Phosphane–Diiodine Complexes

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A Discrete P···I–I···P Assembly: The Large Influence of Weak Interactions on the ^{31}P NMR Spectra of Phosphane–Diiodine Complexes**

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Thioethers, except derivatives of $[7\text{-R-}7,8\text{-}C_2B_9H_{11}]^-$,[1] are more weakly coordinating ligands than phosphanes.[2] This difference is evidenced by the I–I distances in the spoke-shaped charge-transfer (CT) complexes $R_2S{\cdot}I_2$ and $R_3P{\cdot}I_2$ (Figure 1).[3] The I–I distance is sensitive to the strength of the interaction between the σ* LUMO orbital on I_2 and the HOMO orbital of the donor atom:[4] the stronger the donor, the longer the I–I distance. In these spoke CT complexes, the I–I distance varies from 3.2 ± 0.2 Å in $R_3P{\cdot}I_2$ adducts[5] to 2.80 ± 0.05 Å in $R_2S{\cdot}I_2$ adducts,[6] indicating the weaker donor character of the thioether group. Whereas extended I_2 arrays, spoke adducts of I_2, polyiodides, and other structural configurations involving I_2 molecules are well described,[7] examples of discrete assemblies incorporating an I_2 molecule bridging to two donor atoms are limited. The P···I–I···P assembly is unknown, and only a few examples of the S···I–I···S motif have been reported.[8] As thioethers are weaker donors than phosphanes, we predicted that $R_3P{\cdot}I_2{\cdot}PR_3$ adducts could be generated by using a very weakly coordinating phosphane ligand. By using the carboranyl phosphane (Mecarb)*i*Pr_2P (Mecarb = 1-(2-Me-1,2-$C_2B_{10}H_{10}$)), the complex (Mecarb)*i*$Pr_2P{\cdot}I_2$ containing the shortest I–I distance observed in a spoke adduct was produced.[9] A weaker donor ligand than (Mecarb)*i*Pr_2P can be obtained by replacing the isopropyl fragments by electron-withdrawing phenyl groups, as in (Mecarb)Ph_2P (**1**).[10]

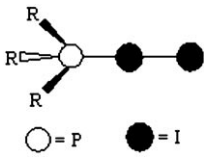

Figure 1. Spoke configuration of $R_3P{\cdot}I_2$ complexes.

Use of ligand **1** allowed the formation of the desired complex **1**·I_2·**1** (**2**), which was isolated as red-brown crystals from a solution of **1** and I_2 (1:1) in CH_2Cl_2 after 2 months at 4 °C. Single-crystal X-ray diffraction confirmed that the structure of **2** consists of one I_2 molecule bridging two molecules of **1** (Figure 2).[11] A nearly linear P···I–I···P arrangement is observed, in which the P···I and I–I distances

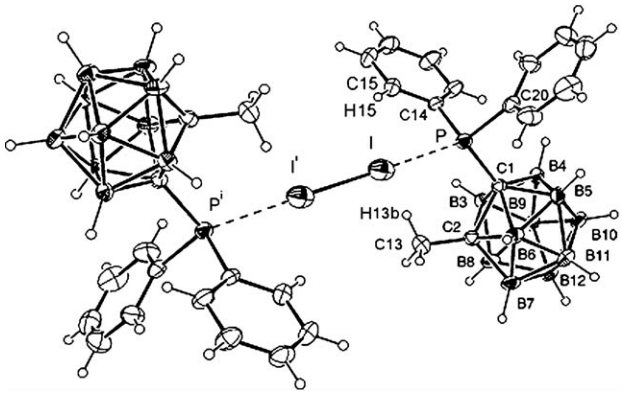

Figure 2. Molecular structure of **2**. The thermal ellipsoids are set at 30% probability. Selected interatomic distances [Å] and angles [°]: I–I^i 2.7753(14) ($i = -x, -y, -z$), P–C1 1.884(6), P–C14 1.831(6), P–C20 1.813(6), C1–C2 1.710(8), I···P 3.3337(18), I···H15 3.15, I···H13b 3.39; P-I-I^i 173.80(4), C1-P-C14 107.6(2), C1-P-C20 101.5(3), C14-P-C20 104.3(3).

are 3.3337(18) and 2.7753(14) Å, respectively. The I–I distance is the shortest found in a phosphane–I_2 adduct, and is only slightly longer than that in solid I_2 at 110 K (2.715(6) Å).[12] The I–I distance in **2** is similar to those in the $R_2S{\cdot}I_2{\cdot}SR_2$ adducts (2.75–2.79 Å).[8] Additionally, two weak I···H(Ph) contacts of 3.15 Å are observed in **2** (Figure 3).

