Diphosphetanes from Monomeric Alkyldene Phosphines

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Bis(trimethylsilyl)phosphines react with acyl chlorides (1), dimethylformamide, benzophenone (2) or carbon disulfide (3) to give [1-(trimethylsiloxy)alkyldene]-, [dimethylaminomethylidene]-, [diphenylmethylidene]-, and [bis(trimethylsilylsulfano)methylidene]phosphines. If the P=C group of these compounds is not shielded sufficiently by bulky substituents, dimerization occurs. Usually 1,3-diphosphetanes are found (4); [1-(trimethylsiloxy)benzylidene]phosphines, however, form 1,2-diphosphetanes. As shown by X-ray structure determinations on characteristic derivatives the molecules (1-4) show different point symmetry; the (E)- or (Z)-arrangement of substituents shown by the monomers is still detectable in the dimers.