Diphosphirane and 1,3-diphosphaallyl anion: geometry and bonding

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Abstract

The unsymmetrical diphosphirane **2a**, obtained by addition of dichlorocarbene to the corresponding diphosphene ArP=PTsi (Ar = 2,4,6-tri-tert-butylphenyl; Tsi = tris(trimethylsilyl)methyl) presents a structure with the shortest P–P bond (2.117 Å) ever observed in the diphosphirane series, and a torsion angle (Ar)CPPC(Tsi) close to 180° (177.0°).

A shortening of intra- and extracyclic P–C bonds, as well as of CCl bonds, is also observed comparative to the symmetrical diphosphirane **1a**. Such short bonds can account for the special chemical behaviour of **2a**.

The anionic ring opening of the diphosphirane **1c** leads to the stable 1,3-diphosphaallyl anion **7c**. The equivalence of the two phosphorus atoms and the existence of a P–Li coupling constant of 41 Hz is an argument for a σ-allylic structure in solution.

Keywords: Diphosphiranes; 1,3-Diphosphaallyl anion; Phosphorous small rings; X-ray crystal structure; Preparation

1. Introduction

The chemistry of phosphorus containing three-membered rings has been considerably developed since 1978 owing to the work of Baudler and Saykowski [1]. Since this date, because of their great synthetic potential in phosphorus chemistry, many studies have been devoted to strained three-membered heterocycles containing one or two phosphorus atoms [2].

The use of bulky groups on phosphorus atoms allowed the stabilization of new types of diphosphirane, generally unstable [3,4], for example *gem*-dihalogeno-diphosphiranes. Such derivatives appear as important synthons since they are good precursors of various low coordinated phosphorus compounds such as phosphaethylenes **3**, **4**, 1,3-diphosphapropenes **5**, **6** [5], diphosphaallylic derivatives **7**, **8** [6] and diphosphaal-lenes **9**, **10** [7] (Scheme 1).

However, as shown in this scheme, the orientation and selectivity of the reactions for **1** or **2** are quite different according to the substituents on phosphorus.

(i) Cheletropic reactions consecutive to simultaneous P–P and P–C bond breaking, observed starting from

1a–d [8b], have never been evidenced in diphosphiranes **2a,b**.

(ii) The photochemical [5b] or thermal [8a] ring-opening of **1** leads to mixtures of *cis* and *trans* diphos-phapropenes **5**, whereas the same reactions from **2** are stereo- and regioselective, leading only to the *trans* 1,3-diphosphapropene **6** in the *syn* conformation [5a,7b].

