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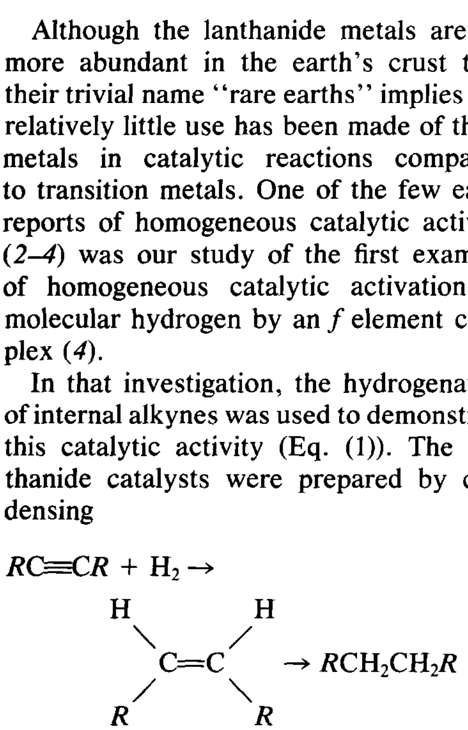
Catalytic Activation of Molecular Hydrogen in Alkyne Hydrogenation Reactions by Lanthanide Metal Vapor Reaction Products

Although the lanthanide metals are far more abundant in the earth's crust than their trivial name "rare earths" implies (*1*), relatively little use has been made of these metals in catalytic reactions compared to transition metals. One of the few early reports of homogeneous catalytic activity (*2–4*) was our study of the first example of homogeneous catalytic activation of molecular hydrogen by an *f* element complex (*4*).

In that investigation, the hydrogenation of internal alkynes was used to demonstrate this catalytic activity (Eq. (1)). The lanthanide catalysts were prepared by condensing lanthanide metal vapor with 3-hexyne at −196°C by the metal vapor technique (*5*) (Eqs. (2) and (3)).



$$RC{\equiv}CR + H_2 \rightarrow \underset{R}{\overset{H}{C}}{=}\underset{R}{\overset{H}{C}} \rightarrow RCH_2CH_2R \quad (1)$$

$$\mathrm{Ln} + CH_3CH_2C{\equiv}CCH_2CH_3 \rightarrow \mathrm{LnC_6H_{10}} \quad (\mathrm{Ln{=}Sm,Yb}) \quad (2)$$

$$\mathrm{Ln} + CH_3CH_2C{\equiv}CCH_2CH_3 \rightarrow \mathrm{LnC_9H_{15}} \quad (\mathrm{Ln{=}Er}). \quad (3)$$

Since our initial report (*4*), we have examined the catalytic behavior of a number of additional lanthanide metal vapor systems. We report here the synthesis and catalytic activity of these complexes.

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 using Schlenk, high vacuum line, and inert atmosphere glove box (Vacuum/Atmospheres, HE-43 Dri-Lab) techniques.

Materials

Lanthanide metals were obtained as ingots from Research Chemicals, Phoenix, Arizona, and filed to a silvery finish in the glove box prior to use. Tetrahydrofuran (THF) and toluene were distilled from solutions of potassium benzophenone ketyl. Pentane, hexane, heptane, and methylcyclohexane were washed with sulfuric acid, dried over magnesium sulfate, refluxed over lithium aluminum hydride, and vacuum transferred. 3-Hexyne was obtained from Chemical Samples Company, Columbus, Ohio, dried over molecular sieves which had been activated by heating overnight under vacuum, and vacuum transferred before use. Bis(trimethylsilyl)acetylene (BTMSA) was obtained from Petrarch Systems Inc., Levittown, Pennsylvania, and was dried similarly. Diphenylacetylene was obtained from Aldrich (Milwaukee, Wisc.) and used without further purification. Triphenylphosphine was obtained from Aldrich and recrystallized from benzene. CCl_4 was dried over molecular sieves and vacuum degassed before use. Research grade hydrogen, 99.9995%, was obtained from

0021-9517/83 $3.00

Air Products and Chemicals, Hillside, Illinois.

