is in complexed form.[31]

Decomposition reactions indicate that a variety of ligands are present in these lanthanide vapor ethene reaction products. Hydrolytic decomposition reactions form complex mixtures of volatile organic products including CH_4, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8, C_4H_8, C_4H_{10}, traces of C_5 hydrocarbons, and as many as 10 different components in the C_6–C_{10} range. Solid polymeric products were also observed in the erbium case. The predominant hydrolytic decomposition products are listed in Table II. Decomposition reactions using D_2O were also examined for these ethene products as well as for the products described in the subsequent sections. As in the case of the chromium propene deuterolysis reactions (vide supra),[22] complex mixtures of monodeuterated, dideuterated, and multiply deuterated hydrocarbons were found in these decompositions. The deuterolysis results indicated a complex pattern of often extensive metal–carbon σ-bond formation but did not provide further insight into reaction mechanisms.

Each of the ethene reaction products was also observed to contain hydride ligands. The presence of these lanthanide hydrides[7,16] was indicated by decomposition reactions with CCl_4,[32] which formed $HCCl_3$, and with $(CH_3)_3SiCl$, which formed $(CH_3)_3SiH$ (Table I). Quantitative information was obtained on the samarium ethene product by measuring the HD generated upon deuterolysis. Four hydride ligands were found for every five metal atoms present.

Table II. Predominant Volatile Hydrolytic Decomposition Products[a]

$H_2C{=}CH_2$

	CH_4	C_2H_6	C_3H_6/C_3H_8	C_4H_8/C_4H_{10}	other minor products
Yb	3	30	15	45	C_2H_4, C_3H_4, C_5, and C_6 hydrocarbons
Sm	5	30	15	45	
Er[b]	90[b]	4		5	

$H_2C{=}C{=}CH_2$

	C_3H_6/C_3H_8	$H_2C{=}C{=}CH_2$	$CH_3C{\equiv}CH$	other minor products
Yb	30	2	60	CH_4, C_2H_4, C_5, and C_6 hydrocarbons
Sm	20	10	65	
Er	30	5	40	

$CH_3CH{=}CH_2$

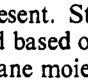
	C_3H_6/C_3H_8	$CH_3C{\equiv}CH$	other minor products
Yb	60	15	CH_4, C_2H_4, C_2H_6, C_5, and C_6 hydrocarbons
Sm	30	60	
Er (insoluble)	80	10	
Er (THF soluble)	95	2	

c-C_3H_6

	C_3H_6/C_3H_8	$CH_3C{\equiv}CH$	c-C_3H_6	other minor products
Er	45	25	30	C_2H_4, C_2H_6, C_4, C_5, and C_6 hydrocarbons

[a] Approximate relative mole per cent of volatile products. Hydrogen also is observed in all cases. [b] The predominant hydrolysis product is a polymeric solid.

Although the precise amounts of all these decomposition products vary slightly from synthesis to synthesis, some general reactivity trends can be discerned from the data obtained. First, the extensive array of hydrolytic decomposition products generated from the lanthanide ethene cocondensation products indicates that these reactions more closely resemble the nickel cluster and zirconium reactions described in the last paragraph of the Introduction than the transition metal and aluminum ethene cocondensations in which π complexes were formed. Clearly, a variety of reaction pathways are traversed in the lanthanide ethene reaction systems. Simple, stable π complexes are not predominant products since ethene is, at best, a trace product in the hydrolysis reactions. Instead, the presence of ethane suggests that σ-bonded linkages such as



or $LnCH_2CH_2Ln$, are present. Structures of this type would be expected to be favored based on Skell's results.[22,24] Since simple metallacyclopropane moieties require the lanthanide to be formally divalent, this bonding situation might be more easily achieved and stabilized with ytterbium and samarium than with erbium.[33] Indeed, ethane is formed in greater

---

(31) Quantitative determination of D_2 generated from deuterolysis of selected samples suggests that the amount of bulk metal present is less than 30% and can be as low as 5% in these reactions. For example, deuterolysis of 1.4 mmol of Sm/C_2H_4 product forms 0.55 mmol of D_2. If the sample contained only samarium metal (and, no Sm^{2+}), 2.10 mmol of D_2 would be expected, i.e., a maximum of 26% samarium metal could be present.