(iii) by analogy with the general synthesis of allenes from *gem*-dihalogenocyclopropanes, the preparation of diphosphaallene **9** from symmetrical diphosphiranes **1a**, **b** (Scheme 1), using RLi [7], RMgX [9], $Cp(CO)_n M^- Na^+$ (M = Mo, Co, W) [6b] is quantitative whereas, under the same conditions, it is not possible to directly obtain the diphosphaallene **10** from the corresponding unsymmetrical diphosphiranes **2a,b** [7b].
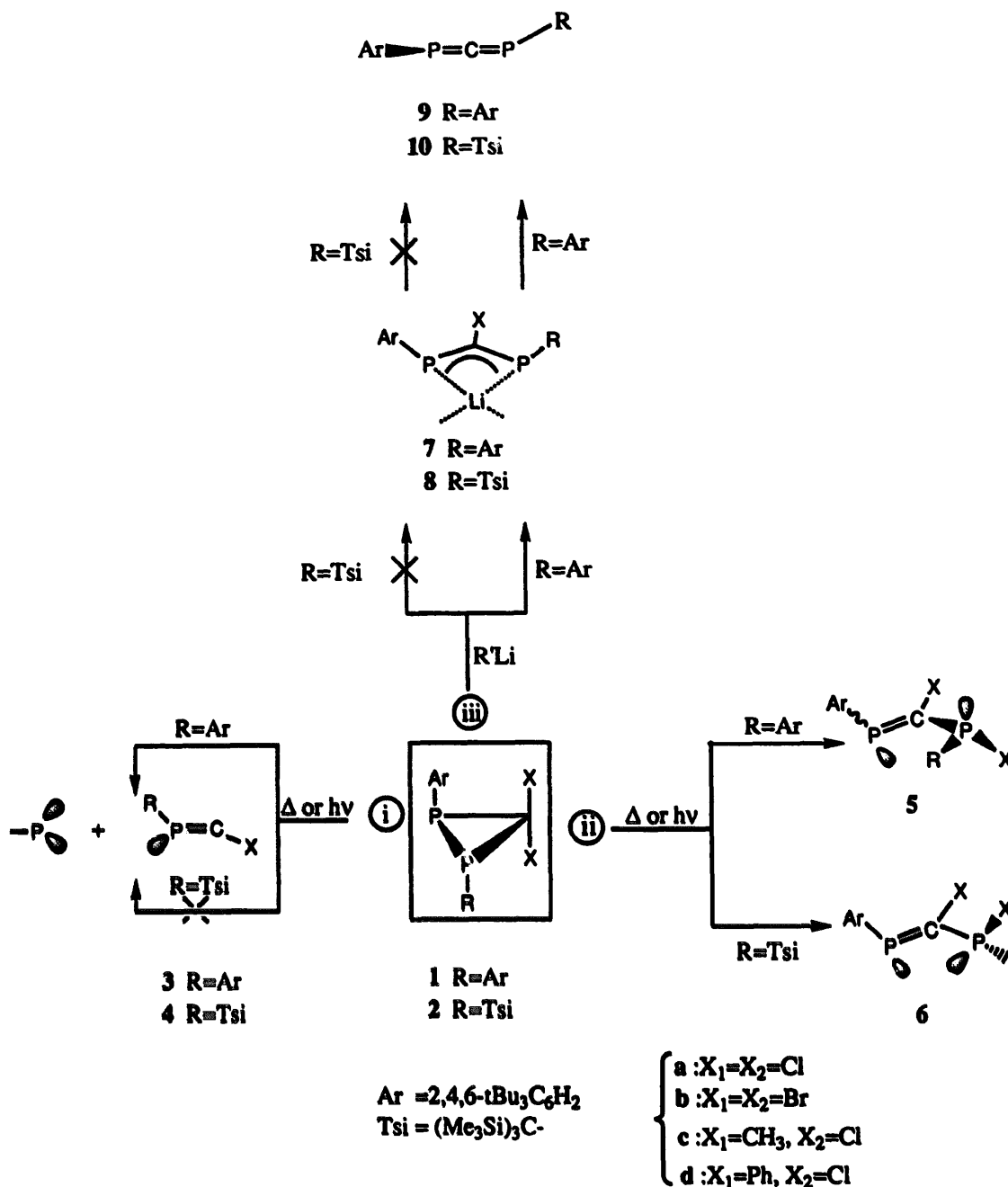
All these observations prompted us to look for an explanation of such chemical behavioural differences in the structure of starting diphosphiranes **1a** and **2a**.

2. Results and discussion

2.1. Diphosphiranes

Diphosphiranes **1a** [3] and **2a** [5a] have been obtained by the same route, involving the addition of

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Ar—P=C=P⟨R

9 R=Ar
10 R=Tsi

R=Tsi ✗   R=Ar

7 R=Ar
8 R=Tsi

R=Tsi ✗   R=Ar

R'Li

(iii)

R=Ar

R=Ar → **5**

3 R=Ar
4 R=Tsi

1 R=Ar
2 R=Tsi

R=Tsi → **6**

Ar =2,4,6-tBu₃C₆H₂
Tsi = (Me₃Si)₃C-

$$\begin{cases} a : X_1=X_2=Cl \\ b : X_1=X_2=Br \\ c : X_1=CH_3,\ X_2=Cl \\ d : X_1=Ph,\ X_2=Cl \end{cases}$$

Scheme 1. General reactivity of the functionalized diphosphiranes 1 and 2.

dichlorocarbene CCl_2 onto the corresponding *trans* diphosphenes symmetric or not. The cyclopropanation reaction is stereoselective and leads in both cases to *trans* diphosphiranes. The nature of the substituent on one of the two phosphorus atoms (Ar or Tsi) is the sole difference between compounds **1a** and **2a** (Scheme 2).

