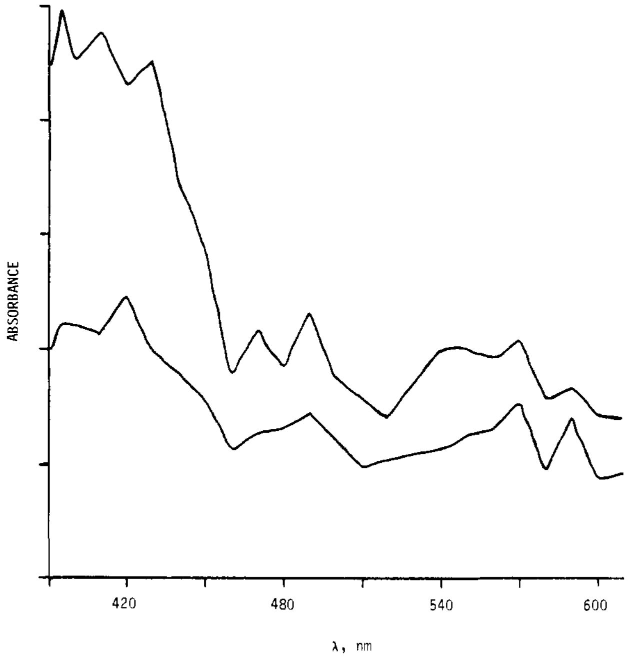


Figure 6. Transient absorption spectra obtained following laser flash excitation of **1** in water-acetonitrile.

impurity. This emphasizes the difficulty in finding a suitable relay to function on both sides of a two-absorber system not employing sacrificial reagents. Thus while for many quinone derivatives the hydroquinone formed in the "anodic" half-reaction does not hinder the buildup of oxidized substrate, it is clear that it will be difficult to find a system in which a reduced substrate is not oxidized by the quinone produced in the "cathodic" half-reaction.

Photoreaction of 1 with Water. The observation that excited states of **1** are reactive toward a number of oxygen-containing substrates prompted us to examine its potential reactivity with water. Through laser flash investigation we find that water both quenches the luminescence of **1** and results in a transient product formation even though no permanent chemical change occurs.[86] The excited-state quenching constant for water in acetonitrile is $k = 1 \times 10^7\ M^{-1}\ s^{-1}$; a transient is produced following the quenching which has the spectrum given in Figure 6. The short-lived transient[87] decays via first-order kinetics and shows general absorption in the visible range. While the spectrum produced is not sufficiently resolved to give any definitive structural information, the lack of congruence between it and that of the RuL_3^+ produced by the other quenchers makes it clear that the quenching is *not* a redox process. Since there appears to be little or no net decomposition upon irradiation of a pure water-acetonitrile solution of **1**, it appears that the photoreaction does not likely involve gross reorganization or decomposition of the complex such as might be expected by water attack at a metal-ligand center.[57-61] It appears much more reasonable that a reversible water attack on the ligand is the origin of the quenching; here again a reasonable possibility appears that the enhanced ligand basicity in the CT excited state can result in a protonation either at a ligand carbon or, more likely, at the oxygen of a carboxy ester group. In parallel with the reduced species, the analogy can be drawn between the charge-transfer excited state and a metal-oxidized ligand radical anion; although interaction with the solvent can furnish a path for nonradiative decay via transient product formation, the interaction does not result in any permanent chemical conversion.

Summary

The results of the present study demonstrate that ligand substituents can produce a variety of effects on the photoreactions of these ruthenium complexes both by "tuning" the redox and excited-state properties of the complex and by providing specific sites for interaction of the complex with solvent or other reagents. The laser flash examination of the complex photoreduction with tertiary amines has demonstrated clearly the occurrence of a mechanism previously suggested by indirect kinetic and ESR spectroscopic evidence; direct observation of the various steps in the process and their importance permit an evaluation of inefficiencies in the overall conversion and sources of energy wastage. The observations made with different oxygen compounds as quencher-reductants for these ruthenium(II) complexes suggest that the range of photoredox reactions available for metal complexes of this or related families should be greatly expandable; while no net chemical conversion occurs in the specific cases examined, it is reasonable to expect that suitable oxygen or other heteroatom-based reductants can be found which lead to net reductive quenching processes analogous to those obtained with amines. Finally, the interactions of both the excited metal complexes and their reduction products with water in nonredox processes occurring at ligand sites suggest the existence of a rich chemistry initiated through ligand-based interactions that has been hitherto unexplored.

---

(86) In neutral aqueous solutions hydrolysis of **1** is extremely slow.

(87) The transient lifetime is 250 ns.

Reactivity of Lanthanide Metals with Unsaturated Hydrocarbons: Terminal Alkyne Reactions[1]

William J. Evans,*[2] Steven C. Engerer, and Kraig M. Coleson

Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois 60637.
Received May 26, 1981

Abstract: The reactions of ytterbium, samarium, and erbium metal vapor with neutral unsaturated hydrocarbons containing acidic hydrogen have been investigated by cocondensation of the metals with 1-hexyne at 77 K followed by isolation and physical and chemical characterization of the organolanthanide products at room temperature. For ytterbium, oxidative addition of the terminal C–H bond of the alkyne is facile, and divalent alkynide hydride complexes are the primary products. Samarium and erbium react with 1-hexyne to form trivalent alkynide hydrides. The catalytic activity of these alkynide hydrides in hydrogenation reactions is also described.

