Monomeric and Dimeric (Aminomethylidene)phosphines and -Arsines

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In (dimethylaminomethylidene)phosphines (1) [1] and -arsines (2) the internal
rotation of the dimethylamino group is hindered by a barrier of 50 to 55
kJmol⁻¹ - analogous to the corresponding amidines. In order to evaluate the in­
fluence of this conjugative effect upon the P=C and (P)-C-N bond lengths, sin­
gle crystal x-ray structure determinations of 1a and 2a have been carried out.
For comparison, the cyclic (aminomethylidene)phosphine 1H-1,3-benzazaphosphole
5 [2] as well as the dimeric compounds 3a, 3b, and 3c [3] have been analyzed,
too, while the arsenic derivative 6 was studied by others [4]. The diarsetanes
4 could not yet be isolated. The structural results indicate the E=C bonds in
1a, 2a, 5, and 6 to be scarcely elongated, the (E)-C-N bonds, however, to be
shortened considerably with respect to the dimers.