

## Homogeneous Catalytic Activation of Molecular Hydrogen by Lanthanoid Metal Complexes†

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**Summary** Co-condensation of lanthanoid metal atoms with internal alkynes generates the first lanthanoid complexes which are capable of homogeneous catalytic activation of molecular hydrogen.

ALTHOUGH the lanthanoid series contains fourteen available metals, few examples of catalytic activity based on these elements have been discovered.<sup>1</sup> Homogeneous catalyses involving the lanthanoids are particularly rare.<sup>2</sup> As part of our programme to investigate the low-valent chemistry of the lanthanoid elements,<sup>3,4</sup> we have examined the interaction of lanthanoid atoms with alkynes. This approach to lanthanoid chemistry has led to the first complexes of *f*-orbital elements which function as homogeneous catalysts for the activation of molecular hydrogen. Catalytic activity is demonstrated using room-temperature atmospheric-pressure hydrogenation reactions involving alkynes and alkenes and is described here specifically for erbium.

Co-condensation of hex-3-yne ( $C_6H_{10}$ ) with erbium metal vapour at  $-196^\circ C$  in a preparative metal atom reactor<sup>5</sup> produces a matrix of brown solids which upon warming is partially soluble in the unchanged hex-3-yne present. In contrast to transition metal-alkyne co-condensation reactions, which usually generate organic oligomers and polymers,<sup>6</sup> hex-3-yne is not polymerized by erbium atoms or by the newly formed reaction product, and the excess of  $C_6H_{10}$  can be removed *in vacuo* leaving a dark brown solid. Successive extraction of this material with pentane, toluene, and tetrahydrofuran (THF) generates three fractions, (A)—(C), respectively. These three products,

which differ only in solubility, are readily interconvertible and may differ only in their degree of association. An empirical formula of  $ErC_9H_{15}$  is suggested for these compounds based on Er,C,H elemental analysis. Cryoscopic and isopiestic molecular weight measurements indicate that the toluene-soluble (B) is dimeric [*e.g.*  $Er_2(C_6H_{10})_3$ ] in benzene and in hex-3-yne whereas molecular weights as high as 3000 (requiring a decameric structure) have been measured for the THF-soluble (C) in THF. I.r. spectroscopy was the most satisfactory spectral method for studying (A)—(C) and indicates that the carbon-carbon multiple bond has been strongly perturbed by the erbium. The similar but non-identical i.r. spectra of (A)—(C) display two broad absorption bands at *ca.* 1875 and 1795  $cm^{-1}$ , of which the lower frequency band is the more intense. In comparison, the  $C\equiv C$  stretching region of the Raman spectrum of hex-3-yne contains absorptions at 2303, 2247, and 2233  $cm^{-1}$ .<sup>7</sup> Lanthanoid-alkyne chemistry has previously been limited to complexes of trivalent lanthanoids with alkynyl ligands derived from terminal alkynes, complexes which have  $C\equiv C$  stretching frequencies lowered by 100  $cm^{-1}$  or less.<sup>8</sup>

The most significant chemical feature of (A)—(C) is their ability to activate catalytically molecular hydrogen under mild conditions in hydrogenation reactions involving alkynes and alkenes. This reactivity was suggested by decomposition studies in which hexane and hexene were the principal volatile products of thermolysis at  $220^\circ C$ , and hydrogen and hex-3-ene were formed by hydrolysis at  $0^\circ C$ . Hence, (A) and (B), neat in hex-3-yne, catalytically

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hydrogenate the alkyne to *cis*-hex-3-ene (97% *cis*) at room temperature and one atmosphere of H<sub>2</sub> at a rate of 0.02–0.04 turnovers/min.<sup>9</sup> Surprisingly, the interaction of (C) with hydrogen and hex-3-yne is not precluded by solvents such as THF which strongly co-ordinate trivalent lanthanoid centres. Although the reaction is slower, catalytic hydrogenation of hex-3-yne can be accomplished using (C) dissolved in THF at a rate of 0.002 turnovers/min. *cis*-Hex-3-ene is also hydrogenated in these systems to form hexane at a rate *ca.* 10 times slower than the alkyne hydrogenation. Maximum turnover numbers have not been measured, but after 480 turnovers these catalysts are still active and soluble.

Co-condensation of samarium and ytterbium with hex-3-yne also generates new organolanthanoid complexes which function as homogeneous catalysts for alkyne hydrogenation. The major products of these reactions are brown, THF-soluble complexes; elemental analyses indicated the empirical formulae SmC<sub>8</sub>H<sub>10</sub> and YbC<sub>8</sub>H<sub>10</sub> and the complexes exhibit i.r. spectra which are very similar to

those of (A)–(C). Complexes which are catalytically active in hydrogenation reactions are also obtained from co-condensation reactions involving lanthanum and hex-3-yne, and erbium and other alkynes such as PhC≡CPh.

Hence, the results described in detail for erbium and hex-3-yne appear to be rather general, and demonstrate that the lanthanoid series of metals have the capacity to function as homogeneous catalysts in reactions involving activation of molecular hydrogen. Obviously, the *f*-orbital metals have a much greater potential in homogeneous catalysis than was previously assumed.

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