(32) Muetterties, E. L. "Transition Metal Hydrides"; Marcel Dekker: New York, 1971.

quantities in the ytterbium and samarium hydrolyses than in the erbium decomposition reactions. Hence, two-electron reduction of the double bond appears to be a more important reaction pathway for ytterbium and samarium than for erbium. Ytterbium and samarium are also differentiated from erbium in that they form relatively larger amounts of homologated three-carbon products and dimerized four-carbon species. The formation of four-carbon products from ethene has precedent in organolithium chemistry: 1,4-dilithiobutane can be generated from ethene and lithium in the presence of naphthalene.[35] In that case, the addition of ethene to $LiCH_2CH_2Li$ is postulated as a favorable reaction pathway which leads to charge separation and the observed $LiCH_2CH_2CH_2CH_2Li$. Hence, formation of C_4 units in the ytterbium and samarium ethene reactions is consistent with the presence of $LnCH_2CH_2Ln$ (or $(-CH_2CH_2LnCH_2CH_2Ln-)$) units.

The primary reactions of erbium with ethene are (1) fragmentation to form monocarbon species and (2) polymerization. Of all the systems examined in this study, the formation of large amounts of carbon–carbon cleavage products is most significant in the erbium ethene reaction. Ethene may be most susceptible to this reaction because it is unable to dissipate the excess energy of the hot metal atom to substituent groups. Erbium may be most active since it is vaporized at higher temperatures than the other metals or since it does not have as stable a divalent state with which to stabilize unfragmented intermediates. Another alternative explanation is that the matrix in the erbium ethene system is the most fluid and the metal atoms may be mobile enough[12] to form clusters which possess this high degree of reactivity.[27] The substantial amount of polymerization found for erbium is consistent with the fact that an erbium ethene unit is an odd-electron species, assuming the metal provides three valence electrons. In contrast, ytterbium and samarium can form predominantly even-electron metal ethene units (e.g., in σ-bonded metallacyclopropane rings) by remaining divalent.

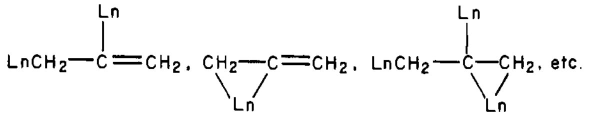
In addition to the reactions discussed above, insertion of the metal into C–H bonds occurs for each metal. The formation of the organometallic lanthanide hydride moieties in these reactions emphasizes the reactivity of the metals in this system.

1,2-Propadiene Reactions. Cocondensation of ytterbium, samarium, and erbium metal vapor with 1,2-propadiene at 77 K generates a black matrix for ytterbium and orange/black matrices for samarium and erbium. As in the ethene reactions, after the products are warmed to room temperature, they are dark brown and insoluble. The ytterbium and samarium products contain 70–75% metal (cf. LnC_3H_4, 79–81% Ln; $Ln(C_3H_4)_2$, 65–69% Ln), whereas the erbium product contains ca. 55% erbium (cf. $Er(C_3H_4)_3$, 58% Er). The infrared spectra of all three products contain strong broad absorptions at 1865–1885 and 1650–1700 cm^{-1}. In comparison, free 1,2-propadiene exhibits a carbon–carbon stretch at 1940 cm^{-1}.

Hydrolytic decomposition of the 1,2-propadiene reaction products indicates that the reactions of this larger three-carbon substrate with the lanthanide metals are less complex than the ethene reactions. The primary hydrolysis products are propene, propane, 1,2-propadiene, and propyne (Table II). CH_4, C_2H_6, and C_4–C_6 hydrocarbons are observed but are present in trace quantities only.