Table 1
Structural data for diphosphiranes **1a** and **2a**

Compound	Bond lengths (Å)				Bond angles and torsion angle (°)				
	P–P	P–C₁	P–R	C₁–Cl	P–C₁–P	(R)P–P–C₁	C₁P–R	P–P–R	R–P–P–R
1a R = Ar	2.245(2)	1.863(4)	1.858(4)	1.766(3)	74.3(2)	52.7(2)	101.8(1)	107.4(1)	176.4(1)
2a R = Ar	2.117(3)	1.808(6)	1.783(6)	1.743(7) (Cl₂)	71.0(2)	53.9(2)	97.8(3)	106.2(2)	177.0(1)
R = Tsi		1.835(6)	1.798(6)	1.760(6) (Cl₁)		55.1(2)	112.4(3)	107.8(2)	

1 a-d   R = Ar,

2 a-b   R = Tsi
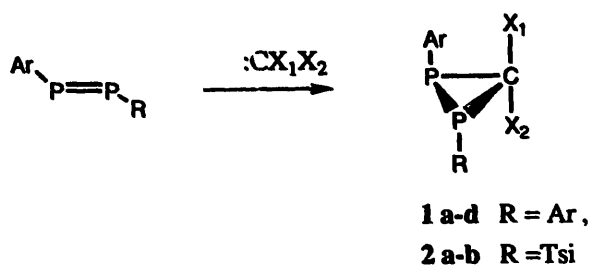
Scheme 2. Synthesis of the diphosphiranes.

Structural data for **2a** (Fig. 1) are displayed in Table 1 and compared with those of **1a** [4b,10].

The main feature observed in **2a** is the very short P–P bond (2.117 Å). Classical P–P bonds are generally around 2.21–2.25 Å [11]. Thus in **2a** the P–P distance is between the double bond in diphosphenes [12a] (for example 2.03 Å [12c] in ArP=PAr) and a single bond. This last value (2.117 Å) corresponds to the shortest P–P bond ever found in a diphosphirane series [2,12d]. By contrast, a normal P–P distance is determined in **1a** (2.245 Å), close to the value (2.21 Å) predicted by Liu and Bachrach [13] from calculations on a model in which substituents are replaced by hydrogen atoms.

The intracyclic P–C bonds in **2a** are unequal (1.808 for ArP_2–C_1 and 1.835 Å for $TsiP_1$–C_1) and shorter than in **1a** (1.863 Å), including in NMR larger $^1J_{CP}$ coupling constants for **2a** (C_1: $\delta = 83.9$, dd, $^1J_{CP_1} = 70.3$ Hz, $^1J_{CP_2} = 77$ Hz [14]) than for **1a** (δ ^{13}C = 86.3, t, $^1J_{CP} = 62$ Hz). The bond shortening is general in compound **2a** since it is also observed in extracyclic bonds (**1a** P–C(Ar) = 1.858 Å, **2a** P–C (Ar) = 1.783 Å, P–C(Tsi) = 1.798 Å). The $^1J_{CP}$ coupling constants are in relation to the short P–C distances observed: **1a** C_2 =

131.9 (t), 1/2 |$J_{CP_1} + J_{CP_2}$| = 68 Hz; **2a** $C_2 = 131.6$ (dd), $^1J_{C_2P_2} = 91$ Hz, $^2J_{C_2P_1} = 7$ Hz, $C_{20} = 13.2$ (dd), $^1J_{C_{20}P_1} = 101$ Hz, $^2J_{C_{20}P_2} = 14$ Hz.

However, these shortenings cause only small changes in intracyclic bond angles (PCP:**1a** 74.3°, **2a** 71.0°; PPC: **1a** 52.7°, **2a** 53.9 and 55.1°). Extracyclic (Ar)CPP bond angles, of about 107° for both **1a** and **2a**, are slightly larger than in the starting diphosphene ArP=PAr (102.8°) [12b]. Torsion angles (Ar)CPPC(Ar) and (Ar)CPPC(Tsi) are close to 180° (**1a** 176.4, **2a** 177.0°), implying that the (Ar)CPPC(Ar or Tsi) mean plane is orthogonal to the three-membered ring.

The quasi-planar (Ar)CPPC(Ar or Tsi) moiety is another characteristic feature of the structures of **1a** and **2a**. These results are in agreement with a mechanism involving an attack of singlet carbene on π-electrons of the P=P double bond rather than an addition onto the phosphorus lone pair followed by the ring closure [15].

