

A Rebel in the Ranks: A Phosphonium Cation with a Planar Tetracoordinate Phosphorus Atom – An Anti van't Hoff-Le Bel Structure

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The shapes and structures of chemical compounds apart from their aesthetic beauty also have a bearing on the way these compounds behave in terms of their chemical reactions or even biological activity. For this reason chemists spend a reasonable amount of their time in trying to determine the structures of chemical compounds which they have synthesized in the laboratory or which may have been isolated from natural sources. Most often the structures of chemical compounds are determined by a combination of techniques such as spectroscopic methods (infrared, Raman, UV – visible, mass, nuclear magnetic resonance, electron spin resonance, Mössbauer), or by the use of X-ray diffraction (powder or single crystal methods). Fortunately, however, the geometric shapes of simple molecules are often easily predicted by the application of simple qualitative theoretical methods. Among the most popular of such methods is the VSEPR (valence shell electron pair repulsion) theory developed by Sidgwick and Powell, which has been very successful in the prediction of geometries of simple main group compounds. The beauty of this theory is its simplicity and extremely high rate of success in predicting the struc-

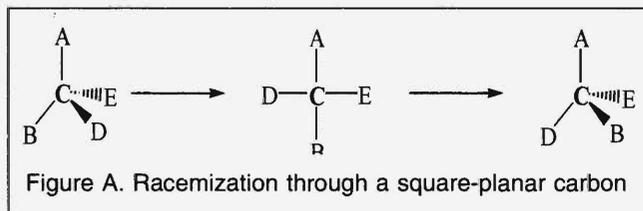
tures of many main group compounds. In fact the exceptions to the predictions of this theory are quite rare. The basic principles of VSEPR and its applications are available from any standard inorganic chemistry textbook (see [1] and [2]).

According to the VSEPR theory, the shape of a molecule is determined by the *electron-pair repulsions* around the atoms present. The basic premise is that the electron pairs surrounding a given atom will tend to keep away from each other to the extent possible. Thus, in this way the most favorable structure is obtained where the electron pair repulsions are minimal. Since the molecule of discussion in this article is a four-coordinate phosphorus-containing compound, let us briefly look at the prediction of the VSEPR theory for such four-coordinate molecules. VSEPR predicts that methane and isoelectronic molecules such as $[\text{PCl}_4]^+$ will have tetrahedral geometries. The most prominent of these kind of molecules belong to the carbon family and are in the realm of organic chemistry. Long before VSEPR was enunciated, in 1877, van't Hoff and Le Bel postulated that the tetracoordinate carbon must be tetrahedral (see [3] and [4]). This postulate remains one of the greatest intellectual contributions to chemistry and has laid the foundation to stereochemical principles in chemistry in general and organic molecules in particular. Incidentally, there have been several theoretical and of late some successful experimental efforts at realizing the planar tetracoordinate carbon (*Box 1*).



Box 1.

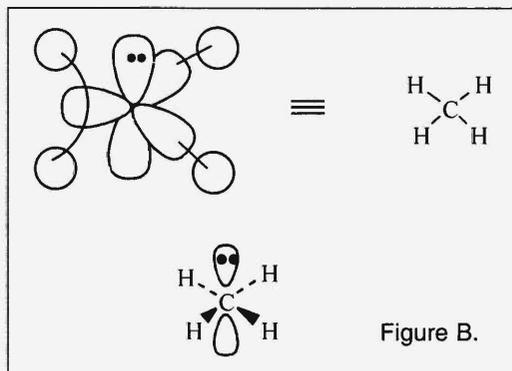
Although the tetrahedral carbon is ubiquitous there has always been the urge to find situations where a square-planar geometry would be preferred. Apart from the esoteric interest one of the motivations for this kind of a study is to assess the role of a square-planar carbon as a thermally accessible transition state for a racemization involving an optically active compound.



