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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.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$.$0^{7,10}$]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 ^{19}F-nmr, uv ($\varepsilon >$4-5000), mass spectrum, and derivation to barrelene type adducts.

2) Treatment of 1,4-diphosphabarrelene with cyclobutadiene derived from tricarbonyl-π-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.