The fact that, in the cyclopropanation of diphosphenes, the main effect on the structure of the C–P=P–C moiety is a little lengthening of the P–P distance corresponds to the observations reported in "olefine π-complexes". As proposed by Dewar and Ford [16], three-membered ring compounds can also be formulated as π-complexes with back-coordination. According to the π-complex theory, compounds of this type can show a continuous range of structures from a π-complex to a "pure" classical ring, so a distinction can be drawn only on the basis of some properties that change along the range.

Concerning the cycloaddition of a carbene on the P=P bond and C=C bond, calculations [15] predict that the discrimination between electrophilic phase (interaction $\pi_{P=P} \leftrightarrow p^*_{CH_2}$) and nucleophilic phase (interaction
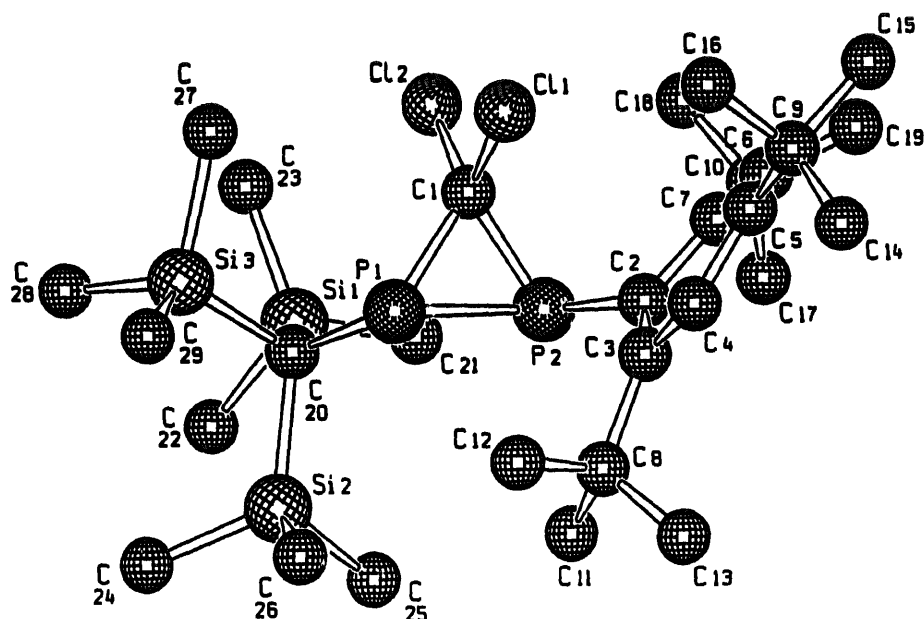
Fig. 1. Molecular structure of **2a**. Selected bond lengths (Å): P_1–P_2 2.117(3), P_1–C_1 1.835(6), P_2–C_1 1.808(6).
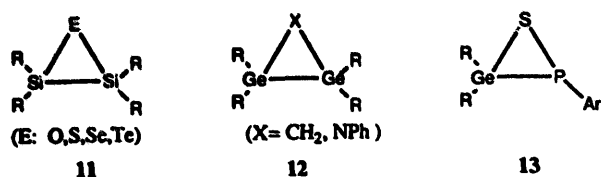
Scheme 3. Heterocyclopropanes analogues with short M–M bond.

$\pi^*_{P=P} \leftrightarrow n_{CH_2}$) is more difficult in diphosphene than in ethylene. The $\pi^*_{P=P}$ orbital level is lower than the $\pi^*_{C=C}$ one, whereas the $\pi_{P=P}$ orbital level is higher than the $\pi_{C=C}$ one; thus we can predict a more important $\pi \leftrightarrow p^*$ electrophilic interaction than $n \leftrightarrow \pi^*$, the latter prevailing at the beginning of the reaction. These conditions, close to those postulated by Dewar and Ford [16] to explain the shortening of the C–C bond of olefines in π-complexes, can explain why the CPPC moiety is still planar as in the starting diphosphenes, and why the P–P bonds, particularly in 2a, are surprisingly short.