During the past few years we have been investigating[3-8] 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

0002-7863/81/1503-6672$01.25/0

complexes and to provide a basis for seeking unusual catalytic transformations which involve the 4f elements. We have used the metal vaporization technique,[9-13] in which metal vapor and a substrate are cocondensed at low temperature, to examine zerovalent lanthanide metal reactivity. These studies have demonstrated that the lanthanide metals interact with a variety of unsaturated hydrocarbons, including alkenes,[8] dienes,[3] and internal alkynes,[5,6] to form preparative scale quantities of new classes of isolable, organolanthanide complexes.[14]

As part of this general study of the interaction of lanthanide metals with unsaturated hydrocarbons, we have investigated the reaction of these metals with unsaturated substrates which contain weakly acidic hydrogen. These reactions allow us to evaluate the viability of oxidative addition of C–H to a lanthanide metal center as a competitive reaction pathway to direct complexation of the metal with the unsaturated carbon–carbon bond. We describe here reactions of 1-hexyne with lanthanide metals which demonstrate that (1) oxidative addition of C–H does occur, (2) the overall reaction is more complex than a simple oxidative addition, (3) products with different stoichiometries and oxidation states are obtained from this reaction depending on the particular lanthanide metal employed, and (4) this approach to lanthanide chemistry provides easy access to soluble lanthanide complexes containing metal/ligand combinations not readily obtained by traditional reaction pathways.

Results and Discussion

Ytterbium. Cocondensation of ytterbium metal vapor with 1-hexyne at −196 °C generates a black matrix which, after warming to room temperature, neither polymerizes nor dissolves in the excess 1-hexyne present. Removal of 1-hexyne leaves a black solid, which is insoluble in pentane and toluene. Extraction of the black solid with diethyl ether forms a purple solution which contains one of the major products, I. Extraction of the remaining ether-insoluble material with tetrahydrofuran (THF) allows isolation of a second major purple product, II, and leaves a small amount of an insoluble black residue. The solids isolated from these purple solutions subsequently display partial solubility in less polar solvents. Extraction of I with toluene gives a purple product, Ia, which has been characterized separately from the remaining diethyl ether soluble material, Ib.

Ia, Ib, and II are similar in many respects. First, complete elemental analyses for each of these products are consistent with the empirical formula $(YbC_9H_{14})_n$. Second, magnetic susceptibility measurements indicate that, in each case, ytterbium is present predominantly as Yb^{2+} with only 8–15% Yb^{3+} present.[17] Third, each complex has a strong infrared absorption in the 2020–2040-cm^{-1} region, which is characteristic of terminal alkynides.[18-21] Fourth, the chemical reactions of each complex (vide infra) indicate the presence of hexynide and hydride ligands.[22]

The main difference among Ia, Ib, and II apparently is solubility, a result which may be due to the differences in the extent of oligomerization. Isopiestic molecular weight studies indicate that these complexes are highly associated in solution, i.e., *n* is large in the above formula. Such behavior has been observed previously in other lanthanide/alkyne systems[5,6] and so far has prevented us from obtaining crystals suitable for X-ray structural analysis. The oligomerization may occur via alkynide bridges (vide infra), since recent studies of bis(cyclopentadienyl)lanthanide alkynide complexes indicate that the alkynide ligand has a strong tendency to form bridged structures. For example, the ytterbium complexes $[(C_5H_5)_2YbC{\equiv}CR]_x$ ($R = C_4H_9, C_6H_{13}$), neither of which could be isolated in crystalline form, were found to have *x* values of 2.5 and 3, respectively, on the basis of cryoscopic molecular weight studies.[20] The erbium complex $[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2$ was found to exist as a dimer in THF[21] rather than as a monomeric THF solvate, as is common for dicyclopentadienyl lanthanide alkyl[23,24] and halide[25] complexes. Furthermore, an X-ray crystallographic study of $[(C_5H_5)_2ErC{\equiv}C\text{-}C(CH_3)_3]_2$[26] shows that it crystallizes from THF as an alkynide-bridged dimer.

The ytterbium complexes Ia, Ib, and II were further characterized by examining the products of their chemical decomposition reactions. Decomposition of Ia and Ib with CCl_4 and $(CH_3)_3SiCl$ indicates the presence of both alkynide and hydride ligands. $HCCl_3$ is obtained from the CCl_4 reaction[27] and $(CH_3)_3SiH$ and $(CH_3)_3SiC{\equiv}CC_4H_9$ from the $(CH_3)_3SiCl$ decomposition. With the latter reagent, quantitative decomposition reactions indicate an alkynide:hydride ratio of at least 3:1. The formula $[Yb(C{\equiv}CC_4H_9)_{1.5}H_{0.5}]_n$ is consistent with the analytical, magnetic, and chemical data presented. Further support for this formulation was obtained by studying quantitative deuterolytic decomposition reactions. Deuterolysis of the ether-soluble I and the THF-soluble II generated 85% and 70%, respectively, of the expected $DC{\equiv}CC_4H_9$, and 85% of the expected HD in each case. Deuterolysis of the insoluble ytterbium–1-hexyne reaction residue also formed $DC{\equiv}CC_4H_9$ and HD, although in lower yield. D_2 was also observed in all of these deuterolyses, consistent with the presence of Yb^{2+}.[28] An analogous deuteride complex was prepared from Yb and $DC{\equiv}CC_4H_9$ to further establish the presence of hydride in these reactions. Upon **hydrolysis**, this complex formed the expected products, HD and H_2. Comparison of the IR and NMR[22] spectra of the hydride and deuteride complexes did not allow definitive assignment of a hydride infrared stretch or NMR absorption.

These data indicate that the reaction of ytterbium vapor with 1-hexyne involves more than a simple oxidative addition of $H{-}C{\equiv}CC_4H_9$ to the metal center (eq 1). This initial oxidative

$$Yb + HC{\equiv}CC_4H_9 \rightarrow H{-}Yb{-}C{\equiv}CC_4H_9 \tag{1}$$

---

(1) Presented in part at the Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 1980; Abstract 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) Evans, W. J.; Coleson, K. M.; Engerer, S. C. *Inorg. Chem.*, in press.