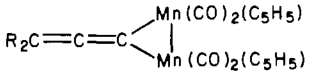
Lanthanide hydrides are also formed in these 1,2-propadiene reactions as indicated by formation of $HCCl_3$ in CCl_4 decomposition reactions. $(CH_3)_3SiCl$ does not decompose these products to a measurable extent, but deuterolysis generates HD in all three systems. Approximately one hydride ligand is found for every four metal atoms present.

As in the lanthanide ethene reactions, several reaction pathways are accessible in the lanthanide 1,2-propadiene systems. The formation of propene and propane upon hydrolysis is consistent with reduction of the double bonds via σ-bonded organolanthanide units such as



$\mathrm{LnCH_2{-}\overset{\overset{Ln}{|}}{C}{=}CH_2,\ CH_2{-}C{=}CH_2\ (\underset{Ln}{\vee}),\ LnCH_2{-}\overset{\overset{Ln}{|}}{C}{-}CH_2\ (\underset{Ln}{\vee}),\ etc.}$

This reaction was also found to be important in the ethene systems. The presence of lanthanide hydride moieties indicates that insertion of the lanthanides into the C–H bonds of propadiene is a second important reaction, which again has precedent in the ethene reaction. The recovery of 1,2-propadiene upon hydrolysis is consistent with this C–H insertion since species such as $(HLn)_2C{=}C{=}CH_2$ or $HLnCH{=}C{=}CHLnH$ could hydrolyze to 1,2-propadiene. Infrared absorptions at 1865–1885 cm^{-1} also suggest such structures by comparison with the dimetalated 1,2-propadienyl complexes



$\mathrm{R_2C{=}C{=}C\langle^{Mn(CO)_2(C_5H_5)}_{Mn(CO)_2(C_5H_5)}}$

which have ν(C–C–C) in the 1862–1887-cm^{-1} region,[36] and the dilithio complex, $LiCH{=}CH{=}CHLi$,[37] which has an absorption at 1870 cm^{-1}. In comparison, transition-metal π complexes of 1,2-propadiene have carbon–carbon stretching absorptions in the 1680–1760-cm^{-1} range.[38] The other infrared absorptions of the lanthanide propadiene product at 1650–1700 cm^{-1} overlap this latter region by 20 cm^{-1}, but since many structural types, including $Li_2C{=}C{=}CLi_2$ (ν(C–C–C) 1675),[37] absorb in this range, definitive evidence for π complexation is lacking. The small amounts of recovered 1,2-propadiene further suggest that little, if any, π-complex formation is occurring. The formation of relatively large amounts of the rearrangement product, propyne, are consistent with the stability of lanthanide alkynide intermediates,[16,39,40] $LnC{\equiv}CCH_3$, but infrared evidence for this discrete moiety is not observed. Since metalated allenyl systems, $MRC{=}C{=}CHM$, are known to form alkynes as well as 1,2-dienes upon hydrolysis,[37,41] the observed propyne may arise from a multiply metalated 1,2-diene unit such as $Ln_2C{=}C{=}CH_2$, as discussed above. Dimerization and fragmentation of carbon–carbon multiple bonds is much less common with this three carbon substrate than with ethene. Polymerization, which is common in many transition-metal 1,2-propadiene reactions,[38] is not observed in these cases.

Propene Reactions. The matrices obtained by cocondensation of ytterbium, samarium, and erbium with propene at 77 K are black, orange/black, and dark brown, respectively. The dark brown, insoluble, ytterbium and samarium products contain ca. 80% metal (cf. LnC_3H_6, 70–80% Ln). In the erbium case, however, extraction of the reaction product with THF provides a soluble complex. Both the soluble erbium complex and the remaining THF insoluble residue were characterized. The soluble and insoluble erbium products contain ca. 57% and 55% erbium, respectively (cf. $Er(C_3H_6)_3$, 57%), and complete elemental analysis of the soluble product is consistent with an empirical formula of ErC_9H_{18}.

