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First example of a discrete P··I··I··P assembly. The large influence of weak interactions on the ³¹P-NMR of iodinated phosphorus compounds.

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Thioethers, except derivatives of [7-R-7,8-C₂B₉H₁₁]⁻,^[1] are weaker coordinating ligands than similar phosphines.^[2] This is also evident focusing on the I··I distance in charge transfer, CT, spoke structures (Figure 1).^[3] The iodine-iodine distance, d(I··I), in these complexes can be interpreted considering the interactions between the σ* LUMO orbital on I₂ and the HOMO of the donor.^[4] The stronger the donor, the longer d(I··I) and vice versa. In spoke charge transfer X··I··I complexes, the d(I··I) varies from 3.2±0.2 Å in P··I··I^[5] to 2.80±0.05 Å in S··I··I,^[6] proving the weaker donor character of the thioether group. Whereas extended I₂, spoke adducts, polyiodides, and other I₂ structural motifs are well described,^[7] examples of discrete assemblies incorporating a bridging I₂ linking two donor atoms are limited. In fact no P··I··I··P example has ever been reported. Conversely, a few examples of S··I··I··S motifs are known.^[8] As thioethers are weaker donors than phosphines, it may be assumed that P··I··I··P may be generated with a very weak phosphine. By using a carboranylphosphine, (1-*i*Pr₂-2-Me-1,2-C₂B₁₀H₁₀), (Mecarb)*i*Pr₂P, the shortest d(I··I) in P··I··I spoke adducts was produced.^[9] A weaker donor than (Mecarb)*i*Pr₂P can be made by replacing the *i*Pr fragments by Ph as in 1-PPh₂-2-Me-1,2-C₂B₁₀H₁₀, **1**.^[10]

Indeed this is what has been found. Complex **2**, **1**·I₂·**1**, was obtained as red-brown crystals from a solution of **1** and I₂ (1:1) in CH₂Cl₂ (DCM) after 2 months at +4 °C. X-ray diffraction analysis of single-crystals of **2** (Figure 2) reveals a I₂ molecule bridging two molecules of **1**. A *pseudo*-linear P··I··I··P array of atoms is observed where the P··I and I-I distances are 3.3337(18) and 2.7753(14) Å, respectively.^[11] This is the shortest d(I··I) in phosphine/I₂ adducts, only slightly longer than solid I₂ at 110K (2.715(6) Å),^[12] but slightly longer than in S··I··I··S adducts.^[8] Additionally, two I-H(Ph) weak contacts of 3.152 Å are also observed (Figure 3).

Is the $P \cdots I \cdots I \cdots P$ motif observed in solid state also stable in solution? Relevant information can be drawn from ^{31}P NMR, conductivity measurements and UV-vis spectroscopy. Titration of **1** with I_2 in dry CDCl_3 , monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR, shows that increasing amounts of I_2 vs. **1** (**1**: I_2) lead to a continuous upfield shift of δ from 11.5 (1:0) to -10.2 (1:1) and to -12.4 ppm (1:2). Higher ratios of I_2 beyond 1:2 do not alter noticeably the -12.4 ppm δ value. This titration does not parallel the usual behavior of other phosphines, even $(\text{Mecarb})i\text{Pr}_2\text{P}$.^[9] Typically, an upfield chemical shift of the ^{31}P NMR resonance upon increasing ratios of I_2 is observed up to the 1:2 ($\text{R}'\text{R}_2\text{P}:\text{I}_2$) ratio, above which δ reverses to lower field due to the formation of $[\text{R}'\text{R}_2\text{PI}]^+\text{I}_3^-$ species.^[13] The same was observed in 1,2-dichloroethane (DCE) and DCM. This means that **1** does not induce the formation of I_3^- . To further confirm this point temperature dependent ^{31}P -NMR studies of **1**: I_2 solutions at 1:0.25, 1:0.5, 1:1 and 1:1.5 ratios to DCM freezing temperature were carried out. With no exception lower temperatures always produce a more negative δ , and this never reversed (see Supporting Information). Likewise, a conductimetric titration of DCM solutions gave very low conductance independently of the **1**: I_2 ratio proving the non formation of ionic species. Finally, the **1**: I_2 solutions were studied by UV/vis spectrometry which confirmed the absence of I_3^- species.^[5a,c] Therefore, and contrarily to other reported phosphines, **1** is incapable to sufficiently polarize the I-I bond in the **1**/ I_2 species in solution for a later splitting even in the presence of large excess of I_2 , but which model, **1**· I_2 or **1**· I_2 ·**1**, would preserve best the $\text{I} \cdots \text{I}$ fragment?.