Physical Measurements

Infrared spectra were obtained as Nujol mulls on NaCl plates contained in an O-ring sealed Barnes Presslok holder using a Perkin–Elmer 283 spectrometer. Optical spectra were obtained on a Cary 14 spectrometer using 2-mm Teflon stoppered cells. ^{1}H NMR spectra were obtained on a Bruker 270-MHz spectrometer. ^{13}C and ^{31}P NMR spectra were obtained on a Bruker 90-MHz spectrometer. Magnetic moments were obtained in solution by the Evans method (*6*) using the 270-MHz spectrometer. Gas chromatography was performed on a Hewlett–Packard 5830A equipped with a thermal conductivity detector using a 6-ft × ¼-in. 5A molecular sieve column and a 20% tricresylphosphate on 60/80 Chromosorb W/dimethyldichlorosilane column. Mass spectra were obtained on a Finnegan 1015 mass spectrometer. A 6-ft × ⅛-in. Porapak Q column was used for the GC-MS (gas chromatography-mass spectral) samples. Complete elemental analyses were performed by Analytische Laboratorien, Postfach 1249, 5250 Engelskirchen, Germany. Complexometric metal analyses were carried out on samples hydrolyzed at room temperature, ashed at 500°C, and dissolved in HCl. Analyses were conducted using hexamethylenetetramine as buffer, xylenol orange as indicator, and 0.01 *M* Na_2 EDTA solution as titrant.

Metal Vapor Reaction Procedure

The static metal vapor reactor and its usage with volatile cocondensation reagents has been described previously (*7*, *8*). In addition to the static reactor, a rotary metal vapor reactor was used in this study. It was built from a Büchi/Brinkmann Rotavapor R modified for high vacuum according to plans kindly provided by Professor P. L. Timms. The rotary evaporator was modified by replacing the condensor with a brass housing which (a) provides a high vacuum seal to the steam pipe, (b) provides the connection to the pumping system, and (c) holds the electrodes in place. The reactor bottom for this system consisted of a 45/50 outer ground glass joint attached to either a 1- or 2-liter round bottom flask via 46-mm glass tubing (7¾ in. and 5⅝ in. long, respectively). Located ½ in. from the joint is a side arm consisting of a greaseless high vacuum right angle stopcock (Kontes K926600) mounted ¾ in. from the wall of the bottom such that the length of the Teflon valve is perpendicular to the length of the reactor bottom and parallel with the wall of reactor bottom. The end of the stopcock which is not attached to the reactor bottom is modified to hold a septum cap. The size of the entire reactor is such that it will fit in the antechamber of a Vacuum/Atmospheres HE-43 Dri-Lab without removing the sliding tray. This design allows the reaction products to be worked up without using septum/syringe techniques.

In a typical reaction, a methylcyclohexane solution of reagent (5% weight/volume) was prepared in the glove box in a 500-ml single neck round bottom flask fitted with a straight stopcock, a septum cap, and a nitrogen inlet. After the space above the stopcock was evacuated and refilled with nitrogen six times, a cannula was inserted through the septum and connected to the nitrogen flushed septum inlet of the reactor bottom. The reagent solution was pressured from the flask into the reactor which previously had been resistively heated until a pressure of less than 6×10^{-4} Torr was attained. The solution was cooled to −123°C with a petroleum ether slush bath and degassed. When the pressure reached 4×10^{-4} Torr or less, resistive heating of the tungsten coil was started.

Synthesis of Catalysts

Cocondensation of erbium metal atoms with 3-hexyne generates three products of formula ErC_9H_{15} differentiated by their solubilities in hexane, **1**, toluene, **2**, and THF, **3**. The synthesis and characterization of these products has previously been described (*5, 9*). SmC_6H_{10}, **5,** and YbC_6H_{10}, **6,** were prepared from 3-hexyne (*5, 9*), $ErC_{12}H_{19}$, **8,** was prepared from 1-hexyne (*7*), and $Er(C_6H_{10})_2$, **10,** was prepared from 2,3-dimethylbutadiene (*10*) as previously described.

Lutetium/3-hexyne, **4.** Cocondensation of lutetium metal (1.5 g, 8.6 mmol) and 3-hexyne (100 ml, 880 mmol) generated a brown solid, which when warmed to room temperature was slightly soluble in the excess 3-hexyne. The reactor was taken into the glove box, and the reaction product was successively extracted with pentane, toluene, and THF. These solvents were removed by rotary evaporation leaving light brown solids of roughly equal amounts (total yield of soluble product: 1.1 g, 40% based on the original weight of metal used). Anal. Calcd for LuC_9H_{15}: Lu, 58.68; C, 36.25; H, 5.07. Found for THF soluble **4**: Lu, 55.68; C, 38.17; H, 5.91. ir (Nujol, cm^{-1}) 2120 (s, br), 1585 (m), 1300 (w), 1250 (w), 1190 (s, br), 1070, (w, sh), 1010 (s, br), 965 (w), 920 (w), 860 (m). The NMR spectrum in C_6D_6 consisted of several featureless humps too broad to be structurally informative.