---

[33] The order of accessibility and stability of the divalent state is Yb > Sm > Er. Ln^{3+}/Ln^{2+}: Yb, −1.04 V; Sm, −1.40 V; Er, not achieved in solution.[34]

[34] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 1007.

[35] Rautenstrauch, V. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 259.

[36] Berke, H. *J. Organomet. Chem.* **1980**, *185*, 75.

[37] West, R.; Jones, P. C. *J. Am. Chem. Soc.* **1969**, *91*, 6156.

[38] Bowden, F. L.; Giles, R. *Coord. Chem. Rev.* **1976**, *20*, 81.

[39] Ely, N. M.; Tsutsui, M. *Inorg. Chem.* **1975**, *14*, 2680.

[40] Evans, W. J.; Wayda, A. L. *J. Organomet. Chem.* **1980**, *202*, C6.

[41] Klein, J.; Becker, J. Y. *Tetrahedron* **1972**, *28*, 5385.

A variety of absorptions are found in the infrared spectra of these propene products. The ytterbium product displays a broad, strong absorption at 1650 cm^{-1} and weaker bands at 1870 and 1525 cm^{-1}. The latter absorption is characteristic of η^3-allyl ligands[42] and is in the range of previously characterized lanthanide allyl complexes.[43,44] The largest absorption in the infrared spectra of the insoluble samarium and erbium products is a single very broad band at 1600–1630 cm^{-1}. The infrared spectrum of the soluble erbium product is much better resolved, although the absorptions are still broad. The strongest band is observed at 1720 cm^{-1}, and weak absorptions are found at 1890 and 1535 cm^{-1}.

Hydrolytic decomposition of these propene products generates primarily the C_3 products, propane, propene, and propyne (Table II), with smaller amounts of dimeric C_6 species as previously reported for Er, Dy, and Tb.[24] Only trace amounts of CH_4, C_2H_6, and C_4 and C_5 hydrocarbons are observed.

The presence of lanthanide hydrides is indicated in all the propene samples by CCl_4 decomposition reactions which form $HCCl_3$. Decomposition of the ytterbium and samarium samples with $(CH_3)_3SiCl$ forms not only $(CH_3)_3SiH$, indicating hydride, but also $(CH_3)_3SiCH_2CH{=}CH_2$, consistent with the presence of allyl groups. Approximately one hydride ligand is found for every two metal atoms present by deuterolysis of these two systems. In contrast, only traces of $(CH_3)_3SiH$ and $(CH_3)_3SiCH_2CH{=}CH_2$ were found in the $(CH_3)_3SiCl$ decomposition of the erbium products.

The decomposition results for the propene reactions indicate that insertion into C–H bonds to form allyl lanthanide hydride units is a major reaction pathway with this substrate. As expected, based on the accessibility and stability of the divalent states, this oxidative addition is more easily achieved for ytterbium and samarium than for erbium. In the erbium reaction, an alternate reaction pathway, namely, reduction of the double bond, may be the more important reaction route. The formation of more propane upon hydrolysis is consistent with this alternative. The formation of propyne upon hydrolysis of these propene reaction products indicates that an additional reaction sequence must be accessible in the lanthanide metal propene reaction system. Hydrolytic formation of propyne is remarkable in that it implies that extensive dehydrogenation of the propene starting material has occurred.

The soluble erbium propene product $[ErC_9H_{18}]_n$ is similar to other soluble erbium metal vapor products derived from dienes[3] and 3-hexyne[5,6] in three respects: (1) it is highly associated in solution ($n > 10$) and has not yielded to crystallization in low molecular weight form, (2) it has a magnetic moment, 8.1 μ_B, which is lower than expected for trivalent erbium complexes (normal range 9.4–9.7 μ_B), and (3) it is much more intensely colored than the typically pale pink-orange trivalent erbium organometallics. A simple trivalent formulation consistent with the analytical and hydrolytic data such as $[Er^{3+}(C_3H_6^-)_3]_n$ would require magnetic coupling between the formally trivalent metal and the anions to reduce the magnetic moment. Such coupling has been previously proposed for bipyridyl lanthanide complexes,[45] but in the absence of further magnetic and structural data, such a postulate is very tentative.

