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Synthesis and Reactions of Phosphorus Substituted Acetylenes

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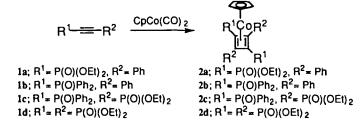
Synthesis and Reactions of Phosphorus Substituted Acetylenes

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To construct phosphorus-functional group substituted π -electron systems, synthesis of acetylenes possessing phosphorus substituents and the reactions with CpCo(CO)₂ were investigated.

Acetylenes 1a, 1b, and 1c were prepared from the corresponding alkynyl Grignard reagents and phosphorus chlorides. On the other hand, 1d was synthesized by the Arbusov-type reaction of triethyl phosphite with dichloroacetylene [1]. Reactions of 1a, 1b, and 1d with $CpCo(CO)_2$ (0.5–0.8 eq.) in refluxing toluene or xylene afforded cyclobutadiene complexes 2a (δ_P 20.6), 2b (δ_P 26.5), and 2d (δ_P 16), respectively. These complexes were isolated in moderate yields and the structure of 2b was confirmed by X-ray crystallographic analysis to indicate that the two diphenylphosphoryl groups are substituted in 1 and 3 positions of the cyclobutadiene ring. On the other hand, the reaction of acetylene 1c under the similar conditions gave a mixture of several products and the corresponding cyclobutadiene complexes could not be isolated probably due to decomposition during chromatographic separation.



References

[1] E.P. Kyba, S.P. Rines, P.W. Owens, and S.S.P. Chou, *Tetrahedron Lett.*, 22, 1875 (1981).