Persistent phosphinyl radicals from a bulky diphosphine: an example of a molecular jack-in-the-box†

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The structure of the phosphinyl radical, $\dot{P}R_2$ [R = $CH(SiMe_3)_2$], has been determined by gas-phase electron diffraction (GED) together with *ab initio* molecular orbital calculations, and that of the corresponding diphosphine, $(PR_2)_2$, has been established by X-ray crystallography; the diphosphine behaves as an energy storage reservoir.

In considering the homolytic cleavage of the E–E single bond of molecules of the general type $R'_nEER'_n$, the formation of the corresponding $R'_nE\cdot$ radicals is expected to be favoured by increased steric bulk of the substituents, R′. The conventional view is that such increases of steric strain would be manifested primarily in elongation of the E–E bond and that beyond a critical point of steric loading this bond would rupture. Herein we describe the X-ray crystal structure of the sterically encumbered diphosphine, $(PR_2)_2$ (**1**) (R = $CH(SiMe_3)_2$), and the gas-phase electron diffraction (GED) structure of the corresponding homolysis product, $\dot{P}R_2$ (**2**), the exclusive species found in both solution and in the gas phase.[1] In conjunction with *ab initio* calculations on **2**, comparisons of the structural features of the radical with those of the cognate dimer **1** provide new insights into the origins of the stabilisation of **2** and related species.

Diphosphine **1** was prepared by the reduction of a hexane solution of $ClPR_2$ (**3**) as described previously[1] or by variations thereof.[2] Slow cooling of the filtered reaction mixture afforded both yellow crystals of **1** and colourless crystals of **3**, which were separated manually. Phosphinyl radical **2** was produced by melting or vaporising **1**.

One of the most interesting features of the crystal structure of **1**‡ (Fig. 1) is the P–P bond length [2.3103(7) Å]. While this is the longest such bond yet reported for a diphosphine, it is only ~ 0.1 Å longer than those reported for other diphosphines. Moreover, this modest lengthening amounts to a diminution of only ~ 4 kJ mol^{-1} in terms of the P–P bond dissociation energy. Previously reported distances for uncoordinated diphosphines $(PR'_2)_2$ include 2.260(1) Å (R′ = Mes),[3a] 2.246(2) Å (R′ = CF_3),[3b] 2.215(3) Å (R′ = Cy),[3c] 2.211(2) and 2.206(2) Å (R′ = Ph,C(O)Bu^t),[3d] 2.212(1) Å (R′ = Me)[3e] and 2.2051(11) Å (R′ = C_4Ph_4).[3f] Another noteworthy feature of the structure of **1** is the *syn,anti* orientation of the R ligands on each PR_2 fragment, which allows for a more efficient packing of the ligands around the P–P core than does the corresponding *syn,syn* orientation.

GED data†§ in conjunction with *ab initio* theoretical results revealed that **2** exists as a single *syn,syn* conformer of symmetry C_2 in the gas phase [*cf.* the *syn,anti* found for $(PR_2)_2$]. The electron diffraction data for **2** in the C_2 geometry were fitted by use of the SARACEN method.[4] The final experimental structure (Fig. 2) is in reasonable agreement with that calculated by the Density Functional Theory (DFT) method at the UB3LYP/DZP level. The computed bond lengths generally exceed the experimental values by ~ 0.01–0.02 Å and the calculated angles within 1–2° of the GED values.

