A New Approach to the Formation of Phosphorus–Phosphorus Double Bonds

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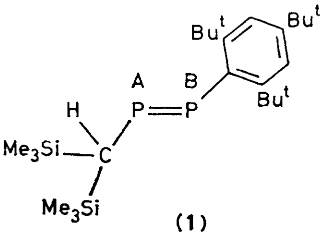
The reaction of $(Me_3Si)_2CHPCl_2$ or $(Me_3Si)_3CPCl_2$ with $(2,4,6\text{-}Bu^t{}_3C_6H_2)PH_2$ in the presence of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) affords the unsymmetrical diphosphene, $(Me_3Si)_2CHP{=}P(2,4,6\text{-}Bu^t{}_3C_6H_2)$.

Despite the current interest in compounds with phosphorus–phosphorus double bonds (diphosphenes),[1–6] only one synthetic approach to these derivatives has been reported so far, *viz.* the coupling of $RPCl_2$ [R = $2,4,6\text{-}Bu^t{}_3C_6H_2$, $(Me_3Si)_3C$] with active metals or organometallic reagents. We now report that diphosphenes can be prepared in high yield by the reaction of $RPCl_2$ with $R'PH_2$ in the presence of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene). Use of this method has permitted the synthesis of an unsymmetrical diphosphene (RP=PR′), a development which has led to measurement of a $^1J_{PP}$ coupling constant for the phosphorus–phosphorus double bond.

Treatment of equimolar quantities of $(Me_3Si)_2CHPCl_2$[7] and $2,4,6\text{-}Bu^t{}_3C_6H_2PH_2$[8] with a 5% excess of DBU in tetrahydrofuran (THF) solution at 0 °C resulted in the formation of a white precipitate. After warming to room temperature and stirring for an additional 12 h, the reaction mixture gradually assumed an orange-yellow colour. Filtration and purification by column chromatography (silica gel, hexane) afforded a 78% yield of orange-yellow solid $(Me_3Si)_2CHP{=}P(2,4,6\text{-}Bu^t{}_3C_6H_2)$ (**1**). Compound (**1**) was characterised by high-resolution mass spectroscopy (M^+ observed 466.2764, calculated 466.2771) and ^{31}P n.m.r. spectroscopy. The $^{31}P\{^1H\}$ n.m.r. spectrum of (**1**) consists of an AB system with δ_A 513.0, δ_B 493.0 p.p.m., and $^1J_{PP}$ 577.5 Hz. The corresponding coupled spectrum comprises the AB portion of an ABX system (with $\frac{1}{2}|J_{AX} + J_{BX}|$ = 16.6 Hz) owing to coupling from the α-hydrogen of the $(Me_3Si)_2CH$ group. Typically, single-bonded trivalent phosphorus compounds exhibit $^1J_{PP}$ values in the range 200—300 Hz.[9] The significantly larger $^1J_{PP}$ value for (**1**) is attributed to shortening of the phosphorus–phosphorus bond length and to π-bond formation rather than to changes in P(3s) character because the P–P–C bond angles in $(2,4,6\text{-}Bu^t{}_3C_6H_2)P{=}P(2,4,6\text{-}Bu^t{}_3C_6H_2)$ (102.8°)[1] and $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (av. 108.5°)[10] are approximately the same as those in the diphosphines $(mesityl)_4P_2$ (av. 104.0°)[11] and $(cyclohexyl)_4P_2$ (av. 104.9°).[12]



(**1**)

$(Me_3Si)_3CP{=}P(2,4,6\text{-}Bu^t{}_3C_6H_2)$
(**2**)

$[(Me_3Si)_2CHP]_3$
(**3**)

$[(Me_3Si)_2CHP]_4$
(**4**)

Interestingly, the reaction of $(Me_3Si)_3CPCl_2$ with $2,4,6\text{-}Bu^t{}_3C_6H_2PH_2$ in the presence of DBU results in (**1**) rather than $(Me_3Si)_3CP{=}P(2,4,6\text{-}Bu^t{}_3C_6H_2)$ (**2**). Although additional studies will be needed to prove this point, we presume that (**2**) is the product formed initially and that the conversion of (**2**) into (**1**) arises *via* Cl^- attack on the $(Me_3Si)_3C$ group followed by elimination of Me_3SiCl and protonation of the resulting carbanion. Diphosphene (**2**) can, in fact, be prepared in low yields by treatment of mixtures of $(Me_3Si)_3CPCl_2$ and 2,4,6-$Bu^t{}_3C_6H_2PCl_2$ with sodium naphthalide in THF solution followed by column chromatography (silica gel, hexane). $^{31}P\{^1H\}$ N.m.r. data for (**2**): AB system, δ_A 533.1, δ_B 530.0 p.p.m., and $^1J_{PP}$ 619.7 Hz.

The use of models indicates that the steric demands of the 2,4,6-$Bu^t{}_3C_6H_2$ and $(Me_3Si)_3C$ groups are adequate to prevent cyclic oligomerisation of diphosphenes. Moreover, a combination of either of these groups with a $(Me_3Si)_2CH$ substituent also results in a kinetically stabilized P=P system. However, two $(Me_3Si)_2CH$ groups are not sufficiently bulky, hence oligomerisation to $[(Me_3Si)_2CHP]_3$ (**3**) and $[(Me_3Si)_2CHP]_4$ (**4**) takes place when $(Me_3Si)_2CHPCl_2$ is treated with Mg or sodium naphthalide in THF. $^{31}P\{^1H\}$ N.m.r. data: (**3**) A_2B system, δ_A -127.4, δ_B -151.8 p.p.m., and $^1J_{AB}$ 204.3 Hz; (**4**) singlet, δ -90.2 p.p.m.

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