

REACTIONS OF DIPHOSPHABARRELENE

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In the study of reactions of 2,3,5,6,7,8-hexakis(trifluoromethyl)barrelene (I), 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (II) and 2,5,7,10,11,12-hexakis(trifluoromethyl)-1,6-diphosphahexacyclo[4.4.2.0<sup>2,5</sup>.0<sup>3,9</sup>.0<sup>4,8</sup>.0<sup>7,10</sup>]dodecene-11 (III) were synthesized.

1) Treatment of 2,3,5,6,7,8-hexakis(trifluoromethyl)-1,4-diphosphabarrelene (I) with rhodium trichloride in methanol gave 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene. Mass spectrum of this adduct shows no peak of molecular ion but shows peaks of  $m/e$  386 [corresponding to 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene] and 194 [corresponding to 1,1,1,4,4,4-hexafluoro-2-methoxybutene-2]. Refluxing this adduct in *n*-hexane in the stream of argon gave 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene and 1,1,1,4,4,4-hexafluoro-2-methoxy-*trans*-2-butene. The structure of diphosphabenzene was determined by <sup>19</sup>F-nmr, uv ( $\epsilon > 4-5000$ ), mass spectrum, and derivation to barrelene type adducts.

2) Treatment of 1,4-diphosphabarrelene with cyclobutadiene derived from tricarbonyl- $\pi$ -cyclobutadiene iron gave two 1:1 adducts (*endo*- and *exo*-form). Irradiation of the *endo* adduct gave a new cage compound but that of the *exo* adduct did not.