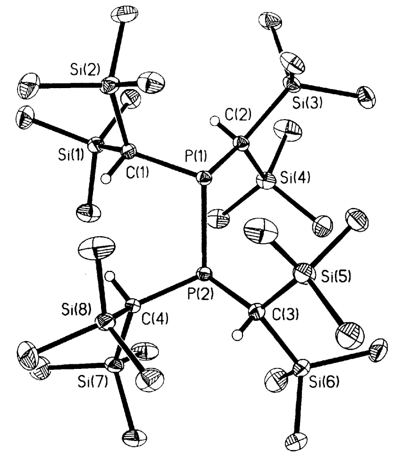

Fig. 1 Thermal ellipsoid plot (30% probability level) of $(PR_2)_2$ (**1**; R = $CH(SiMe_3)_2$). Selected bond lengths (Å), bond angles (°) and dihedral angles (°): P(1)–P(2) 2.3103(7), P(1)–C(1) 1.892(2), P(1)–C(2) 1.896(2), P(2)–C(4) 1.892(2), P(2)–C(3) 1.893(2), Si(1)–C(1) 1.905(2), Si(2)–C(1) 1.915(2), Si(3)–C(2) 1.918(2), Si(4)–C(2) 1.894(2), Si(5)–C(3) 1.892(2), Si(6)–C(3) 1.926(2), Si(7)–C(4) 1.921(2), Si(8)–C(4) 1.896(2), C(1)–P(1)–C(2) 103.57(9), C(1)–P(1)–P(2) 107.92(7), C(2)–P(1)–P(2) 104.83(6), C(4)–P(2)–C(3) 103.00(9), C(4)–P(2)–P(1) 106.98(6), C(3)–P(2)–P(1) 105.27(7), C(1)–P(1)–P(2)–C(4) 32.0(1), C(2)–P(1)–P(2)–C(3) 109.0(1), H(111)–C(11)–P(1)–C(12) 124.6, H(112)–C(12)–P(1)–C(11) 7.8, H(113)–C(13)–P(2)–C(14) −4.6, H(114)–C(14)–P(2)–C(13) 122.9.

The change from the *syn,syn* to the *syn,anti* conformation represents the most obvious difference between the local geometries of the PR_2 fragments in **1** and **2**, and is a consequence of the packing requirements of the ligands about the P–P core of **1**. However, the price of this packing is that there is substantial steric strain, (a) within each R group, *i.e.* between the two $SiMe_3$ groups, (b) between the two R groups attached to each P atom, and (c) between the R groups on the two halves of the molecule. The steric strain is considerably greater in the diphosphine than in the radical, as evidenced by the distortions of the metrical parameters of **1** compared with those of **2**. For example, in **2** the root-mean-square variances from the means of the angles at carbon and silicon are 3.9 and

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† Electronic supplementary information (ESI) available: summary of GED details and theoretical results. See http://www.rsc.org/suppdata/cc/b0/b004889p/

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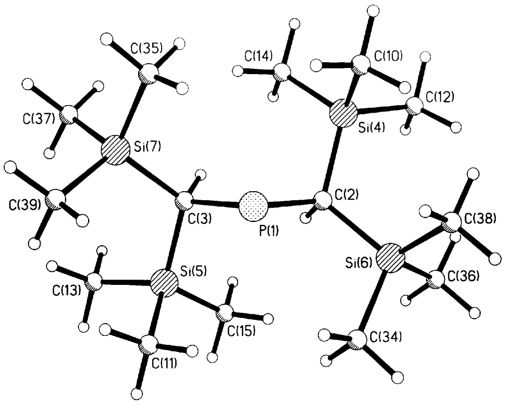

Fig. 2 Gas-phase electron diffraction structure of $\dot{P}R_2$ (**2**; R = $CH(SiMe_3)_2$). Selected bond lengths (Å), bond angles (°) and dihedral angles (°): P(1)–C(2) 1.856(9), C(2)–Si(6) 1.902(2), C(2)–Si(4) 1.905(2), Si(4)–C(10) 1.878(2), Si(4)–C(12) 1.878(2), Si(4)–C(14) 1.876(2), Si(6)–C(34) 1.880(2), Si(6)–C(36) 1.879(2), Si(6)–C(38) 1.875(2), C(2)–P(1)–C(2a) 103.9(10), P(1)–C(2)–H(8) 108.1(13), avg. P(1)–C(2)–Si 109.4(4), avg. Si(4)–C–Si(6) 117.5(5), H(8)–C(2)–P(1)–C(3) −26.4(8).

2.4° respectively, whereas in **1** they are significantly larger (15.3 and 4.1°). There are also increases in many of the bond lengths of the R ligands in **1**, the largest of which are close to the P–P core. In general, there is an attenuation of such bond length increases towards the molecular periphery.

