Von Ketazinen zu 1,2-Diaza-3-phospha-cyclopent-5-enen, -penta-3,5-dienen, 1,5-Diaza-2,6-diphospha-bicyclo[3.3.0]octa-3,7-dien und einem Cyclohexaphosphan

From Ketazines to 1,2-Diaza-3-phospha-cyclopent-5-enes, -penta-3,5-dienes, 1,5-Diaza-2,6-diphospha-bicyclo[3.3.0]octa-3,7-dien, and Cyclohexaphosphane

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The dilithium salt of di(*tert*-butyl-methyl)ketazine **1** reacts with the bimolar amount of $ClSiMe_3$ to give the di(*tert*-butyl-trimethylsilylmethylen)ketazine, **2**. In the reaction of lithiated **2** and $F_2PN(iPr)_2$ the 1,2-diaza-3-phosphacyclopent-5-ene (**3**) is formed. The dichlorophosphanes $Cl_2PC_6H_5$ and Cl_2PCMe_3 react with **1** in boiling toluene to give the 1,2-diaza-3-phosphacyclopentenes **4** and **5**. The oxygen of the air oxidizes **5** to the 1,2-diaza-3-phosphacyclopent-5-ene **6**. Equivalent amounts of H_2O cleave the ring skeleton of **5**, the *tert*-butyl-methyl-(*tert*-butyl-(*tert*-butylphosphino)methyl-ketazine **7** being formed. The 1,2-diaza-3-phosphacyclopenta-3,5-diene **8** and the 1,5-diaza-2,6-diphospha-bicyclo[3.3.0]octa-3,7-diene **9** are the reaction products of **1** and PCl_3 in toluene. **1** forms with HCl the hydrochloride **10**. The 5-*tert*-butyl-1,2-diaza-3-phospha-cyclopenta-3,5-diene **11** is isolated from the reaction of **9** and MeLi. **11** is also obtained from PCl_3 and *tert*-butyl-methyl-hydrazone in good yields. The cyclohexaphosphane **12** was formed in the reaction of **9** with Na/K alloy. The results of the crystal structure analyses of **2**, **3**, **6**, **10**, and **12** are reported.

Key words: Ketazine, Diaza-phospha-cyclopentenes, Diaza-phospha-cyclopenta-dienes, Cyclohexaphosphane