The first theoretical attempt in this regard was made by the Nobel laureate R Hoffman. He began the quest by trying to understand the electronic structure of a square-planar methane (Figure A). Hoffman proposed that carbon utilizes a $sp^2 + p$ type of hybridization in this molecule.

Using two of the sp^2 hybrid orbitals and two out of its four valence electrons carbon forms regular 2c-2e covalent bonds with two hydrogen atoms. The third sp^2 hybrid orbital is involved in a 3c-2e bond with the other two hydrogen atoms. For this the carbon does not contribute any electrons. After this exercise the carbon is left with two electrons which are in an out-of-plane p_z orbital (it is out of plane since the p_z orbital is perpendicular to the molecular plane (Figure B)).

Hoffman has also arrived at a qualitative molecular orbital diagram for the square-planar methane and other molecules of this type. This is similar to the one obtained for the planar phosphonium ion. The lower two molecular orbitals are of the bonding type. The HOMO (highest occupied molecular orbital) is a carbon centered p orbital containing a pair of electrons. Because of this type of electronic arrangement the planar tetracoordinate carbon is an electron poor center in its molecular plane and electron rich out of plane. Consequently the square-planar methane is destabilized with respect to the tetrahedral one by a considerable amount of energy. How is it possible to realize the square-planar carbon experimentally? There are two strategies suggested for the stabilization of this rare configuration. One, design of sterically constrained molecules where the square planar geometry is forcibly adopted. This is a brute-force approach and some of the examples that have been suggested as possible candidates are given in Figure C.



The second approach involves the replacement of the hydrogens on methane by substituents that are in-plane s -donors and out-of-plane p -acceptors. This would allow a transfer of electron density inplane towards carbon and dissipation of the excess π -electron density out of plane. Experimentally observed examples incorporating some of the above suggestions are given in Figure D.

Box 1. continued...

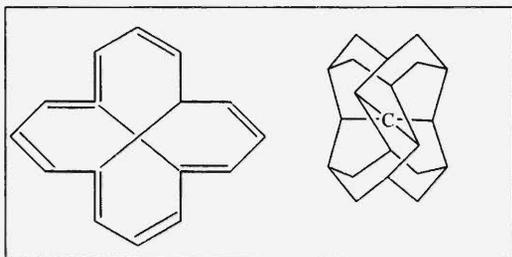
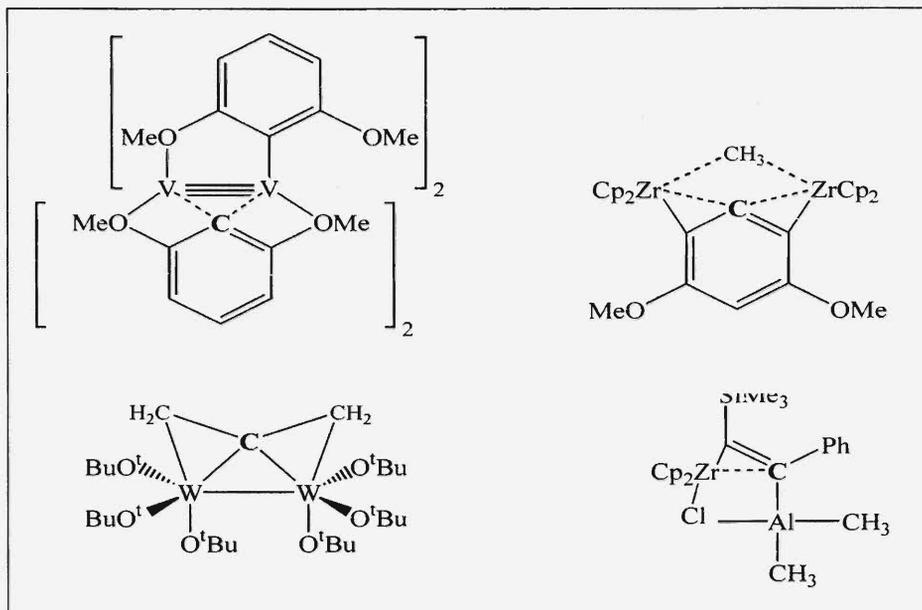


Figure C. Some of the suggested synthetic targets for brute-force approach of stabilising square-planar carbon.