Neodymium/3-hexyne, **7.** Cocondensation of neodymium metal (2.5 g, 17.3 mmol) and 3-hexyne (100 ml, 880 mmol) generated a dark brown solid which was insoluble in the excess 3-hexyne when warmed to room temperature. In the glove box, the product was found to be insoluble in pentane, and only slightly soluble in toluene. Extraction with THF gave 0.57 g of a brown solid. This solid did not remain completely soluble in THF, however, and a second extraction was necessary to obtain totally soluble material, **7.** (0.4 g, 35% based on measured 0.6 g metal vaporized). Anal. Calcd for NdC_9H_{15}: Nd, 53.93; C, 40.42; H, 5.65. Found: Nd, 51.29; C, 42.92; H, 5.33. ir (Nujol, cm^{-1}) 2040 (w), 1865 (s, br), 1740 (s, br), 1690 (m, sh), 1540 (w, sh), 1305 (w), 1250 (m, br), 1060 (w), 1030 (m), 970 (m), 920 (w), 870 (m), 780 (w),750 (s).

Samarium/$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$, **9.** Vaporization of samarium (2.6 g, 17.3 mmol) into a solution of bis(trimethylsilyl)acetylene, BTMSA, (25 g, 147 mmol) in methylcyclohexane (500 ml) generated a black solid which was insoluble in methylcyclohexane, toluene, and diethyl ether. Extraction with THF gave a dark brown solution, which upon removal of solvent by rotary evaporation yielded a brown solid, **9.** Virtually all of the reaction product was soluble in THF (2.3 g, 90% based on metal vaporized). Anal. Calcd for $Sm_2C_{12}H_{27}Si_2$: Sm, 56.93; C, 27.28; H, 5.15; Si, 10.63. Found: Sm, 56.27; C, 27.03; H, 5.11; Si, 10.57. ir (Nujol, cm^{-1}): 1750 (s, v br), 1560 (w, sh), 1240 (s), 1070 (w, sh), 1030 (s), 965 (w), 910 (w), 840 (s, br), 750 (m), 660 (m). $\chi_M^{296\,K} = 1210 \times 10^{-6}$; $\mu_{eff} = 1.7$ B.M. The near infrared visible spectrum of **9** was dominated by a charge-transfer-like band. Extinction coefficients were measured at several wavelengths along this band: 1200 nm, 30; 1600 nm, 10. Broad peaks were observed in the near ir at 1090, 1250, 1380, and 1490 nm.

An erbium slurry, **11,** was prepared by vaporizing erbium into pentane. The product had no solubility in THF.

Samarium/$P(C_6H_5)_3$, **12.** Vaporization of samarium metal (3.0 g, 20 mmol) into a solution of $P(C_6H_5)_3$ (15 g, 57 mmol) in methylcyclohexane (300 ml) at −120 ± 5°C in a rotary reactor generates a blue solution which becomes black within approximately 5 min. After 1 hr, the reaction was stopped and the reactor was warmed to room temperature, detached from the vacuum line, and taken into the glove box. The black solution was filtered through a 350-ml medium porosity frit leaving the black, hydrocarbon insoluble product. This material was washed with toluene to remove unreacted phosphine and then extracted with THF. Removal of THF from the brown-black solution gave 3.6 g of a brown powder (90% based on samarium vaporized). Anal. Calcd for $Sm_2[P(C_6H_5)_2](C_6H_5)H_4$: Sm, 53.03; P, 5.46; C, 38.13; H, 3.38. Found: Sm, 52.53; P, 5.20; C, 38.00; H, 3.53. Found: Sm, 51.14; P, 5.22; C, 37.13; H, 3.68. Found: Sm, 50.10; P, 7.13; C, 38.64; H, 3.65. Isopiestic molecular weight in THF: 1400. The magnetic susceptibility was measured to be $\chi_M^{296\,K} = 1580 \times 10^{-6}$, $\mu_{eff} = 1.95$ B.M. The ^{1}H NMR spectrum in C_4D_8O contained a broad resonance at δ7.3 ppm. The near ir-VIS spectrum exhibited a strong charge transfer band starting at 1630 nm. ir (Nujol, cm^{-1}): 1950 (w), 1880 (w), 1810 (w), 1575 (s), 1435 (s), 1367 (s), 1300 (w), 1175 (m), 1150 (m), 1065 (m), 735 (m), 690 (s).