In essence, the whole structure of **1** represents an energy storage reservoir, somewhat like a compressed spring, which, upon dissolution, melting or evaporation, is used to effect cleavage of the P–P bond. In sharp contrast, other diphosphines $P_2R'_4$ with sterically demanding substituents retain their P–P bonding in both solution and the gas phase. To gain further insights, we estimated the magnitude of steric relaxation in the dissociation process using DFT calculations, summarised in Fig. 3 (see ESI† for details). Single-point calculations on **1** (C–H bond lengths fixed at 1.08 Å) and the two fragments formed by breaking the P–P bond, $\mathbf{1A_1}$ and $\mathbf{1A_2}$, predict a P–P homolysis energy of 95 kJ mol^{-1}. The hydrogen atom positions in $\mathbf{1B_2}$ were then optimised. This energy change, which reflects the correction for unrefined placement of hydrogen atoms in the crystal, was 239 kJ mol^{-1}. The remaining atom positions in $\mathbf{1B_2}$ were then relaxed, to give structure $\mathbf{1C_2}$ releasing 52 kJ mol^{-1}. Finally, rotation of one of the R ligands around the P–C bond to form the optimised *syn,syn* conformation (**2**), analogous to that observed experimentally, releases a further 33 kJ mol^{-1} per radical. Thus, while the initial step in the homolysis reaction is endothermic, the relaxation and rotation of the R ligands releases at least 135 kJ mol^{-1}, more than sufficient to render the overall process exothermic.

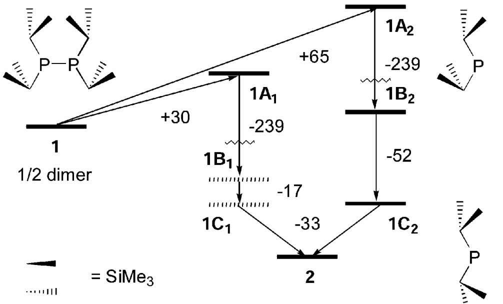

Fig. 3 Summary of DFT calculation results for diphosphine **1** in the solid-state geometry, the *syn,anti* phosphinyl radicals with solid-state geometries $\mathbf{1A_1}$ and $\mathbf{1A_2}$, with hydrogen atom positions relaxed ($\mathbf{1B_1}$ and $\mathbf{1B_2}$), the *syn,anti* phosphinyl radical in the optimised geometry **1C** (the same for both radical fragments), and the *syn,syn* phosphinyl radical in the optimised geometry **2**. Energies in kJ mol^{-1}.

An informative comparison can be made with some closely-related group 14 species. Analogous *syn,anti* to *syn,syn* conformational changes and similar dissociation energies are observed in the cleavage of $(MR_2)_2$ (M = Ge, Sn) into the MR_2 carbenoid fragments.[5] Again, the M–M distances in the solid are very similar to those in sterically less encumbered $M_2R'_4$ molecules. In contrast, the related $\{M[N(SiMe_3)_2]_2\}$ (M = Ge, Sn, Pb) species, while remaining monomeric in both the gas and the solid, change their conformations.[6]

In conclusion, the homolytic behaviour of **1** permits a new understanding concerning the functioning of bulky substituents. The shape and flexibility of the $CH(SiMe_3)_2$ ligands allows for the formation of the P–P bond in **1**. However, in the process of bond formation (and crystallisation) the molecule accumulates a large store of potential energy and is primed to spring apart upon release from the solid state. The potential energy of steric repulsion is not manifested in an elongated P–P bond, but is evidenced primarily by the deformation of the ligands. In this sense, the malleable R substituents act as the springs in a molecular jack-in-the-box.

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Notes and references

‡ *Crystal data* for **1**: $C_{28}H_{76}P_2Si_8$, M = 699.55, yellow blocks, monoclinic, $P2_1/c$, a = 18.341(2), b = 13.4240(10), c = 19.033(2) Å, β = 110.650(10)°, V = 4385.0(7) Å^3, Z = 8, D_{calcd} = 1.060 g cm^{-3}, μ(Mo-Kα) = 0.335 mm^{-1}. A suitable single crystal of **1** was covered with mineral oil and mounted on a Siemens P4 diffractometer at 183 K. A total of 9263 reflections was collected in the range 2.38° < 2θ < 50.13° using Mo-Kα radiation (λ = 0.71073 Å). Of these, 7709 were considered observed ($I > 2.0\sigma(I)$) and were used to solve (direct methods) and refine (full matrix, least squares on F^2) the structure of **1**; R_w = 0.1159, R = 0.0375. CCDC 182/1770. See http://www.rsc.org/suppdata/cc/b0/b004889p/ for crystallographic files in .cif format.

§ *GED data* for **2**: Electron scattering intensities for **2** were recorded on the Balzers' gas electron diffraction apparatus in Oslo. See ESI for details.†

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