Is the P···I–I···P structural motif observed in the solid state also stable in solution? Monitoring the titration of **1** with I_2 in dry $CDCl_3$ by $^{31}P\{^1H\}$ NMR spectroscopy revealed that increasing the ratio of I_2:**1** leads to a continuous upfield shift of the P-atom signal, from $\delta = 11.5$ (I_2:**1** = 0:1) to −10.2 (1:1) to −12.4 ppm (2:1). The same trend was observed for titrations in 1,2-dichloroethane and CH_2Cl_2. Ratios of I_2:**1** greater than 2:1 do not noticeably alter the chemical shift. These results do not parallel the behavior of other phosphanes, including (Mecarb)*i*Pr_2P,[9] for which an upfield shift of the P-atom resonance is observed when the ratio of I_2:R_3P is increased, up to a ratio of 2:1. Above this ratio, the signal shifts downfield, owing to the formation of $[R_3PI][I_3]$ species.[13] This difference in behavior implies that **1** does not induce the formation of the $[I_3]^-$ ion. To further confirm this point, temperature-dependent ^{31}P NMR spectroscopic studies of solutions of I_2:**1** in CD_2Cl_2 at ratios of 0.25:1, 0.5:1, 1:1, and 1.5:1 were carried out from 1–175 °C. In general, lower temperatures produced an upfield shift of the P-atom signal (see Supporting Information). Likewise, in conductometric titrations of solutions of I_2:**1** in CH_2Cl_2, very low conductance was observed, independent of the I_2:**1** ratio, which is inconsistent with the formation of ionic species. Finally, the I_2:**1** solutions were studied by UV/Vis spectros-

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copy, which confirmed the absence of $[I_3]^-$ ions.[5a,c] Therefore, in contrast to other phosphanes, **1** is incapable of sufficiently polarizing the I–I bond to allow the splitting required for the formation of $[I_3]^-$ ions, even in the presence of a large excess of I_2. But which species in solution, $\mathbf{1}\cdot I_2$ or $\mathbf{1}\cdot I_2\cdot\mathbf{1}$, best preserves the I–I fragment?

To learn more about the forces that bind phosphane–I_2 adducts, we combined experimental data with density functional theory (DFT) to calculate theoretical NMR spectra for $Ph_3P\cdot I_2$ (in spite of the difficulties encountered in the calculation of accurate NMR spectra for compounds containing P–I interactions using current computational methods[14]). Note that our attempts to reproduce the experimentally observed P···I–I arrangement in $Ph_3P\cdot I_2$ were unsuccessful; therefore, we decided to use geometric parameters from the crystal structure of $Ph_3P\cdot I_2$[5c] as input in our DFT calculations using gauge-including atomic orbitals (GIAO) (see Supporting Information). The calculated chemical shift of the donor P atom depends strongly on the positions of each of the two I atoms along the line defined by the other two atoms in the P···I(1)–I(2) assembly. When the P···I(2) distance is kept constant, moving the I(1) atom towards the P atom increases the shielding of the P nucleus. When the P···I(1) distance is fixed, moving the I(2) atom away from the P atom (and hence increasing the I(1)···I(2) distance) decreases the shielding at the P nucleus. Clearly, a larger number of I atoms in the near proximity of the P donor atom increase its shielding significantly. The results of the calculations are consistent with the upfield shift of the P-atom signal observed when the ratio of I_2:Ph_3P is increased in the titration of Ph_3P with I_2.[13] The removal of I(2) from the Ph_3P···I(1)–I(2) molecule to give the $[Ph_3PI]^+$ ion (along with an $[I_3]^-$ ion) deshields the P nucleus. The $[Ph_3PI]^+$ ion was examined in a separate set of calculations based on geometric parameters from the crystal structure of $[Ph_3PI][I_3]$.[15] The computed chemical shift of the P atom of the naked cation is $\delta = -282$ ppm, far from the experimental value of $\delta = 44$ ppm.[5c] However, if the $[I_3]^-$ ion is incorporated into the calculation the computed chemical shift of the P atom is $\delta = 36$ ppm. Therefore, the chemical shift is very dependent on weak interactions. All of these results suggest that when **1** and I_2 are combined in solution the moiety formed is P···I–I···P, and that the continuous decrease in the chemical shift of the P atoms with either increasing ratios of I_2 or lower temperatures arises from an increase in the number or strength of weak interactions between the P atoms in **1** and I_2 molecules or other I-containing species.