The product described above (0.8 g, 5.3 meq of Sm) was hydrolyzed by condensing degassed H_2O (1 ml) onto the powder at 77 K. Extraction of the organic products with $CDCl_3$ formed a solution of $(C_6H_5)_2PH$, identified by ^{1}H NMR (δ7–7.4, 5.06 (J_{PH} = 220 Hz) ppm) and its subsequent air oxidation to $(C_6H_5)_2P({=}O)OH$ (δ8.9 ppm) (*11*). Extraction of the hydrolysis product with xylene and GC analysis revealed the presence of benzene.

Deuterolysis of the samarium triphenylphosphine product (0.58 g, 2 meq of Sm) was accomplished by condensing degassed D_2O (1 ml) onto the powder in a vacuum flask attached to a Toepler pump. The gas produced (0.44 mmol) was analyzed by GC as HD (0.21 mmol) and D_2 (0.23 mmol).

In another decomposition reaction, CCl_4 was condensed onto the samarium phosphine reaction product in THF at 77 K. After reacting 1 day, $HCCl_3$ was identified by GC-MS analysis.

Ytterbium/P(C₆H₅)₃, **13.** Vaporization of ytterbium metal (2.6 g, 15 mmol) into a solution of $P(C_6H_5)_3$ (7.3 g, 28 mmol) in methylcyclohexane (150 ml) at −120 ± 5°C generated a black solution within a few minutes. Vaporization was continued for ¼ hr and the reaction was subsequently handled as described above for samarium. The product was again soluble in THF forming a green-black solution. Removal of THF left a black powder (0.36 g, 8% based on starting Yb). Anal. Calcd for $Yb_3[P(C_6H_5)_2](C_6H_5)_2H_4$: Yb, 60.21; P, 3.59; C, 33.44; H, 2.81. Found: Yb, 58.60; P, 5.40; C, 32.57; H, 3.12. Found: Yb, 60.64; P, 3.77; C, 32.57; H, 3.30. Isopiestic molecular weight in THF: 1120, $\chi_M^{296\,K} = 1790 \times 10^{-6}$; $\mu_{eff} = 2.0$ B.M. The ^{1}H NMR spectrum in $CD_3C_6D_5$ (**13** is soluble in arenes after treatment with THF) exhibited a broad peak at δ7.06 ppm. The near ir-VIS spectrum contained a strong charge transfer band starting at 1200 nm. ir (Nujol, cm^{-1}): 1955 (w), 1885 (w), 1815 (w), 1575 (w), 1435 (s), 1430 (m), 1375 (s), 1308 (w), 1180 (w), 1155 (w), 1090 (m), 1060 (w), 740 (s), 695 (s).

Hydrolysis of the ytterbium product formed $(C_6H_5)_2PH$ and C_6H_6 which were isolated and identified as described above for samarium. Deuterolysis of the ytterbium product (52 mg, 0.18 meq Yb) formed HD (0.08 mmol) and D_2 (0.04 mmol). Reaction of CCl_4 with the ytterbium product formed $HCCl_3$.

Lanthanum/3-hexyne, **14.** Cocondensation of lanthanum metal (2.1 g, 15.1 mmol) and 3-hexyne (100 ml, 880 mmol) generated a brown solid which when warmed to room temperature was insoluble in the excess 3-hexyne. The reactor was taken into the glove box and the reaction product was found to be insoluble in pentane and toluene. Extraction with THF gave a brown solution, which upon removal of solvent by rotary evaporation yielded a brown solid, **14** (0.15 g). ir (Nujol, cm^{-1}): 2040 (w), 1865 (s, br), 1750 (s, br), 1690 (s, br), 1550 (m), 1310 (w), 1260 (w), 1060 (w, sh), 1030 (s), 970 (w), 870 (w), 760 (s). In the presence of **14** in THF, catalytic hydrogenation of 3-hexyne to 10% hexane and 90% 3-hexene which was 84% *cis* was observed to occur at rates similar to system **3.**