A similar phenomenon (short M–M bonds and torsion angles RM–MR close to 180°) has been reported in other organometallic three-membered ring compounds with one or two Group 14 elements (for example by West and coworkers in compounds 11 [17], Tsumuraya and coworkers in compounds 12 [18] and some of us in the three-membered ring derivative 13 [19] with a short Ge–P bond and R–Ge–P–Ar torsion angle of the same value as in the starting germaphosphene) (Scheme 3). Thus, such a phenomenon appears completely general in this type of three-membered ring compound containing main group elements. Calculations by Grev and Schaefer [20] confirm such an interpretation.

However, even if the Dewar and Ford model is in good agreement with the shortening of the P–P bond, it cannot alone explain either the large difference observed between 1a and 2a for the P–P bond length or the shortening of the intracyclic P–C bonds of 2a. A reason for the bond shortenings observed in 2a relatively to 1a could be the rather strong attractive effect of the trisyl group. A similar phenomenon has previously been reported in diphosphenes [12a] or diazenes [21] substituted by silyl groups.

In the case of phosphorus-containing three-membered ring systems, the first bands observed in photoelectron spectra (PES) could be assigned to a linear combination of the phosphorus lone pairs and the Walsh orbitals; owing to the low symmetry of the compounds, a strong mixing of lone pairs and Walsh orbitals was predicted [22] involving a shortening of the corresponding bonds. This shortening would be enhanced by the electroattractive effect of substituents on phosphorus atoms.

The structure observed in 2a looks like the structures of η^2-complexes of diphosphenes, in which the P–P

bond length is generally between 2.12 and 2.15 Å [12a]. It is important to note that the P–P bond distance in 2a is, surprisingly, even shorter than in such η^2-complexes.

It seems that the general shortening of extracyclic and intracyclic bonds, and particularly the extremely large steric hindrance around this P–P bond, are responsible for the special reactivity of 2a, particularly the absence of cheletropic reactions which easily occur in 1a. The stereoselectivity observed in the formation of 1,3-diphosphaproprenes by photolysis or thermolysis of 2a, whereas cis and trans diphosphapropenes are obtained from 1a, can also be understood by the particular effect of the huge Tsi group in 2a.

2.2. 1,3-Diphosphaallyl anion

As noted previously, diphosphiranes 1 and 2 have a different chemical behaviour particularly towards lithio compounds [7b]; whereas the reactions of RLi with dihalogenated diphosphiranes 1a,b lead quantitatively to the corresponding allene 9 (Scheme 1), the reactions with diphosphiranes 2a,b only afford unidentified products. The unsymmetrical diphosphaallene ArP=C=PTsi 10 can only be obtained by another route, involving dehydrohalogenation of the corresponding diphosphapropene [7b].

In a previous work [7a], we have postulated that the formation of diphosphaallene 9 was not the result of a carbenic insertion reaction, but occurred via the transient 1,3-diphosphaallyl anion 7

When the carbon is substituted by only one halogen atom, the diphosphaallyl anions 7c,d have been characterized by ^{31}P NMR and 7c has even been isolated, but unfortunately with solvent inclusion (hexane) in the form of rather unstable crystals. Thus, the X-ray analysis of 7c that we have performed at low temperature was too rough for a detailed structural analysis. However, as 7c and 7d have been characterized by NMR, some information about their structure can be obtained. In ^{31}P NMR at room temperature the compounds 7c,d give two singlets respectively at 64.1 and 54.0 ppm. At low temperature ($-70°C$) we have observed in each case one quartet 1.1.1.1 with $^1J_{PLi}$ of respectively 41 Hz (7c) and 48 Hz (7d) (Fig. 2). The existence and order of the size of this P–Li coupling constant seems to show that a covalent character predominate in Et_2O solution [23]. The single signal—observed at 32.4 and 101.2 MHz—for the two phosphorus atoms indicates that we have a fluxional system with the lithium bonded to the two equivalent phosphorus atoms. Consequently, the Ar substituents are in exo–exo (or endo–endo) position. Because of the very bulky substituents the most likely is the configuration in which the Ar substituents are in exo–exo position relatively to the P–C–P bond angle (Fig. 2). This configuration confirms the conrotatory
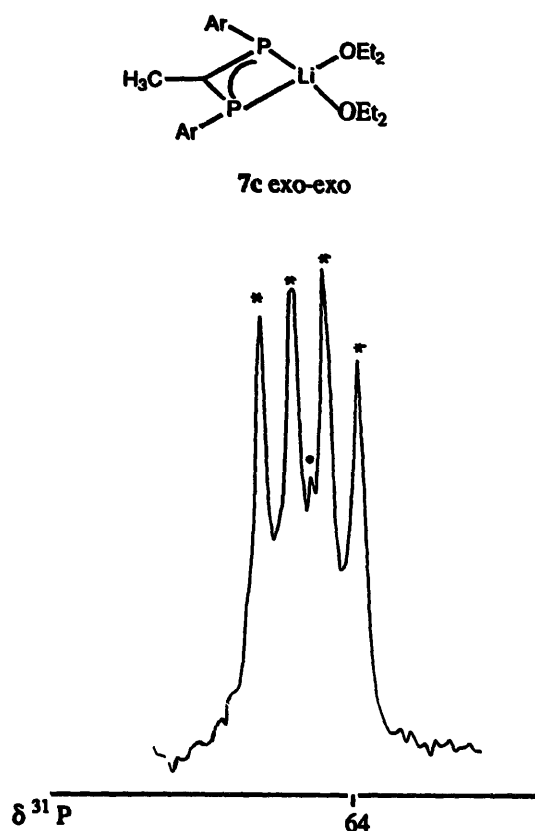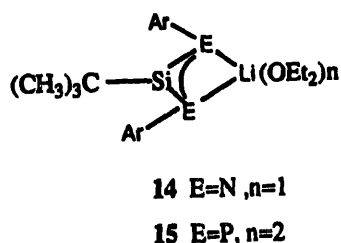
7c exo-exo