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

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

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

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

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

(14) Preparative-scale lanthanide metal vapor studies of cyclooctatetraenyl[15] and acetylacetonate[16] complexes have also been reported.

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

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

(17) A χ_M value of 8400×10^{-6} for Yb^{3+} was used in this calculation.

(18) Ely, N. M.; Tsutsui, M. *Inorg. Chem.* **1975**, *14*, 2680.

(19) Deacon, G. B.; Koplick, A. J. *J. Organomet. Chem.* **1978**, *146*, C43.

(20) Fischer, R. D.; Bielang, G. *J. Organomet. Chem.* **1980**, *191*, 61.

(21) Evans, W. J.; Wayda, A. L. *J. Organomet. Chem.* **1980**, *202*, C6.

(22) The NMR spectra of these complexes also indicate the presence of hexynide ligands, but the three observed resonances are too broad for definitive assignment based on coupling constants. The broadening may be due either to the presence of small amounts of Yb^{3+} in the sample or to the existence of multiple alkynide environments.

(23) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54.

(24) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 292.

(25) Maginn, R. E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 672.

(26) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.*, in press.

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

(28) The observed yields of D_2 were inexplicably lower than those expected: I, 42%; II, 20%.

addition product, $HYbC{\equiv}CC_4H_9$, is coordinatively unsaturated and would be expected to react further to increase its coordination. This could be accomplished via a ligand redistribution reaction, a type of reaction common in f element chemistry.[29,30] Equation 2 is one such reaction which accounts for the observed product.

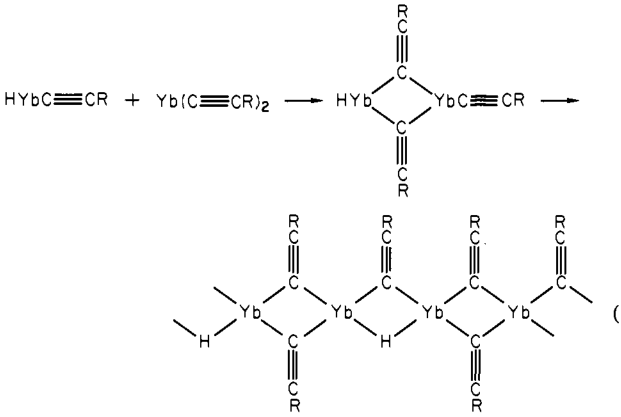
$$3HYbC{\equiv}CC_4H_9 \rightarrow HYb_2(C{\equiv}CC_4H_9)_3 + [YbH_2] \quad (2)$$

No evidence for YbH_2 or ytterbium metal, formed from decomposition of YbH_2, is observed, however. Reaction 2, therefore, would require that the YbH_2 would be completely consumed in some subsequent reaction such as reaction with additional 1-hexyne to form H_2 and $HYbC{\equiv}CC_4H_9$.

A more attractive reaction sequence for the initially formed $HYbC{\equiv}CC_4H_9$ is reaction with additional 1-hexyne to form $Yb(C{\equiv}CC_4H_9)_2$ (eq 3) and subsequent coupling of this bis-

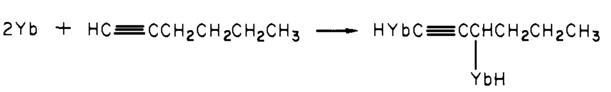
$$HYbC{\equiv}CC_4H_9 + HC{\equiv}CC_4H_9 \rightarrow H_2 + Yb(C{\equiv}CC_4H_9)_2 \quad (3)$$

(alkynide) intermediate with $HYbC{\equiv}CC_4H_9$ to form the final observed product (eq 4, R = C_4H_9). Subsequent oligomerization of this product would serve to futher increase the coordination around the ytterbium as shown in eq 4. Reactions 3 and 4 involve structures with precedence in the literature. Bis(alkynide)ytterbium complexes have previously been reported,[19] and, as discussed above, there is crystallographic evidence which supports the tendency of alkynide ligands to form bimetallic bridged structures.[26]



(4)

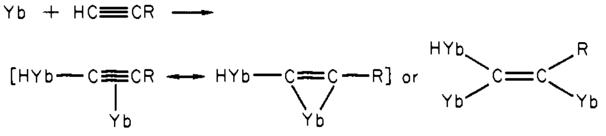
In this study, we were particularly interested in determining the importance of competitive reaction pathways which involved sites of reactivity other than the terminal C–H bond of the alkyne. One alternative reaction was additional metalation at the α-CH_2 group (reaction 5). A high metal to ligand ratio would be



$$2Yb + HC{\equiv}CCH_2CH_2CH_2CH_3 \rightarrow HYbC{\equiv}C\underset{\displaystyle YbH}{\underset{|}{C}}HCH_2CH_2CH_3 \quad (5)$$

expected to favor such a reaction. Indeed, when ytterbium was rapidly vaporized (3 g, 0.5 h) into the 1-hexyne matrix, broad infrared absorptions at 1840 and 1730 cm^{-1} were observed in addition to the predominant $\nu(C{\equiv}C)$ absorption at 2000–2040 cm^{-1}. Absorptions similar to these lower frequency bands have been observed previously in multiply lithiated derivatives of alkynes. In the specific case of propyne, such absorptions have been attributed to rearranged allenyl forms of the di-, tri-, and tetralithiated propyne.[31,32] For a direct comparison in the 1-hexyne case, the reaction of excess *tert*-butyllithium with 1-hexyne in hexane was examined. The hexane-soluble product, III, exhibited very intense broad absorptions at 1855 and 1745 cm^{-1}. Deuterolysis of III gave primarily dideuterated 1-hexyne, $DC{\equiv}CHDCH_2CH_2CH_3$, with smaller amounts of the mono- and trideuterated species. Comparison of the intensities of the 1840- and 1730-cm^{-1} absorptions of the ytterbium 1-hexyne product with the intensity of the $\nu(C{\equiv}C)$ band and the intensities observed for III suggested that the amount of multiply metalated products in the ytterbium reaction is small. Deuterolysis studies supported this contention. The 1-hexyne obtained by deuterolysis of I and II contains only trace amounts of dideuterated product on the basis of NMR and GC/MS analysis.