Figure D. Some of the experimentally realized examples of compounds containing a square-planar carbon.

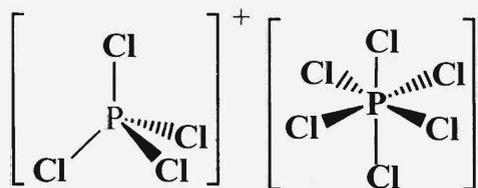


The interested readers may consult the original references cited below for more information on the planar tetracoordinate carbon:

- [1] R Hoffman, R W Alder, C F Wilcox Jr., *J. Am. Chem. Soc.*, **92**, 4992, 1970.
- [2] J B Collins, J D Dill, E D Jemmis, Y Apeloig, P v R Schleyer, R Seeger, and J A Pople, *J. Am. Chem. Soc.*, **98**, 5419, 1976.
- [3] G Erker, R Zwettler, C Krüer, R Noe and S Werne, *J. Am. Chem. Soc.*, **112**, 9620, 1990.
- [4] M P McGrath and L Radom, *J. Am. Chem. Soc.*, **115**, 3320, 1993.
- [5] I-H Kryspin, R Gleiter, M-M Rohmer, J Deveny, A Gunale, H Pritzkow and W Seibert, *Chem. Eur. J.*, **3**, 294, 1997.

As shown in Scheme 1 $[\text{PCl}_4]^+$ belongs to the AB_4 type of molecule similar to methane or silicon tetrachloride and therefore is predicted to have a tetrahedral structure and

indeed structural determination of a number of phosphonium ions have shown that invariably all of them have tetrahedral geometries around the phosphorus.



Prediction of geometry for $[\text{PCl}_4]^+$

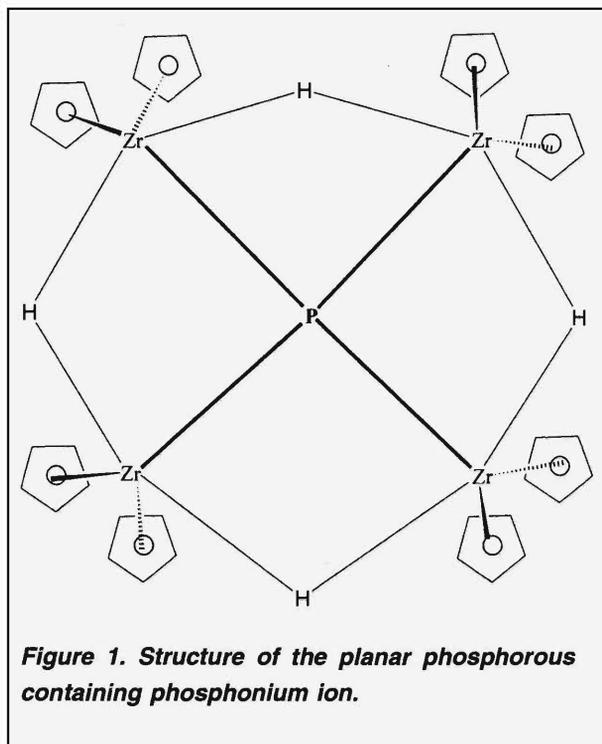
- | | |
|---|-------------|
| 1. Central atom: P | |
| 2. Valence electrons on P | = 5 |
| 3. 4 Cl contribute 1 electron each to form P-Cl bonds | = 4 |
| | = 9 |
| 4. Less one electron for positive charge | = -1 |
| 5. Total | = 8 |
| 6. Bond pairs around P | = $8/2 = 4$ |

Structure predicted: Tetrahedral

Scheme 1. Solid-state structure of PCl_5 . Tetrahedral arrangement around phosphorus in $[\text{PCl}_4]^+$ and Octahedral arrangement around phosphorus in $[\text{PCl}_6]^-$.