Fig. 2. Evidence of the magnetical equivalence of the two phosphorus atoms of 7c by ^{31}P NMR at −70°C in ether. Major signal (∗), a quadruplet with $^1J_{P-Li}$ constant centred at $\delta = 64.1$. Minor signal (●), only one peak appears at the same chemical shift, so $^1J_{P-Li}$ is not detectable.

anionic ring opening process. The structure of 7c looks like the structures of 1,3-diaza-2-silaallyllithium (14) described by West and coworkers [24] and 1,3-diphospha-2-silaallyllithium (15) described by Niecke et al. [25] (Scheme 4).

Of course the kind of structure in the 1,3-diphosphallyl complex remains open. Calculations made by von Rague Schleyer and coworkers [26] on unsolvated allyllithium compounds, predict two possible structures: a σ-type structure, with an important covalent character, and a π-type structure, with a large ionic character. In such conditions of calculation, the π-allyl system ap-

pears more stable than the σ-allyl system by about 18 kcal mol^{-1}. The previous studies have been extended by Liu and Bachrach [13], by ab initio calculations, to 1,3-diphosphaallyllithium compounds; they also confirmed in this case the π-structure, with the lithium atom being above the P–C–P plane, at a distance of 2.46 Å from the phosphorus. More recently, ab initio SCF + CI calculations of total charges, made by Pfister-Guillouzo and coworkers [15] on 1,3-diphosphaallylic anion show that, by contrast with allyllithium compounds, negative charges are located both on phosphorus and central carbon atoms: the highest charge (−0.4) is on the carbon, whereas the lowest ones (−0.26) are on every phosphorus. Such a distribution is in favour of a π-structure.

However, such calculations are made on simple models (H instead of substituents, no complexation of lithium by solvent), whereas in the case of 7c, phosphorus atoms are substituted by extremely bulky Ar groups and the lithium is solvated by two Et_2O molecules which can destabilize the π-complex. It seems necessary to be careful about the effect of bulky groups, since Appel et al. [27] and we [6b] have stabilized 1,3-diphosphaallyl π-type cationic complexes by transition metals.

An equilibrium between a σ- and a π-structure could also be considered since recently, in a cationic complex, such an equilibrium has been evidenced [28,6b]. However, our experimental data are in better agreement with a σ-allyl structure.

3. Conclusion

In conclusion, diphosphiranes obtained by the addition of carbenes on the P=P double bond of diphosphenes present a short P–P bond (particularly 2a, 2.117 Å) with a CPPC torsion angle close to 180°. These experimental data can be interpreted in terms of "Dewar/Ford type adducts". The preferential P–P bond breaking leads to the 1,3-diphosphaallyl anion. In the latter, the exo–exo position of the phosphorus substituents confirms the conrotatory anionic ring-opening process predicted by calculations. A σ-allyl character is in good agreement with the P–Li coupling constant.