A second alternative reaction site for ytterbium atoms in their reaction with 1-hexyne is the multiple bond. Ytterbium addition to the triple bond via π complexation of a single metal or 1,2-addition of two metals (eq 6), would form organometallics which would be expected to generate $D_2C{=}CDC_4H_9$ upon deuterolysis. Indeed, 1-hexene is observed as a minor deuterolysis product, and GC/MS analysis of the 1-hexene so obtained showed it to be trideuterated.



(6)

In summary, in the ytterbium–1-hexyne reaction, the data suggest that the predominant reactions involve the terminal C–H bond as shown in eq 1, 3, and 4. Alternative reaction pathways such as α-CH_2 metalation and addition to the triple bond appear to be accessible, but are less important for this lanthanide.

Samarium. Cocondensation of samarium with 1-hexyne at 77 K forms a matrix which varies in color from orange to black depending on the concentration of metal. The brown-black solid left after warming the reaction to room temperature and removing the excess 1-hexyne is insoluble in pentane, toluene, and diethyl ether. Most of the reaction product dissolves in THF, however, to form a brown solution of a samarium complex, IV. Following removal of THF by rotary evaporation, IV is totally soluble in pentane. IV is formulated as a trivalent alkynide hydride, e.g., $[Sm(C_6H_9)_2H]_n$, on the basis of complete elemental analysis, magnetic susceptibility measurement, and D_2O, $(CH_3)_3SiCl$, and CCl_4 decomposition reactions which form $DC{\equiv}CC_4H_9$ and HD, $(CH_3)_3SiC{\equiv}CC_4H_9$ and $(CH_3)_3SiH$, and $HCCl_3$, respectively. The infrared spectrum of IV contains a strong absorption at 2040 cm^{-1} assignable to $\nu(C{\equiv}C)$ of 1-hexynide, but it also consistently contains broad lower frequency absorptions at 1865 and 1760 cm^{-1}, as were observed in the ytterbium reaction involving rapid deposition of the metal. In the samarium case, these low-frequency absorptions are more intense than in the ytterbium case, and clearly, the samarium reaction is not as clean as the ytterbium system.[33] Analysis of the products formed by deuterolysis of IV supports this contention. Although the 1-hexyne obtained upon deuterolysis is primarily monodeuterated, it is recovered in only 40% yield in this case. Small amounts (3%) of C_2, C_3, C_4, and C_5 fragmentation products are observed,[8] and the remainder of the organic decomposition products are oligomeric species. The yield of HD formed upon deuterolysis, 25%, was also low. On the basis of these chemical decomposition data, and the infrared spectrum, the formula of IV might be better represented as $[Sm(C_6H_9)_{2-x}(C_6H_8)_xH_{1-x}]_n$ $(0 < x < 0.5)$ to account for the increased amount of dimetalation with this metal. Like the ytterbium alkynides, IV also is a high molecular weight species, and an alkynide-bridged oligomeric structure is presumably present.

The more complex nature of the samarium reaction compared to the ytterbium case can be understood by comparing the relevant properties of the two metals. First, the divalent oxidation state of samarium is more reactive than that of ytterbium: Ln^{3+}/Ln^{2+} reduction potentials are −1.50 and −1.10 V, respectively.[34] Second, samarium is larger than ytterbium. In a comparably coordinated complex, samarium will be less coordinatively saturated and, hence, more reactive. If the initial reaction involves oxidative addition

---

[29] Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Organomet. Chem.* **1980**, *192*, 65.

[30] Ernst, R. D.; Kennelly, W. J.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2656.

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

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

[33] As in the ytterbium case, neither IR nor NMR provided signals definitively attributable to the hydride.

[34] Morss, L. R. *Chem. Rev.* **1976**, *76*, 827.

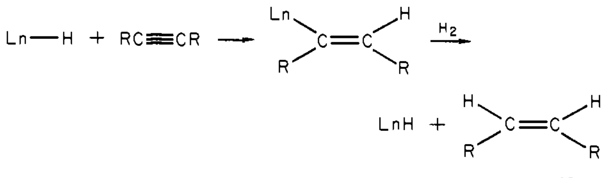
of $HC{\equiv}CC_4H_9$ to samarium to form $HSmC{\equiv}CC_4H_9$ (analogous to eq 1), this product would be expected to be much more reactive than $HYbC{\equiv}CC_4H_9$. There also may be alternative reaction pathways which lead directly to trivalent products (vide infra).

Erbium. The metal vapor reaction of erbium with 1-hexyne is similar in many respects to the samarium reaction. The matrix varies in color from orange to black at low temperature, and a brown product is obtained when the reaction is warmed to room temperature. The crude reaction product is insoluble in pentane, toluene, and diethyl ether but dissolves readily in THF. Removal of THF from this solution leaves a brown solid, V, which is subsequently soluble in pentane. Complete elemental analysis, magnetic susceptibility measurement, and chemical decomposition with $(CH_3)_3SiCl$ and CCl_4 are consistent with a formula for V which is analogous to IV, namely $[Er(C_6H_9)_{2-x}(C_6H_8)_xH_{1-x}]_n$. The infrared spectrum of V is also similar to that of IV, containing strong absorptions at 1875 and 1770 cm^{-1} in addition to the strong terminal alkynide absorption at 2060 cm^{-1}.