Samarium/C₆H₅C≡CC₆H₅, **15.** Vaporization of samarium (4.3 g, 28.6 mmol) into a solution of $C_6H_5C{\equiv}CC_6H_5$ (10.3 g, 57.8 mmol) in heptane (500 ml) generated a black solid which was insoluble in the heptane. Extraction with toluene and removal of solvent by rotary evaporation yielded a brown solid (0.44 g, 5%). Anal. Calcd for $SmC_{42}H_{30}$: Sm, 21.95; C, 73.64; H, 4.41. Found: Sm, 23.15; C, 72.27; H, 4.31. Extraction of the remaining product with THF left 1.1 g insoluble material and a second soluble brown product (0.86 g, 10%). Anal. Calcd for $SmC_{21}H_{15}$: Sm, 36.00; C, 60.38; H, 3.62. Found: Sm, 33.00; C, 63.01; H. 4.20. ir (Nujol, cm^{-1}, similar for both products): 3050 (w), 3020 (w), 1950 (w), 1875 (w), 1805 (w), 1750 (w), 1575 (s, br), 1490 (sh), 1440 (s), 1310 (s, br), 1170 (m), 1155 (w), 780 (w), 760 (s), 700 (s), 670 (w). For the THF soluble product, $\chi_M^{296\,K} = 3000 \times 10^{-6}$, $\mu_{eff} = 2.7$ B.M. The visible spectrum was dominated by a charge transfer band extending into the near infrared. Extinction coefficients at several wavelengths along this band were: 1200 nm, 175; 1600 nm, 35. Broad peaks were observed in the near infrared at 1265 and 1510 nm.

Catalytic Hydrogenation

In a typical experiment, 0.1 mmol of the lanthanide metal vapor product was dissolved in 5 ml of solvent and placed in a 70-ml tube fitted with a greaseless high vacuum stopcock. 3-Hexyne (1 ml, 9 mmol) (or another substrate) was added, and the tube was attached to a high vacuum line, cooled to −196°C, and evacuated. The tube was warmed to room temperature and hydrogen (750 Torr, room temperature) was added. The solution was magnetically stirred as the drop in pressure was monitored on a manometer. At the end of a run, hydrogenation products were vacuum transferred to another vessel and analyzed by GC. The rates and product yields of the various systems examined are listed in Tables 1 and 2.

RESULTS AND DISCUSSION

As shown in Tables 1 and 2, the reactions of lanthanide metal vapor with alkynes, dienes, and phosphines generate a variety of new complexes which have the capacity to catalytically activate molecular hydrogen in hydrogenation reactions. As described previously (*5*, *9*), attempts to characterize the metal vapor reaction products by the physical methods commonly used for organometallic complexes, i.e., NMR spectroscopy and X-ray crystallography, have been hampered by the paramagnetic nature of the complexes and their tendency to oligomerize under crystallization condi-

TABLE 1

Catalytic Hydrogenation of 3-Hexyne under Ambient Conditions

System	Lanthanide metal/ cocondensation reagent	Solvent	Rate turnovers/metal/min	Percent conversion	Percent hexane	Percent of *cis* isomer in 3-hexene
1	Er/3-hexyne	neat	0.02	100	0	96
2	Er/3-hexyne	toluene	0.02	99	3	96
3	Er/3-hexyne	THF	0.002–0.003	93	1	99
4	Lu/3-hexyne	neat	0.02	100	10	99
5	Sm/3-hexyne	THF	0.008	25	0	96
				35	0	95
6	Yb/3-hexyne	THF	0.005			99
7	Nd/3-hexyne	THF	0.0045	100	7	93
				100	20	75
8	Er/1-hexyne	toluene	0.0025–0.0035			
9	Sm/BTMSA	THF	0.0005	100	7	83
10	Er/DMB	THF	0.0005	100	11	—
11	Er slurry	neat	0.0002	50	0.5	—
12	Sm/$P(C_6H_5)_3$	THF	0.0002	—	—	>95
13	Yb/$P(C_6H_5)_3$	THF	0.00005	—	—	>95

TABLE 2

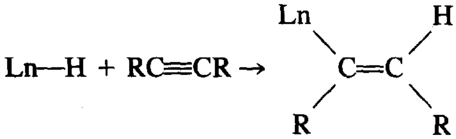
Catalytic Hydrogenation of Other Substrates