Cyclopropane Reaction. Cocondensation of erbium metal vapor with cyclopropane at 77 K was investigated to see if this erbium system would also form a soluble product. The reaction generates a black matrix which is dark brown and insoluble at room temperature. The infrared spectrum contains a single, strong, broad absorption at 1680 cm^{-1}. Decomposition of this product with $(CH_3)_3SiCl$ forms $(CH_3)_3SiH$ and hydrolytic decomposition generates cyclopropane, propane, propene, and propyne.

This erbium cyclopropane cocondensation, like the unsaturated hydrocarbon reactions, follows several different pathways. The formation of $(CH_3)_3SiH$ from $(CH_3)_3SiCl$ and generation of cyclopropane upon hydrolysis are consistent with C–H insertion to form cyclopropyl erbium hydride groups. The presence of propane, propene, and propyne in the hydrolysis products indicates that ring cleavage occurs with considerable hydrogen migration.

Conclusion

Several reaction patterns recur in these small hydrocarbon lanthanide metal vapor reactions. The two most common reactions are two-electron reduction of unsaturated carbon–carbon bonds and oxidative addition of C–H linkages. Extensive ligand fragmentation via C–C and C–H bond cleavage, comparable to that observed for nickel clusters and zirconium atoms, can occur in specific systems, but this reactivity is not as general as the above two reactions. Oligomerization and dimerization reactions are generally less important and are more dependent on which specific metal ligand combination is examined. The most unusual reactions observed are the dehydrogenation reactions, which lead to hydrolysis products deficient in hydrogen compared to the starting material, and the homologation reactions, which generate odd-carbon products from even-carbon precursors.

Clearly, zerovalent lanthanide metals have the potential to effect a variety of interesting transformations on hydrocarbon substrates. The reactivity of the low-valent lanthanide is much more extensive than that of trivalent lanthanide complexes and suggests that this low-valent approach will be useful in developing new f element chemistry. In this study, we have defined a set of conditions under which a variety of hydrocarbon activation reactions take place in the presence of the lanthanide metals. Obviously, the challenge in this area is to control this reactivity so that it can be used selectively.

Experimental Section

The reaction products described herein are all extremely air and moisture sensitive. All manipulations were carried out with rigorous exclusion of air and water with use of high-vacuum and glovebox techniques.

Physical Measurements. Infrared spectra were obtained as Nujol mulls on NaCl plates contained in an O-ring sealed Barnes Presslok holder with use of a Perkin-Elmer 283 spectrometer. Optical spectra were obtained on a Cary 14 spectrometer using 2-mm Teflon stoppered cells. Magnetic moments were determined on a Faraday balance. Gas chromatography (GC) was performed on a Hewlett Packard 5830A equipped with a thermal conductivity detector using a 6 ft × $^1/_4$ in. 5 Å molecular sieve column and a 20% tricresylphosphate on 60/80 Chromosorb W/dimethyldichlorosilane column. Mass spectra (MS) were obtained on a Finnegan 1015 mass spectrometer. A 6 ft × $^1/_8$ in. Porapak Q column was used for the GC–MS samples. Complete elemental analyses were performed by Analytische Laboratorien, Engelskirchen, Germany. Complexometric metal analysis were carried out on samples hydrolyzed at room temperature, ashed at 500 °C, and dissolved in HCl. Analyses were conducted with hexamethyltetramine as buffer, xylenol orange as indicator, and ethylenediaminetetraacetic acid as titrant.[46]

Materials. Lanthanide metals were obtained as ingots from Research Chemicals, Phoenix, AZ, and filed to a silvery finish in a Vacuum/Atmospheres, Inc. recirculating glovebox prior to use. Reagent gases were obtained from Linde. Ethene and propene were CP grade. CCl_4 and $(CH_3)_3SiCl$ were dried over molecular sieves and vacuum degassed before use. THF was dried over potassium

---

(42) Maslowsky, E., Jr. "Vibrational Spectra of Organometallic Compounds"; Wiley: New York, 1977.