Hence, the reaction of erbium with 1-hexyne, like that of samarium, is more complex than the ytterbium reaction. This is not unexpected for several reasons. If the reaction proceeds initially by two-electron oxidative addition, the intermediate, $HErC{\equiv}CC_4H_9$, would be expected to be extremely reactive, since Er^{2+} is much less stable than Sm^{2+} or Yb^{2+}. The Er^{3+} to Er^{2+} reduction potential is estimated to be −2.96 to −3.1 V.[34] Alternatively, if the reaction proceeds via a direct three-electron oxidation of erbium via two-electron oxidative addition of the terminal C–H bond of the alkyne, a complex reaction involving at least three reactants is required.

The reaction of erbium vapor with $DC{\equiv}CC_4H_9$ further indicates the complex nature of this reaction. Only 40% of the expected noncondensible gas is evolved upon hydrolysis, and rather than analyzing as pure HD, a substantial amount of H_2 is present. This is consistent with the formation of erbium hydrides via metalation at the α-CH_2 as discussed above for samarium. There are also similarities to the samarium reaction in the organic hydrolysis products. Although 1-hexyne is still the primary product, it is recovered in lower than expected yield, 25%. A substantial amount of insoluble material is also formed upon hydrolysis in this erbium system.

Catalysis. The catalytic activity of these alkynide hydride complexes was surveyed by using the hydrogenation of 3-hexyne as a test reaction. Catalytic hydrogenation of 3-hexyne at room temperature under 1 atm of hydrogen occurred in the presence of complexes IV and V. 3-Hexene is the primary hydrogenation product and is found to be >96% *cis*-3-hexene. Small amounts of hexane are also formed. The rates of these catalyses are low, however, (2–4) × 10^{-3} turnovers/min. Faster lanthanide-catalyzed hydrogenation rates were observed with the products of cocondensation reactions of lanthanide metals with 3-hexyne.[5,6] The hydrogenation of 3-hexyne by IV and V can be readily explained by addition of the hydride to the unsaturated bond and hydrogenolysis of the resulting alkenyl complex (eq 7). Both reactions have precedent in alkali metal organometallic chemistry,[35-38] and the hydrogenolysis has been previously observed with both lanthanide[39] and actinide[40] alkyls.



(7)

Conclusion

The reactions described above demonstrate several important conclusions regarding the utility of metal vapor synthesis in organolanthanide chemistry. First, organic substrates with C–H bonds as acidic as terminal alkynes will oxidatively add to zerovalent lanthanide metals under these reaction conditions. The oxidative addition is more favored than the formation of a π complex between the unsaturated bond and the lanthanide metal. Two-electron reduction of the unsaturated bond (via a π metallocyclopropene complex or via two separate metal centers) and oxidative addition of weakly acidic carbon–hydrogen bonds (e.g., the α-CH_2 bonds) are less favored, alternative reaction pathways which vary in importance depending on the specific lanthanide involved. Second, the initially formed C–H oxidative addition product is coordinatively unsaturated and consequently reactive. Unless an extremely large organic group, R, is used in the oxidative addition of R–H to an elemental lanthanide, the product is likely to be more complex than the simple H–Yb–R oxidative addition product. Third, these reactions are highly dependent on the particular metal used in the reaction. It is clear that the lanthanide metals cannot be viewed simply as a homologous series of chemically similar metals when their zerovalent chemistry is considered. Fourth, the metal vapor reaction provides a useful route to lanthanide hydrides. We have recently prepared organolanthanide hydrides by solution methods,[39] but the synthesis of stable, soluble trivalent species in high yield has not been easy. In contrast, the metal vapor technique allows good yields of soluble hydride complexes. Moreover, in the ytterbium case, the metal vapor synthesis provides the first divalent organolanthanide hydride complexes. We anticipate that other new classes of organolanthanide complexes will be similarly accessible in the future by using this low-valent metal vapor approach to f element chemistry.

Finally, the results of this study emphasize the differences between zerovalent lanthanide chemistry and zero valent transition-metal chemistry. The reactions of terminal alkynes with transition-metal vapor invariably form oligomeric and polymeric organic species and rarely form isolable organometallic complexes.[9-13,41-45] The formation of alkynide hydrides from lanthanide metal vapor clearly indicates that the zero valent chemistry of these elements is distinct from that of the transition metals.

Experimental Section

The reaction products described herein are all extremely air and moisture sensitive. All manipulations are carried out with rigorous exclusion of air and water by using high-vacuum and glove-box techniques.

Physical Measurements. Infrared spectra are obtained as Nujol mulls on NaCl plates contained in an O-ring sealed Barnes Presslok holder by using a Perkin-Elmer 283 spectrometer. Optical spectra are obtained on a Cary 14 spectrometer using 2-mm Teflon-stoppered cells. Magnetic moments are obtained in solution by the Evans method[46] by using a Bruker 270-MHz spectrometer. Gas chromatography is performed on a Hewlett-Packard 5830A equipped with a thermal conductivity detector using a 6 ft × 0.25 in. 5-Å molecular sieve column and a 20% tricresyl phosphate on 60/80 Chromosorb W/dimethyldichlorosilane column. Yields of volatile products are determined with pentane or hexane as an internal standard. Mass spectra are obtained on a Finnegan 1015 mass spectrometer. Complete elemental analyses are performed by Analytische Laboratorien, Postfach 1249, 5250 Engelskirchen, Germany. Complexometric metal analyses are carried out on samples hydrolyzed at room temperature, ashed at 500 °C, and dissolved in HCl. Analyses are conducted with hexamethyltetramine as buffer, xylenol orange as indicator, and ethylenediaminetetraacetic acid as titrant.[47] Molecular

---

(35) Gilman, H.; Jacoby, A. L.; Ludeman, H. *J. Am. Chem. Soc.* **1938**, *60*, 2336.

(36) Podall, H. E.; Petree, H. E.; Zietz, J. R. *J. Org. Chem.* **1959**, *24*, 1222.