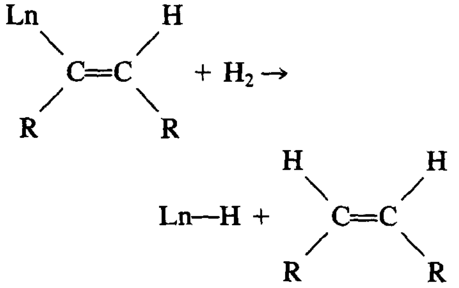
System	Lanthanide metal/ cocondensation reagent	Substrate	Solvent	Rate	Percent conversion	Product
1	Er/3-hexyne	3-hexene	neat	0.002	98	hexane
2	Er/3-hexyne	$C_6H_5C{\equiv}CC_6H_5$	toluene	0.0015	100	50% 1 : 2 *cis* : *trans* stilbene 50% diphenylethane
10	Er/DMB	DMB	toluene	0.001	47	70% 2-butene, 2% butane
					92	75% 2-butene, 10% butane

tions. Information on the ligand components in these products is obtainable by infrared spectroscopy and hydrolytic decomposition, but a particular structure is not specified by these data. Discussions of the precise nature of the C_6 ligands in the 3-hexyne products, **1–7**, and the 2,3-dimethylbutadiene product, **10**, have already been presented (*9, 10*). Characterization of the erbium 1-hexyne product, **8**, as $[HEr(C_6H_9)_2]_n$ has also been described (*7*). The triphenylphosphine reaction products, **12** and **13**, are best described as $Ln_a[P(C_6H_5)_2]_b(C_6H_5)_cH_d$ complexes. These compounds are presumably formed by initial insertion of the lanthanide metal into a P–C bond to form a divalent diphenylphosphido phenyl complex, $(C_6H_5)_2PLnC_6H_5$, which subsequently abstracts hydride. The P–C cleavage reaction (*12*), the oxidation of the lanthanide metal vapor to the divalent state (*7, 8, 13*) and the hydrogen abstraction reaction (*7, 8, 13–16*) all have precedent in the literature.

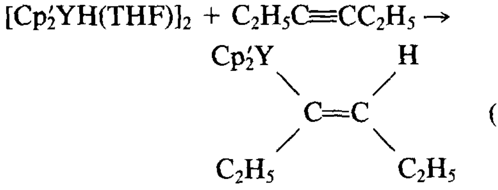
Several generalizations on the catalytic activity of lanthanide metal complexes in hydrogenation reactions are suggested by the data in the tables. These can best be evaluated by considering a simple reaction sequence for catalytic hydrogenation involving *cis*-1,2 addition of Ln–H to the unsaturated bond followed by hydrogenolysis (Eqs. (4)–(6)):

$$Ln{-}R + H_2 \rightarrow Ln{-}H + RH \qquad (4)$$

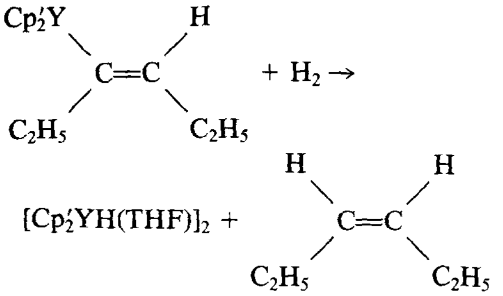

(5)


(6)

Hydrogenolysis of a metal alkyl bond (Eq. (4)) is a well established organometallic reaction for *f* orbital metals (*17, 18*) as well as for transition metals (*19*) and alkali and alkaline earth metals (*20*). 1,2 addition of a metal hydride to an unsaturated hydrocarbon (Eq. (5)) is also a well-documented reaction in the literature (*21–23*). The 1,2 addition pathway is particularly applicable to systems in which a two electron oxidative-addition reductive-elimination route is not accessible. The final step in the catalysis (Eq. (6)) is of course a special case of M–*R* hydrogenolysis. With regard to lanthanide catalysis, it is noteworthy that Eqs. (4) and (5) have been demonstrated in the stepwise fashion shown above with the crystallographically characterized hydride $[(CH_3C_5H_4)_2YH(THF)]_2$, **16** (eqs. (7), (8); Cp′ = $CH_3C_5H_4$) (*17, 24*).