(43) Tsutsui, M.; Ely, N. *J. Am. Chem. Soc.* **1975**, *97*, 3551.

(44) Poggio, S.; Brunelli, M.; Pedretti, U.; Lugli, G., paper presented at NATO AST, Sogesta, Italy, Sept 1978.

(45) Feistel, G. R.; Mathai, T. P. *J. Am. Chem. Soc.* **1968**, *90*, 2988.

(46) Schwarzenbach, G.; Flaschka, H. "Complexometric Titrations"; Methuen: London, 1969; p 194.

benzophenone ketyl and vacuum degassed before use.

Metal Vapor Reactor. The metal vapor reactor was modeled after reactors described in the literature.[47,48] It consists of a glass test-tube-shaped bottom, 125 mm in diameter × 300 mm long, fitted with a 75-mm O-ring joint. This seals to a round stainless-steel plate, 110 mm in diameter and 10 mm thick, which contains holes for the vacuum connection, the ligand inlet tubes, and the electrodes. The apparatus is attached to a high-vacuum line by a connecting assembly consisting of a 24/40 joint, which is sealed to a 6-mm high-vacuum stopcock, which is sealed to a Kovar glass-to-metal seal, which is welded to the plate. The ligand inlet tubes are $^1/_4$-in. copper tubes which are soldered to the plate. On the outside of the reactor, each ligand inlet tube is connected to another part of the vacuum line (to which the ligand flask is attached) by a series of Cajon ultra-Torr connectors, flexible stainless-steel tubing, and a Kontes stopcock (K826600). On the inside of the reactor, the ligand inlet tubes descend to within 1 in. of the metal vapor source. At $^1/_2$-in. intervals starting at the bottom of the ligand tube, three rings of six $^1/_{16}$-in. holes are drilled around the tube circumference. One electrode is soldered to the steel plate; the other is insulated by a ceramic spacer and sealed with epoxy on both sides. The hollow $^1/_4$-in. copper electrodes are water cooled via an inner $^1/_8$-in. copper tube as in a condenser. A 1 × $^1/_2$ × $^1/_4$ in. copper block is attached to the top of each electrode to allow the attachment of the electrical leads. The bottom inch of each electrode is solid copper and contains a tapped hole for the screw which holds the tungsten coil or boat. A lava block is suspended beneath the electrodes, attached by screws which tap into the botton of each electrode. Erbium is vaporized from a tungsten wire coil basket (GTE Sylvania BC 1004) coated with alumdum cement. Samarium and ytterbium are vaporized from a tungsten boat (R.D. Mathis S20A) 0.005 in. thick.

The power source is a 0-280V Variac and a stepdown transformer which delivers 5 V at a rating of 230 A or 10 V at a rating of 115 A. Current is monitored with an Amprobe RS-2 obtained from Newark Electronics. The tungsten coil or boat is degassed prior to use by heating the evacuated system until a pressure of less than 5×10^{-4} torr is obtained.

Reaction Procedure. In a typical reaction, a layer of the hydrocarbon reagent is initially condensed on the walls of the reactor cooled to 77 K. The current in the electrodes is gradually increased until the metal begins to vaporize. The metal and hydrocarbon are cocondensed over a $^3/_4$–2 h period. After the metal has been vaporized, the reactor is warmed to room temperature while the excess ligand is removed to a 77 K trap in another part of the vacuum line. The reactor is detached from the vacuum line and brought into the glovebox. The reaction product is scraped from the reactor, weighed, and divided into portions for subsequent analysis. CCl_4 and $(CH_3)_3SiCl$ decompositions are carried out on a vacuum line by condensing a tenfold excess of these reagents along with THF or diethyl ether onto the solid metal vapor reaction product at 77 K. The flask is warmed to room temperature, and after 3–5 days, volatile reaction products are vacuum transferred to a gas collection vessel for GC analysis. Products were identified by comparison with authentic samples. Hydrolytic decomposition is accomplished by condensing H_2O (or D_2O) onto the reaction product at 77 K, allowing the reaction to warm to room temperature, and similarly analyzing the volatile products.