(37) Clauss, K.; Bestian, H. *Liebigs Ann. Chem.* **1962**, *654*, 8.

(38) Slaugh, L. H. *Tetrahedron* **1966**, *22*, 1741.

(39) Evans, W. J.; Wayda, A. L.; Bloom, I. and Coleson, K. M. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, Georgia, March, 1981; INOR 219.

(40) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939.

(41) Simons, L. H.; Lagowski, J. J. *J. Org. Chem.* **1978**, *43*, 3247.

(42) Simons, L. H.; Lagowski, J. J. In "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M.; Ishii, Y. Ed.; Plenum Press: New York, 1978; Vol. 2, p 73.

(43) Mixed-ligand metal cocondensation reactions involving a metal, an alkyne, and CO[44] or C_5H_6[45] have yielded isolable alkyne carbonyls and alkyne cyclopentadienyls, respectively.

(44) Klabunde, K. J.; Groshens, T.; Brezinski, M.; Kennelly, W. *J. Am. Chem. Soc.* **1978**, *100*, 4437.

(45) Freeman, M. B.; Hall, L. W.; Sneddon, L. G. *Inorg. Chem.* **1980**, *19*, 1132.

(46) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Becconsall, J. K. *Mol. Phys.* **1968**, *15*, 129.

weights are determined in THF by an isopiestic method with a Signer apparatus (SGA Scientific Inc.) modified for air-sensitive compounds by attaching greaseless high-vacuum stopcocks to each side. Ferrocene purified by sublimation was used as the standard.

Materials. Lanthanide metals are obtained as ingots from Research Chemicals, Phoenix, AZ, and filed to a silvery finish in a Vacuum/Atmospheres, Inc. recirculating glove box prior to use. 1-Hexyne is obtained from Chemical Samples Co., Columbus, OH, and dried over molecular sieves which have been activated by heating overnight under vacuum. CCl_4 and $(CH_3)_3SiCl$ are dried over molecular sieves and vacuum transferred before use. THF and toluene are dried over potassium benzophenone ketyl and vacuum transferred before use. Diethyl ether is heated to reflux over lithium aluminum hydride and vacuum transferred before use. Pentane is washed free of olefins with concentrated sulfuric acid, dried over magnesium sulfate, heated to reflux over lithium aluminum hydride, and vacuum transferred before use.

Metal Vapor Reactor. The metal vapor reactor is modeled after reactors described in the literature.[48,49] 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 0.5-in. intervals starting at the bottom of the ligand tube, three rings of six $^1/_{16}$-in. holes are drilled around the 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 × 0.5 × 0.25 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 bottom of each electrode. The metal is vaporized from either a tungsten wire coil basket (GTE Sylvania BC 1004) coated with alumdum cement or a tungsten boat (R. D. Mathis S20A) 0.005 in. thick.

The power source is a 0–280-V 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 1-hexyne 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 1-hexyne are cocondensed over a 0.75–2 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 products are isolated as described below.

$(YbC_9H_{14})_n$, I. Cocondensation of Yb metal (2.6 g, 15.0 mmol) and 1-hexyne (115 mL, 1000 mmol) as described above gives after removal of excess 1-hexyne a black residue which is insoluble in pentane and toluene. Extraction of this black solid with diethyl ether gives a purple solution containing one of the major products, I (0.25 g, 0.86 mmol, 6% based on Yb vaporized[50]). Following removal of the ether by rotary evaporation, approximately half of I is soluble in toluene. The remainder is still soluble in diethyl ether. The purple solids remaining after removal of solvent from these solutions have been designated Ia and Ib, respectively. Anal. Calcd for YbC_9H_{14}: Yb, 58.61; C, 36.61; H, 4.78. Found for Ia: Yb, 57.56; C, 36.44; H, 4.76. Found for Ib: Yb, 57.36; C, 36.64; H, 4.63. Mol wt, calcd for $(YbC_9H_{14})_8$: 2360. Found for Ia: 2300. Calcd for $(YbC_9H_{14})_{32}$: 9440. Found for Ib: 9300. IR (cm^{-1}) 2020, 2040 (sharp unresolved doublet found for both Ia and Ib). Magnetic susceptibility, $10^6\chi_M$ (cgs): Ia, 1280; Ib, 690. Near-IR–vis: The visible spectrum of I was dominated by a charge-transfer band extending into the near-infrared. A broad peak rises out of this band at λ = 525 nm.

II. THF extraction of the solid remaining after the removal of I gives a purple solution containing the second major product. Removal of THF gives a purple solid, II[51] (2.40 g, 8.14 mmol, 54% based on Yb vaporized[50,52]). Anal. Calcd for YbC_9H_{14}: Yb, 58.61; C, 36.61; H, 4.78. Found for II: Yb, 58.15; C, 36.47; H, 4.95. IR (cm^{-1}) 2020 s, 1850 w, br, 1740 w, br. Magnetic susceptibility, $10^6\chi_M$ (cgs): 1260. Near-IR–VIS: A charge-transfer-like absorption dominates the spectrum as in I. A shoulder is observed at 525 nm and a small peak is observable at 985 nm due to the small amounts of Yb^{3+} present.

$(SmC_{12}H_{19})_n$ IV. Cocondensation of Sm metal and 1-hexyne as described above generates a brown solid which is insoluble in pentane, toluene, and diethyl ether. Extraction with THF gives a brown solution which contains the major product, IV. Following removal of solvent, IV is found to be soluble in pentane. As in the ytterbium reaction,[52] the yield is found to be dependent on rate of metal deposition and metal/ligand ratio. Vaporization of 1.8 g (12.0 mmol) of Sm in 30 min yields 1.35 g (4.3 mmol) of IV, 35% yield. Vaporization of 0.9 g (6.0 mmol) of Sm in 80 min yields 0.92 g (2.9 mmol) of IV, 50% yield. Anal. Calcd for $SmC_{12}H_{19}$: Sm, 47.94; C, 45.95; H, 6.11. Found for IV: Sm, 48.22; C, 46.02; H, 6.10. IR (cm^{-1}) 2040 m, 1865 s, br, 1765 m, br. Magnetic susceptibility, $10^6\chi_M$ (cgs): 1100. Near-IR (nm) 1090, 1250, 1385, 1510.

