

Reaction of terminal phosphinidene complexes with acetylenic alcohols: Intramolecular hydrophosphination of a phosphirene ring

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Abstract

The transient phosphinidene complex [PhP-Mo(CO)₅], as generated from the appropriate 7-phosphanorbornadiene complex at 110°C in toluene, selectively reacts with the C≡C triple bond of 4-phenyl-3-butyn-1-ol to give the corresponding phosphirene complex 4. Upon further heating, this phosphirene evolves via two pathways. The minor pathway involves the formal addition of the OH bond of the alcohol function onto the phosphirene P-C ring bond to give the 3-benzylidene-1,2-oxaphospholane complex 5. The major pathway involves the reaction of a second molecule of [PhP-Mo(CO)₅] with the OH group of 4, giving an intermediate phosphirene with an additional secondary alkoxyphosphine functionality (7). An intramolecular hydrophosphination of one P-C bond of the phosphirene ring then immediately takes place to give the cis-1,2-bis(phosphino)ethene [MoCCO] 4 complex 8 as a mixture of two diastereomers. After methylation of the PH group of 8, decomplexation can be efficiently achieved by reaction with sulfur. Structures have been ascertained by X-ray analysis for 5, 8, and the disulfide 10.

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