Table I lists typical amounts of reagents, product yields, metal analyses, prominent infrared absorptions, and nonhydrolytic decomposition results. The erbium propene system is described below in detail along with representative deuterolytic decomposition reactions.

Erbium/Propene. Erbium metal (2.9 g, 17.3 mmol) is cocondensed with propene (ca. 0.6 mol) over a 1-h period at 77 K. Extraction of the dark brown product with diethyl ether gives a faint yellow solution, but too little of this material was available for proper characterization. Extraction of the product with THF generates a red-orange solution which contains 100 mg of product upon solvent removal. Anal. Calcd for ErC_9H_{18}:Er, 56.99; C, 36.83; H, 6.18. Found: Er, 57.37; C, 36.55; H, 5.96.[49] The yield, based on metal, is 2%. Magnetic susceptibility at 295 K is $\chi_M = 27\,600 \times 10^{-6}$ ($\mu_{eff} = 8.1\ \mu_B$). The near-infrared–visible spectrum contains no maxima but rather a charge-transfer like absorption with ϵ 11 at 900 nm, ϵ 43 at 750 nm, and ϵ 110 at 650 nm. IR (cm^{-1}): 1890 w, 1720 s, br, 1535 w, 865 w. The insoluble component of this reaction product is a brown material (0.62 g, 11% yield) which contains 53% metal, has infrared absorptions at 1730 w, br, 1600 w, br, 865, and 795 cm^{-1}, reacts with CCl_4 to form $HCCl_3$, and reacts with Me_3SiCl to form traces of Me_3SiH and $Me_3SiCH_2CH{=}CH_2$.

Deuterolyses. Deuterolysis of the samarium ethene cocondensation product (0.275 g, 1.4 mmol of Sm based on the metal analysis) generated HD (1.12 mmol), D_2 (0.55 mmol), methane (0.06 mmol), ethene (0.015 mmol), ethane (0.09 mmol), 0.03 mmol of C_3 hydrocarbons, 0.03 mmol of butane, 0.12 mmol of butenes, 0.009 mmol of C_5 hydrocarbons, and less than 5 μL (ca. 0.04 mmol) of C_6 and higher hydrocarbons (10 components obseved by GC). Deuterolysis of the samarium 1,2-propadiene cocondensation product (0.610 g, 3 mmol) formed HD (0.87 mmol), D_2 (0.40 mmol), methane (0.1 mmol), ethene (0.02 mmol), ethane (0.04 mmol), propene/propane (0.16 mmol), 1,2-propadiene (0.06 mmol), propyne (0.5 mmol), and 30 μL (ca. 0.3 mmol) of C_5–C_6 hydrocarbons (five components). Deuterolysis of the samarium propene cocondensation product (0.208 g, 1.1 mmol) formed HD (0.66 mmol), D_2 (0.36 mmol), methane (0.02 mmol), ethane (0.02 mmol), propene/propane (0.12 mmol), propyne (0.24 mmol), and small amounts (ca. 0.03 mmol) of C_4, C_5, and C_6 hydrocarbons.

Acknowledgment. We thank the National Science Foundation for support of this research and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (to W.J.E.).

Registry No. $H_2C{=}CH_2$, 74-85-1; $H_2C{=}C{=}CH_2$, 463-49-0; $CH_3CH{=}CH_2$, 115-07-1; Yb, 7440-64-4; Sm, 7440-19-9; Er, 7440-52-0; c-C_3H_6, 75-19-4.

---

[47] Skell, P. S.; Wescott, L. D., Jr.; Golstein, J.-P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.

[48] Timms, P. L. *J. Chem. Educ.* **1972**, *49*, 782.

[49] Higher rates of erbium deposition form soluble products with slightly high metal content.