It is against such a background that we now consider a path breaking discovery of a planar four-coordinate phosphorus in a phosphonium ion which breaks all the rules [5] Matthias Driess at the Ruhr University, Bochum, Germany, has been interested in the preparation of tetrametallated phosphonium salts, $[\text{PR}_4]^+ \text{X}^-$; R = organometallic ligand, X = counter anion. In their search for a suitable synthetic route for such compounds, Driess and coworkers decided to

interact the well-known organometallic zirconium compound $[(\text{C}_5\text{H}_5)_2\text{ZrHCl}]$, known as the Schwartz reagent with an unusual triphosphonium ion, $[(\text{NMe}_2)_3\text{P}=\text{P}-\text{P}(\text{NMe}_2)_3]^+ [\text{BPh}_4]^-$ [see 6]. A 1:9 reaction ratio between the Schwartz reagent and the triphosphonium ion in the presence of the tertiary base triethylamine was carried out. A ^{31}P NMR of the reaction mixture showed a resonance at +123.9 ppm. This can be assigned to the released $\text{P}(\text{NMe}_2)_3$ indicating that the reaction is proceeding as per the plan. However, a quintet was observed at a very low field +254.2 ppm. The separation between the quintet was 29.5 Hz. This suggests that the phosphorus is coupled to four other equivalent nuclei. Only one pure compound was isolated from this mixture. This was identified as $\{\text{P}[\text{Zr}(\text{H})\text{Cp}_2]_4\}^+ [\text{BPh}_4]^-$. The structure of this compound in the solid-state was determined by single crystal X-ray diffraction analysis and is shown in *Figure 1*. The most remarkable feature of this structure is that the central phosphorus atom is completely planar. The Zr-P-Zr angles are very close to 90° . A closer inspection of the structure shows that the central phosphorus is in fact part of a wheel like arrangement where the outer ring of the wheel is made up of an eight-membered Zr-H cyclic ring. The hydrogens serve to bridge the zirconium centers and complete the cycle. The spokes of the wheel are formed by the Zr-P bonds. Thus, for the first time an unprecedented structural type was isolated where the central phosphorus in a phosphonium cation does not adopt the normal tetrahedral structure