$(ErC_{12}H_{19})_n$, V. Cocondensation of Er metal and 3-hexyne as described above generates a product which is insoluble in pentane, toluene, and ether. Extraction with THF gives a brown solution which contains the major product, V. As in the samarium reaction, following removal of solvent V is found to be soluble in pentane. Anal. Calcd for $ErC_{12}H_{19}$: Er, 50.60; C, 43.60; H, 5.79. Found for V: Er, 50.34; C, 43.79; H, 5.79. IR (cm^{-1}) 2055 s, 1870 s, br, 1770 w, br. Magnetic susceptibility, $10^6\chi_M$ (cgs): 31 700.

Decomposition Reactions. CCl_4 and $(CH_3)_3SiCl$ decompositions are carried out on a vacuum line by condensing a 10-fold excess of these reagents into a THF solution of the 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.

I, II, IV, and V produce $CHCl_3$ on decomposition with CCl_4. Decomposition of I, II, IV, and V with $(CH_3)_3SiCl$ produces $(CH_3)_3SiH$ and $(CH_3)_3SiC{\equiv}CC_4H_9$, identified by comparison with authentic samples.

Hydrolytic decomposition is accomplished by condensing an excess of H_2O or D_2O onto the solid reaction product at 77 K and allowing the reaction to warm to room temperature. Gaseous products are collected in two fractions on a Toepler pump. The first fraction, which passes through a liquid N_2 trap, contains hydrogen and methane. The second fraction, which passes through a dry ice/2-propanol trap, contains C_2–C_5 hydrocarbons. The remaining volatile products are vacuum transferred to another flask and all three fractions are analyzed by GC.

Deuterolysis of I (138 mg, 0.47 mmol) generates 0.2 mmol of HD, 0.1 mmol of D_2, less than 0.01 mmol of C_1–C_5 hydrocarbons, 0.61 mmol of 1-hexyne an 0.08 mmol of 1-hexene. This gives 85% of the theoretical amount of hydride and 98% of the theoretical amount of C_6H_9. NMR and MS analysis of the 1-hexyne indicates that it is $DC{\equiv}CC_4H_9$, with only 2–3% deuteration of the α-CH_2 position.

Deuterolysis of II (784 mg, 2.65 mmol) generates 1.12 mmol of HD, 0.28 mmol of D_2, 0.02 mmol of C_1–C_5 hydrocarbons, 2.72 mmol of 1-hexyne, and 0.87 mmol of 1-hexene. This gives 85% of the theoretical amount of hydride and 90% of the theoretical amount of C_6H_9. NMR and MS analyses of the 1-hexyne indicate that it is $DC{\equiv}CC_4H_9$, with only 2–3% deuteration at the α-CH_2 position. NMR and MS analyses of the 1-hexene indicate that it is $D_2C{=}CDC_4H_9$.

Deuterolysis of IV (368 mg, 1.17 mmol) generates 0.3 mmol of HD, 0.03 mmol of C_1–C_5 hydrocarbons (50% 1-butene), 0.90 mmol of 1-hexyne, and 0.07 mmol of 1-hexene. This constitutes 25% of the theoretical amount of hydride and 40% of the theoretical amount of C_6H_9. NMR analysis of the 1-hexyne indicates that it is completely deuterated at the terminal hydrogen and 40% deuterated at the α-CH_2 position. NMR analysis of the 1-hexene shows deuteration of all the olefinic positions. Pentane extraction of the involatile residue from this deuterolysis yields 80 mg of a yellow oil of low volatility. The IR spectrum of

---

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

(48) Skell, P. S.; Wescott, L. D., Jr.; Golstein, J.-P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.

(49) Timms, P. L. *J. Chem. Educ.* **1972**, *49*, 782.

(50) The relative amounts of I and II vary. In some cases, I is the major product, and in other cases I and II are produced in roughly equal amounts.

(51) II frequently becomes less soluble in THF after initial solvent removal. The insoluble portion retains the other characteristics of II, however.

(52) The total yield of I and II is 60% on the basis of metal vaporized. If the vaporization rate is lower, e.g., 0.9 g in 60 min instead of 2.6 g in 30 min, the yield is higher. For example, in one case 0.9 g (5.2 mmol) of Yb yielded 1.4 g (4.75 mmol) of total product, a 90% yield.

J. Am. Chem. Soc. **1981**, *103*, 6677-6685

this oil contains absorptions characteristic of conjugated polyenes.

Hydrolysis of the analogue of V prepared from Er and $DC\equiv CC_4H_9$ (175 mg, 0.53 mmol) generates 0.21 mmol of H_2, 0.02 mmol of HD, 0.09 mmol of C_1–C_5 hydrocarbons, 0.06 mmol of 1-hexene, and 0.27 mmol of 1-hexyne. This gives 40% of the theoretical amount of hydride of which 10% is deuteride and 30% of the theoretical amount of C_6H_9.

Catalytic Hydrogenation. In a typical experiment, 0.1 mmol of the compound to be studied is dissolved in 5 mL of toluene (or THF, if the compound is insoluble in toluene) in a 70-mL tube fitted with a greaseless high-vacuum stopcock. 3-Hexyne (1 mL, 9 mmol) is added, and the system is attached to a high-vacuum line. Hydrogen (~750 torr, room temperature) is added, and the solution is magnetically stirred. Approximate hydrogenation rates are obtained by monitoring the drop in hydrogen pressure. Products are analyzed by GC. IV and V are catalytically active in this system, hydrogenating 3-hexyne to greater than 96% *cis*-3-hexene at a rate of 0.002–0.004 turnovers/min. Other products are *trans*-3-hexene, 2%, and hexane, 2%. I and II are not catalytically active under these conditions over a 2 week period.