4. Experimental

4.1. Synthesis of 2a

Compound 2a was prepared by the procedure previously described [5a]. Single crystals were obtained by crystallization in benzene. Calculations have been performed on a micro-vax using SHELX-TL [29] and SCHAKAL [30].

14 E=N ,n=1

15 E=P, n=2

Scheme 4. Configuration of 1,3-diphospha- (or diaza) 2-silaallyllithium.

4.2. X-ray crystallography of 2a

Compound 2a, $C_{29}H_{56}Cl_2P_2Si_3$, FW 621.88, crystallizes in the triclinic crystal system (space group $P\bar{1}$): $a = 9.761(7)$, $b = 11.038(10)$, $c = 15.675(12)$ Å, $\alpha = 89.11(6)$, $\beta = 87.09(6)$, $\gamma = 78.67(6)°$, $V = 1654$ Å^3, $Z = 2$, $D_x = 1.249$ mg m^{-3}, μ (Mo K α) = 0.420 mm^{-1}. Intensity measurements were performed by Siemens AED2 4-cycle diffractometer, 2θ range from 3.0 to 48.0°, 4958 reflections with 4330 ($F > 2\sigma(F)$) classified as observed. The structure was solved by direct methods and refined using anisotropic temperature coefficients for all non-hydrogen atoms, the latter atoms calculated in reasonable atomic positions with a common U-value. Only 27 hydrogen atoms were introduced in the calculated structure; the disordered other ones are omitted. The R-values obtained are $R = 0.0655$ ($R_W = 0.0643$) using $W^{-1} = \sigma^2(F) + 0.0001F^2$ with the largest remaining difference peak equal to 0.59 eÅ^{-3}. In this refinement a split atom model has been used for the tris(trimethylsilyl)methyl group with side occupation factors (SOF) of 0.8 and 0.2, giving 393 parameters.

4.3. Synthesis of 7c

At $-70°C$, 1.4 ml (3.5 mmol) of a 2.5 M hexane solution of n-butyllithium was added dropwise to a solution of diphosphirane 1c (0.220 g, 3.6 mmol) in 5 ml of anhydrous ether. The precipitate of LiCl was removed by filtration. The resulting solution was concentrated and cooled at $-20°C$. Compound 7c crystallized as red crystals, extremely air- and moisture-sensitive.

5. Supplementary material available

Final atomic coordinates, thermal parameters, lists of observed and calculated structure factors and tables of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgement

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^{1}H NMR (80.13 MHz, C_6D_6): δ 0.47 (s, 27H (Si(CH$_3$)$_3$)$_3$), 1.23 (s, 9H, p-^{t}Bu), 1.47 (s, 18H, o-^{t}Bu), 7.37 (d, 2H, $^4J_{H-P}$ = 2.6 Hz, Ar). ^{13}C NMR (62.86 MHz, C_6D_6): δ 6.5 (d, $^3J_{CP_2}$ = 4 Hz, $C_{21}-C_{29}$), 13.2 (dd, $^1J_{CP_1}$ = 101 Hz, $^2J_{CP_2}$ = 14 Hz, C_{20}), 31.6 (s, $C_{14}-C_{16}$), 33.6 (s, $C_{17}-C_{19}$ or $C_{11}-C_{13}$), 35.0 (s, C_9), 36.3 (s, $C_{11}-C_{13}$ or $C_{17}-C_{19}$), 38.9 (s, C_{10} or C_8), 39.6 (s, C_8 or C_{10}), 83.9 (dd, $^1J_{CP_1}$ = 70.3 Hz, $^1J_{CP_2}$ = 77.0 Hz, C_1), 121.7 (s, C_6 or C_4), 123.9 (s, C_4 or C_6), 131.6 (dd, $^1J_{CP_2}$ = 91 Hz, $^1J_{CP_1}$ = 7 Hz, C_2), 150.0 (s, C_5), 157.5 (s, C_7 or C_3), 160.3 (s, C_3 or C_7). ^{31}P NMR (32.44 MHz, C_6D_6): δ -29.4 (d, P_1), -77.8 (d, P_2), $^1J_{P_1P_2}$ = 144 Hz.
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