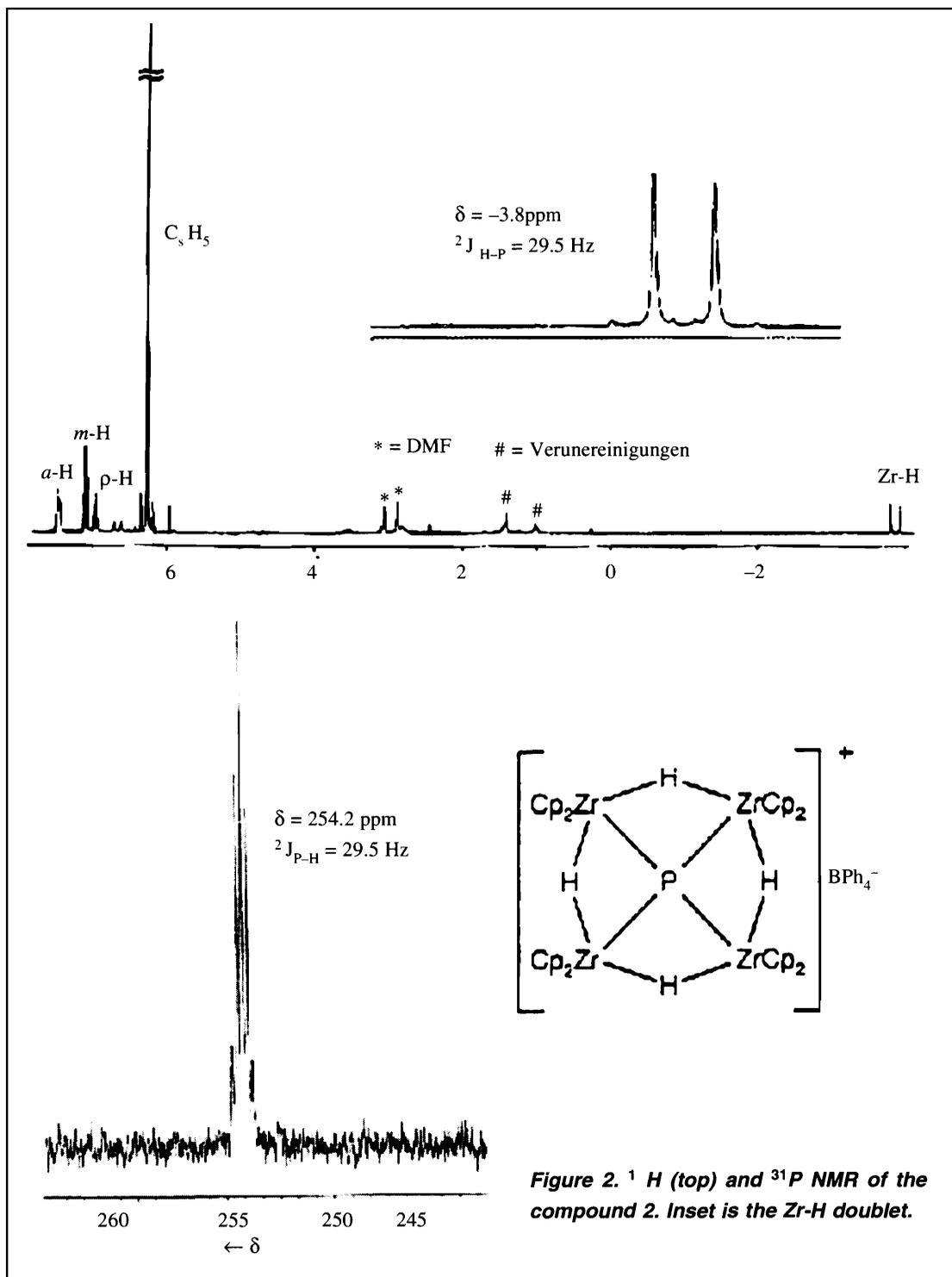
but prefers to form a square planar structure. The next question that Driess and co-workers addressed is whether this structure is retained in solution as well? NMR spectroscopy is a powerful technique to answer this question. The ^1H and ^{31}P NMR of this compound are shown in *Figure 2*. A resonance at -3.8 ppm in the proton NMR confirms the fact that bridging hydrogens persist in solution. This resonance is a signature for the bridging hydrides. Also it can be seen that this resonance appears as a doublet with a coupling constant of 29.5 Hz. In the phosphorus NMR a quintet corresponding to the coupling of the four equivalent hydrogens with the central phosphorus atom is seen with the same coupling constant of 29.5 Hz. Thus it is quite unambiguously proven that