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.).

Use of Silyloxydienes in Synthesis. Total Syntheses of the Sesquiterpene (±)-Seychellene

Michael E. Jung,*[1] Charles A. McCombs, Yukiko Takeda, and Yuh-Guo Pan

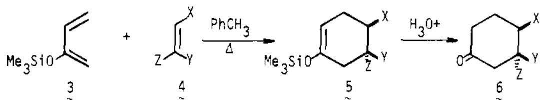
Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024. Received March 5, 1981

Abstract: 2-Silyloxy-1,3-dienes, e.g., **3**, can be prepared from the corresponding enones and undergo facile Diels–Alder cycloaddition with typical dienophiles. The cyclic enol silyl ethers thus produced, e.g., **5**, can be readily converted into several functionalized ketone derivatives, e.g., 7. By starting with 2,3-dimethylcyclohex-2-enone (**12**), one can produce rapidly, via the 2-silyloxydiene **13**, bicyclo[2.2.2]octane systems in which the endo isomer **16** generally predominates over the exo isomer **17**. These bicyclo[2.2.2]octane systems permit one to prepare the structurally interesting sesquiterpene (±)-seychellene (**1**) by two general procedures. The methyl vinyl ketone adduct **16b** was converted into a 1:1 mixture of the isomeric bromo ketones **22b** and **23b** which were cyclized to norseychellanone (**2**) and epinorseychellanone (**25**). Conversion of **2** into seychellene (**1**) completed a nonstereoselective 10-step synthesis with an overall yield of 20%. Alternatively, the divinyl ketone adduct **16c** was transformed into the tricyclic dione **26** by a Lewis acid-promoted internal Michael addition in 31% yield. This dione could be converted with a high stereoselectivity (80:20) into a mixture of **2** and **25**. Completion of this route produced seychellene **1** via seven steps in an overall yield of 9%.

Introduction

(−)-Seychellene (**1**), a plant sesquiterpene isolated from patchouli oil, has been often used as a model compound on which to test new general methods of synthesis because of its interesting tricyclic structure.[2-4] Seven syntheses[5-11] have been reported since the pioneering work of Piers in 1969,[5] and several other routes to the substituted tricyclo[5.3.1.0^{3,8}]undecane ring system have been described.[12] From the outset of our work in this area, we envisioned a rapid synthesis of the tricyclic system involving essentially only two operations, namely, a Diels–Alder cycloaddition between a 3,4-dimethyl-2-silyloxycyclohexa-1,3-diene (i) and a vinyl ketone (ii) to produce as the major product the adduct iii which would then be converted into the tricyclic system, e.g., norseychellanone (**2**), by an intramolecular cyclization. We now report the full details of our work,[13] including a very much improved procedure for the intramolecular Lewis-acid-catalyzed Michael addition of a silyl enol ether to a vinyl ketone.

Table I. Preparation and Hydrolysis of the Diels–Alder Adducts of 3



	X	Y	Z	yield, %	hydrolysis, %
a	COMe	H	H	60	81
b	CO_2Me	H	H	35	99
c	CO_2Me	H	CO_2Me	71	95
d	CO_2Et	H	CO_2Et	77	100
e	CO_2Et	CO_2Et	H	39	*a*

[a] No yield determined.

Results and Discussion

Simple Silyloxydienes.[14] Before beginning the work on seychellene itself, we first investigated the preparation and reactions

---

(1) Camille and Henry Dreyfus Teacher-Scholar, 1978–83; Fellow of the Alfred P. Sloan Foundation, 1979–81.

(2) Tsubake, N.; Nishimura, K.; Hirose, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 597.

(3) Wolff, G.; Ourisson, G. *Tetrahedron Lett.* **1968**, 3849; *Tetrahedron* **1969**, *25*, 4903.

(4) Guenther, E. "The Essential Oils", Van Nostrand: New York, 1949; Vol. IIID.

(5) Piers, E.; de Wall, W.; Britton, R. W. *Chem. Commun.* **1969**, 1069; *J. Am. Chem. Soc.* **1971**, *93*, 5113.

(6) Schmalzl, K. J.; Mirrington, R. N. *Tetrahedron Lett.* **1970**, 3219. Mirrington, R. N.; Schmalzl, K. J. *J. Org. Chem.* **1969**, *34*, 2358; **1972**, *37*, 2877.

(7) Fukamiya, N.; Kato, M.; Yoshikoshi, A. *Chem. Commun.* **1971**, 1120; *J. Chem. Soc., Perkin Trans. 1*, **1973**, 1843.

(8) Frâter, G. *Helv. Chim. Acta* **1974**, *57*, 172; **1979**, *62*, 1893.

(9) Jung, M. E.; McCombs, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 5207.

(10) Yamada, K.; Kyotani, Y.; Manabe, S.; Suzuki, M. *Tetrahedron* **1979**, *35*, 293.

(11) Jung, M. E.; Pan, Y.-G. *Tetrahedron Lett.* **1980**, 3127.

(12) (a) Spitzner, D. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 197; *Tetrahedron Lett.* **1978**, 3349. (b) White, K. D.; Reusch, W. *Tetrahedron* **1978**, *34*, 2439.

(13) Preliminary communications; see ref 9 and 11.

(14) (a) Preliminary communication: Jung, M. E.; McCombs, C. A. *Tetrahedron Lett.* **1976**, 2935. (b) See also: Jung, M. E.; McCombs, C. A. *Org. Synth.* **1978**, *58*, 163.

0002-7863/81/1503-6677$01.25/0