(7)



(8)

Complex **16** is a catalyst for *cis* hydrogenation of 3-hexyne with a rate of 0.0025 turnovers/metal/min (*24*).

One trend obvious in the 3-hexyne reaction products, **1**–**7**, is that the rate of hydrogenation is slower in THF solvent. Systems **1**, **2**, and **4** run neat or in toluene are the fastest catalysts in this series. In studies of the hydrogenolysis of $[(RC_5H_4)_2YCH_3]_2$ and $(RC_5H_4)_2YCH_3(THF)$ (*24*; R = H or CH_3) we have found that the degree of coordination unsaturation and solvation are important factors in determining the rate of hydrogen addition to the metal methyl bond. Hydrogenolysis occurs most rapidly when a coordinatively unsaturated, unsolvated species such as $(RC_5H_4)_2YCH_3$ is accessible. All three of equations (4)–(6) could be inhibited by THF solvation of the lanthanide center leading to a slower rate. Therefore, if the above mechanism were operative, the observed solvent dependence of the rate would be reasonable. Hydralumination of alkynes is also found to occur more slowly in THF (*22*). It is interesting to note that Er/3-hexyne is found to be more highly associated in THF than in arene or alkyne solvents. Hence, the observed rate trend is also consistent with the degree of association (which may be related to the degree of coordinative unsaturation) of the catalyst independent of the role of THF in solvating the metal center.

A second trend discernible from the 3-hexyne products is that the rates do not vary regularly with the size of the metal. Metallic radius decreases monotonically with increasing atomic number of the lanthanide and often can be used to explain the small variances in chemistry within the series (*25*). For the 3-hexyne systems run in THF, the order of decreasing radial size is **7**, **5**, **3**, **6**, whereas the order of decreasing rate is **5**, **6**, **7**, **3**. Therefore, size factors seem less important in determining rates in this system.

Another interesting trend is that the complexes which contain significant amounts of chemically identifiable hydride, **8**, **12**, **13**, and **16**, do not have the fastest rates. Complexes **12** and **13** have the slowest rates in this series and the rates of **8** and **16** are comparable to the slower rates of the Ln/3-hexyne/THF systems. Since hydrogenolysis (Eq. (4)) is a common reaction with lanthanide metal complexes (*17*, *24*), the presence of hydride in the starting catalyst is not necessary for activity according to Eqs. (5) and (6). It is possible that all the systems studied hydrogenate by Eqs. (4)–(6) and the hydride forming step is not rate determining.

Alternatively, it is possible that the products containing substantial amounts of hydride proceed via Eqs. (4)–(6) and the other systems hydrogenate by a completely different mechanism. Related to this, the enediyl complex $[(C_5Me_5)_2Sm](C_6H_5)C{=}C(C_6H_5)[Sm(C_5Me_5)_2]$, formed from $(C_5Me_5)_2Sm(THF)_2$ (*13*) and $C_6H_5C{\equiv}CC_6H_5$, is observed to catalytically hydrogenate alkynes faster than the corresponding hydride $[(C_5Me_5)_2SmH]_2$ (*26*). It is interesting to note that this enediyl, although formally a Sm(III) complex, does not have the yellow or orange color characteristic of Sm(III). Instead it is black due to an intense charge-transfer-like absorption in the near infrared visible region. The metal vapor products described here also fail to have the colors and absorption spectra characteristic of the simple trivalent ions and are intensely colored brown-black due to a strong charge-transfer-like absorption.

A more complete understanding of the precise mechanism(s) of catalytic hydrogenation of alkynes and alkenes by lanthanide metal vapor products depends on obtaining more definitive structural information on the complexes involved and more kinetic data. Our preliminary survey study does indicate that catalytic reaction chemistry is available to these metals in a wide range of coordination environments. As this field becomes more fully developed, and the trends in reactivity better understood, the diversity in metal and in coordination environment available within the lanthanide series can be more fully exploited.

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William J. Evans[1]
Ira Bloom
Steven C. Engerer

Departments of Chemistry
University of California
Irvine, California 92717, and
University of Chicago
Chicago, Illinois 60637

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[1] Camille and Henry Dreyfus Teacher–Scholar; Alfred P. Sloan Research Fellow; to whom correspondence should be addressed at the University of California, Irvine, Calif. 92717.