



Oxidative addition of (bromoethynyl)benzene to κ^2 -acetylacetonatobis(trimethylphosphine)rhodium(I)

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ABSTRACT

The reaction of (bromoethynyl)benzene with κ^2 -acetylacetonatobis(trimethylphosphine)rhodium(I), [Rh(acac)(PMe₃)₂] **1**, was followed by *in situ* ¹H and ³¹P NMR spectroscopy. The kinetic product is that of *cis*-oxidative addition of the C–Br bond to Rh, and this species rearranges to the thermodynamically more stable *trans*-oxidative addition product *trans*-[Rh(acac)(Br)(CCPh)(PMe₃)₂] **3**. The structures of both **1** and **3** have been determined by single-crystal X-ray diffraction.

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1. Introduction

Our group has been interested in the synthesis of rhodium–acetylide complexes for many years. We have reported several examples of hydrido–acetylide and bis(acetylide) rhodium(III) complexes, including mono-, dinuclear and oligomeric rigid-rods [1] and rhodium(I)–acetylide [2] complexes, and have recently used the Rh(I) acetylides as precursors to prepare novel, highly fluorescent 2,5-bis(arylethynyl)rhodacyclopentadienes [3]. Typical syntheses of the rhodium acetylide complexes included oxidative addition of terminal alkynes to Rh(I) [1a], elimination of methane from Rh–Me complexes [1b,d,e,2], and deprotonation of hydrido–acetylide complexes by KOH [2]. Unsymmetrically substituted bis(acetylide)rhodium(III) were difficult to obtain in pure form via these synthetic pathways [1b] and the mechanism of the acetylide scrambling process has been studied in some detail [4]. While we were successful in isolating unsymmetrical donor–acceptor

substituted platinum bis(acetylide) complexes for studies of their nonlinear optical properties [5], other methods to access related rhodium complexes are still required. Herein, we present the first step of a possible route to unsymmetrically substituted bis(acetylide)rhodium(III) complexes by oxidative addition of (bromoethynyl)benzene to κ^2 -acetylacetonatobis(trimethylphosphine)rhodium(I).

2. Experimental

2.1. General

All syntheses and purifications were performed in a nitrogen-filled Innovative Technology Inc. glovebox or using standard Schlenk techniques. [RhCl₃·3H₂O] was purchased from Precious Metals Online, Australia, and used without further purification. [RhMe(PMe₃)₄] was synthesized according to a published method [6]. The compound (bromoethynyl)benzene was synthesized using a variation of a published method [7]. HPLC grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated, dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze–pump–thaw method. THF-d₈ and C₆D₆ were purchased

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