To learn more on the forces that hold the phosphine/ I_2 adducts, we have combined crystallographic and NMR data with DFT studies and calculated NMR chemical shifts. In spite of the difficulty^[14] of current computational methods to match NMR data in compounds having P-I interactions, we thought positive to use these tools to get information on this interaction. To start with it,

it is necessary to indicate that after many unfruitful attempts to reproduce experimental P··I··I motifs from pure computation, we decided to take geometrical parameters from X-ray and use them as input in the calculations (see Supporting Information). By using DFT and GIAO we observe a strong ^{31}P NMR δ dependence upon altering the position of one of the two I atoms along the line defined by the remaining two elements in the P··I(1)··I(2) motif. When P··I(2) is kept constant, the effect of moving I(1) towards P produces a shielding on ^{31}P NMR. We then assume that a large number of iodine atoms in the near immediacy of P contribute to its NMR shielding. Conversely, for P··I(1) fixed, a strong ^{31}P -NMR δ deshielding is observed by increasing the I(1)··I(2) distance. This parallels the experimental data described above concerning the titration of Ph_3P with I_2 .^[13] The segregation of I(2) in $\text{Ph}_3\text{P} \cdots \text{I}(1) \cdots \text{I}(2)$ to produce I_3^- reverses δ producing a deshielded ^{31}P NMR resonance. A second relevant example concerns $[\text{PPh}_3\text{PI}]^+$. The computed ^{31}P NMR δ of the naked ion, for which calculation the geometric parameters from the crystal structure of $[\text{PPh}_3\text{PI}][\text{I}_3]$ have been taken,^[15] is -282 ppm, far from the experimental value at +44 ppm.^[5c] However if $[\text{I}_3]^-$ is incorporated into the calculation, at the geometric distances provided by the crystal structure, the computed δ is at +36 ppm. Therefore δ is very much dependent on weak interactions. This explains the continuous δ dependence upon altering the P/ I_2 ratio or even the temperature. All this suggests that when **1** and I_2 are combined in solution the existing moiety is P··I··I··P, and that the continuous upfield shift either with high ratios of I_2 or lower temperature is due to weak interactions nearby the phosphorus with other I_2 or other I containing molecules. The computed NPA charges calculated at the B3LYP/6-311+G(d,p) level of theory on P in Ph_3P and **1**, 0.90 vs. 0.92, respectively, suggest, as expected, a higher donating capacity of P in PPh_3 but this would not explain the very dissimilar P··I··I and P··I··I··P motifs (Figure 3). A further stabilization is required and

this may arise from the hydrogen *C-H* charges on the Ph groups in PPh₃ and in **1**. Charges ranging from 0.237 to 0.245 have been calculated in PPh₃ whereas they drop to the range 0.131 to 0.202 in **1**. Relevant NPA values corresponding to free PPh₃ and **1** are on display in Figure 3. In support of the importance of *C-H* aryl charges in the stabilization of the P··I··I··P arrangement is the absence of (Ph)C-H··I(1) interactions in Ph₃PI₂ while they are present in **2** as found in their X-ray crystal structures. On the contrary I(2) in Ph₃PI₂ interacts with (Ph)C-H groups in *para* positions from independent molecules (Figure 3).

Then, with regard to the influence of the carboranyl group in **1** and the formation of the P··I··I··P motif, it can be said that in addition of having a stronger electron-withdrawing character than Ph rings, it redistributes the charges on the neighbouring phenyl rings. So, the more negative *C-H* moieties in **1** are in *ortho* which are adequately placed for a weak interaction with I. This is not the case on a phenyl ring in PPh₃ in which the negative *C-H* sites are in *para*. These do participate in weak interaction with I(2) in the spoke motif.

The combination of experimental and computational techniques has shed some light into the Phosphorus-Iodine interactions and the importance of weak interactions in the interpretation of ³¹P NMR, but what can be said about the short d(I··I) in S··I··I··S and P··I··I··P motifs, which is shorter than in the spoke-type adducts?. A simple explanation results after considering that the combination of the two sp filled orbitals on both P will only lead to one filled orbital with the right symmetry to combine with σ* on I₂. Therefore the number of possible electrons transferred from donors is equal in P··I··I··P and P··I··I, however in the latter the sp electrons from the donor are necessarily more basic, therefore producing the longer I-I distance. This explanation accounts also for the similar d(I··I) distances, 2.754(2) and 2.816(2) encountered in (1,4,7-trithiacyclononane)₂(I₂)₄,^[3d] where equivalent thioethers produce spoke and I₂ bridging moieties within the same entity. An alternative but equivalent

explanation is given in the Supporting Information considering the butadiene model.

This research has substantiated the importance of the carboranyl moiety to get unknown structural motifs. Thanks to this, the P··I··I··P arrangement has been described for the first time. It is definitely proven in the solid state, and through a combination of experimental techniques and computational methods it appears that it also exists in halogenated solvents, at least. Furthermore it has been shown that the ^{31}P -NMR of phosphorus iodinated compounds depends enormously on the weak interactions with iodine containing species. This seems to be of great relevance when calculating the ^{31}P NMR by computational methods.