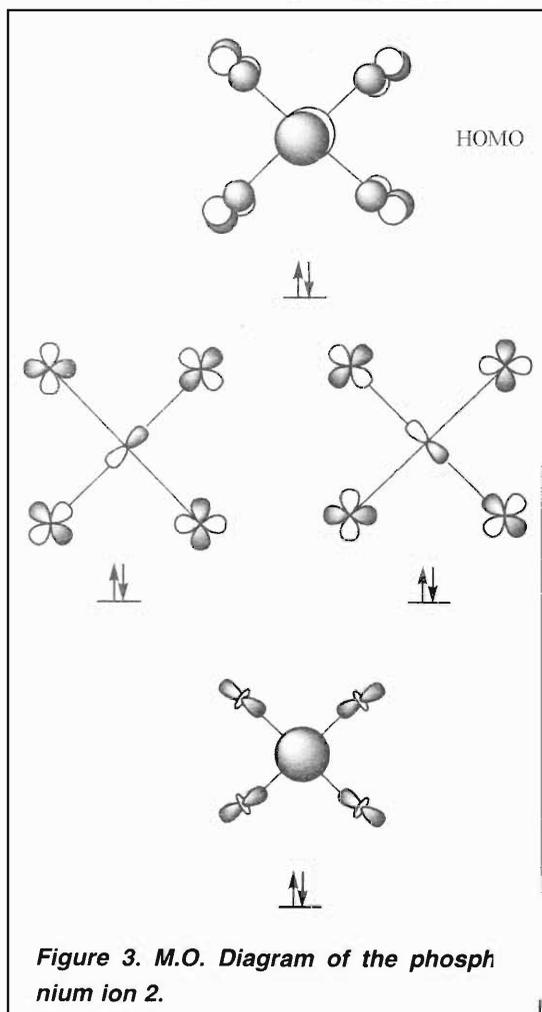
the planar phosphonium ion structure is retained in solution as well.

In order to understand the preference for the square-planar geometry for this compound, theoretical *ab initio* calculations were carried out on the model cation $[\text{P}\{\text{Zr}(\text{H})(\text{Cl})_2\}_4]^+$ for the two extreme structural possibilities viz., the tetrahedral structure and the square-planar structure. It has been found that the square planar structure is energetically more favored by about 74 kcal mol $^{-1}$. It is interesting to compare these results with that obtained for similar calculations on the $[\text{PH}_4]^+$ cation. For the latter the tetrahedral structure is the preferred one. What are the factors that tip the balance for $[\text{P}\{\text{Zr}(\text{H})$

$(\text{Cl})_2\}_4]^+$ in favor of the square planar structure?

An examination of the MO diagram of this cation (*Figure 3*) shows its similarity with that of the planar tetracoordinate carbon (see *Box 1*). The highest occupied molecular orbital is located on the phosphorus and contains a pair of electrons. The other electrons are involved in three-center Zr-P-Zr bonds. The HOMO electrons on phosphorus (in a p_z orbital) are involved in a facile π -back bonding with the symmetry adapted empty d orbitals of the metal center (*Figure 3*). Thus it is the π -acidity of the metal center in the organometallic fragment that tilts the balance towards the square planar structure. Two more crucial observations vindicate this view. One, as already stated above, theoretical cal-





calculations on $[\text{PH}_4]^+$ (where hydrogen cannot have π bonding) show that the tetrahedral structure is more favored over the planar structure by over $276 \text{ kcal mol}^{-1}$. Secondly, the calculations on the hypothetical $[\text{AlR}_4]^-$ and SiR_4 ($\text{R} = \text{Zr}(\text{H})\text{Cl}_2$), which are isoelectronic with the phosphorus compound, show that even in these cases the planar molecules are preferred over the tetrahedral ones by over 60 and 66 kcal mol^{-1} , respectively. This

underscores the importance of the π -accepting organometallic fragment towards stabilizing the planar structures.

The importance of Driess's discovery lies not only in the fact that a universal ligand for the stabilization of the non-conventional square-planar geometries for the heavier Group 14 and 15 elements has been discovered but more importantly it alerts us to the importance of challenging the accepted dogma. More often than not it is by such challenges that genuine progress in science is achieved.

Acknowledgements

V Chandrasekhar thanks Prof. Matthias Driess for providing the proton and phosphorus NMR spectra of compound 2 for being reproduced in this article.

Suggested Reading

- [1] J E Huheey, E A Keiter and R L Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, Fourth Edn. Harper Collins, New York, USA, 1993.
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