Cyclometallated Ir(III), Rh(III) and Ru(II) complexes as catalysts for the cyclotrimerisation of 1,6-diynes with monoynes

Ronald Grigg,[a*1] Colin Kilner,[a] Meena Senthilnanthanan,[a] Ché R. Seabourne,[a] Visuvanathar Sridharan,[a] and Barry A. Murrer[b]

[a] *Molecular Innovation, Diversity and Automated Synthesis (MIDAS) Centre, School of Chemistry, The University of Leeds, Leeds LS2 9JT*
[b] *Johnson Matthey, Blounts Court, Sonning Common, Reading RG4 9NH*
E-mail: r.grigg@leeds.ac.uk

Abstract
A new series of Rh, Ir and Ru precatalysts for the [2+2+2] cyclotrimerisation of 1,6-diynes with monoynes is reported. The precatalysts are reduced in situ to the active catalysts by reduction with alcohols. The precatalysts activity is in the order Ru>Rh>Ir which reflects the ease of this reduction. The Rh and Ir precatalysts require temperature in excess of 140 ^{o}C allowing their preparation in 2-methoxymethanol at 125 ^{o}C. The mechanism of this process is discussed.

Keywords: Cyclometallated complexes, cyclotrimerisation, diynes, precatalysts

Introduction

The exploitation of cyclometallated complexes in catalysis has recently evolved as a broad new strategy. A variety of palladacycles incorporating cyclometallated phosphines,[1] phosphites,[2] carbenes,[3] imines,[4] heterocycles,[5] thioethers,[6] and oximes[7] have been reported to catalyse carbon-carbon (Heck, Suzuki) and carbon-nitrogen bond forming processes with high turnover numbers.[8,9] Additionally, chiral palladacycles have been shown to catalyse carbon-carbon bond forming processes such as the aldol reaction,[10] Michael addition[11] and cyclopropanation reactions[12] with high enantiomeric excesses. Studies on the synthesis and catalytic behaviour of orthometallated complexes of Rh(II)[13], Rh(III)[14], Ir(I)[15] , and Ru(II)[16] have revealed active catalysts of high efficiency. For example, Nishiyama *et al.* reported that the chiral orthometallated rhodium (III) complex **1** effects the catalytic enantioselective allylation of aldehydes.[17] Other useful applications of the cyclometallated transition metal complexes include electroluminescent/photoluminescent devices[18] and antibacterial agents.[19]

[1] Ron Grigg was Chairman of the RSC Heterocyclic Group during the period 1983-1985.