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LEGENDS FOR FIGURES

Figure 1. Solid state structure for spoke CT phosphine-diiodine complexes.

Figure 2. Molecular structure of **2** showing the atom labeling scheme. The thermal ellipsoids are set at 30% probability level. Selected interatomic distances [Å] and angles [°]: I··P 3.3337(18)), I-Iⁱ 2.7753(14) (i = -x, -y, -z), P-C(1) 1.884(6), P-C(14) 1.831(6), P-C(20) 1.813(6), C(1)-C(2) 1.710(8), P-I··Iⁱ 173.80(4), C(1)-P-C(14) 107.6(2), C(1)-P-C(20) 101.5(3), C(14)-P-C(20) 104.3(3), I··H(15) 3.1523, I··H(13b) 3.392.

Figure 3. Schematic representation of $1 \cdot I_2 \cdot 1$ and $Ph_3P \cdot I_2$ showing the contacts shorter than van der Waals radii. Numbers in parenthesis indicate NPA charges on the free ligands for phosphorous and defined hydrogen atoms.

Figure 1. Solid state structure for spoke CT phosphine-diodine complexes.

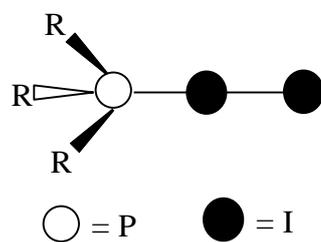


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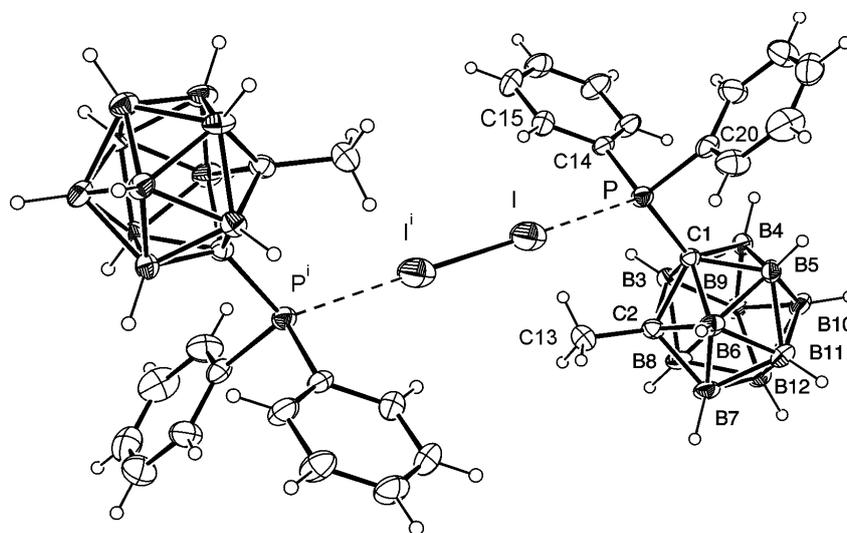
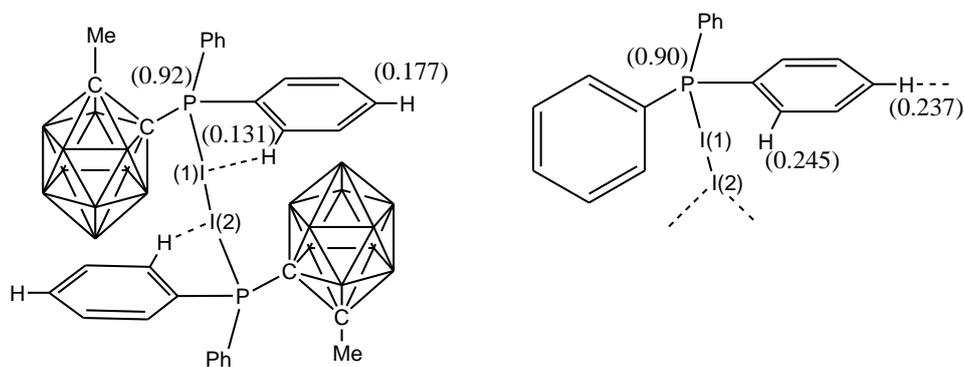


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TEXT FOR THE TABLE OF CONTENTS

The carboranylphosphine containing two electron-withdrawing phenyl groups is a very weakly coordinating phosphine. Its reaction with I₂ has permitted to demonstrate for the first time, the P··I··I··P motif in solid-state. Through a combination of experimental techniques and DFT calculations, it seems that this also exists in solution. It is also described the enormous influence of weak interactions in the ³¹P NMR of phosphorous-iodine compounds.

Keywords: boron, carboranes, diiodo-phosphines, ³¹P NMR, weak interactions.

GRAPHICAL MATERIAL