The natural population analysis (NPA) charges on the P atoms in the free ligands Ph_3P and **1**, calculated at the B3LYP/6-311+G(d,p) level of theory, are 0.90 and 0.92, respectively (Figure 3; see Supporting Information). These values suggest that, as expected, the P atoms in PPh_3 are slightly better donors than those in **1**, but do not explain why very dissimilar P···I–I and P···I–I···P motifs are formed (Figure 3). The stabilization of one arrangement over the other may arise from differences in the charges on the phenyl hydrogen atoms in PPh_3 and in **1**. Charges ranging from 0.237 to 0.245 are calculated for those in PPh_3, whereas lower charges of 0.131 to 0.202 are calculated for those in **1** (some of these data are shown in Figure 3). The X-ray crystal structures of $Ph_3P\cdot I_2$[5c] and **2** also demonstrate the importance of the phenyl hydrogen atoms in PPh_3 and **1** for the stabilization of the P···I–I···P arrangement. Intramolecular I···H(Ph) interactions are absent in $Ph_3P\cdot I_2$ but present in **2**. In $Ph_3P\cdot I_2$, I(2) participates in intermolecular interactions with hydrogen atoms in the *para* positions on phenyl groups from two different molecules (Figure 3).

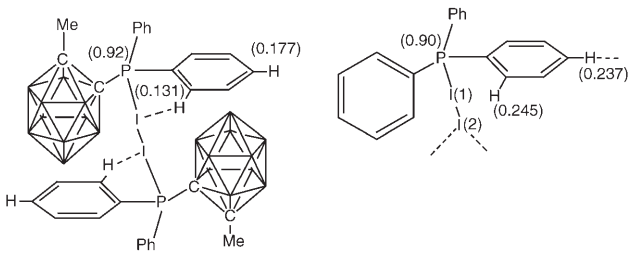

Figure 3. Schematic representation of $\mathbf{1}\cdot I_2\cdot\mathbf{1}$ (**2**) (left) and $Ph_3P\cdot I_2$ (right). Weak I···H contacts shorter than the sum of the van der Waals radii are indicated with dashed lines; those in $Ph_3P\cdot I_2$ are intermolecular contacts. The numbers in parentheses indicate the calculated NPA charges for the P atoms and selected H atoms of the free ligands **1** and PPh_3.

With regard to the influence of the carboranyl group in **1** on the formation of the P···I–I···P motif, it is noted that in addition to having a stronger electron-withdrawing character than a phenyl ring, the carboranyl group also redistributes the charges on the phenyl rings connected to the same P atom. The phenyl hydrogen atoms in **1** with the lowest charges are in the *ortho* positions, and are thus appropriately placed for a weak I···H(Ph) interaction involving a partial electron donation into the σ* orbital on the I_2 molecule in the adduct **2**. This is not the case for the phenyl rings in PPh_3, in which the hydrogen atoms with the lowest charges occupy the *para* positions. Some of these hydrogen atoms do participate in weak intermolecular interactions with I(2) in the crystal structure of the spoke adduct $Ph_3P\cdot I_2$.

The combination of experimental and computational techniques has shed some light on the P–I interactions in $R_3P\cdot I_2$ and $R_3P\cdot I_2\cdot PR_3$ complexes, and on the importance of weak interactions in the interpretation of their ^{31}P NMR spectra, but what can be said about the I–I interactions in these complexes? The I–I distances in $R_3P\cdot I_2\cdot PR_3$ (and $R_2S\cdot I_2\cdot SR_2$) are generally shorter than those in the spoke adducts $R_3P\cdot I_2$. This observation can be explained by considering the orbitals involved in the interaction between the donor P atoms and the I_2 molecule. The combination of the filled lone-pair sp^3 orbitals on each of the two P atoms leads to two filled orbitals, only one of which has the correct symmetry to interact with the σ* orbital on the I_2 molecule. Therefore, the number of electrons transferred from the donor atoms to the I_2 molecule is equal in $R_3P\cdot I_2\cdot PR_3$ and $R_3P\cdot I_2$. However, in $R_3P\cdot I_2$ the electrons in the sp^3 orbital on the donor atom are necessarily more polarizable, and therefore, produce a longer I–I bond. This explanation also accounts also for the similarity of the I–I bond lengths in the spoke $R_2S\cdot I_2$ (2.816(2) Å) and bridging $R_2S\cdot I_2\cdot SR_2$ (2.754(2) Å) adducts with equivalent thioethers in (1,4,7-trithiacyclononane)$_2(I_2)_4$.[3d] An alternative, but equivalent, explanation of

the bonding in $R_3P{\cdot}I_2{\cdot}PR_3$, based on the butadiene model, is given in the Supporting Information.

This research has substantiated the importance of ligands containing the carboranyl moiety in the formation of phosphane–I_2 adducts with novel structural motifs. Through the use of a carboranyl phosphane ligand, the P···I–I···P assembly was isolated for the first time. X-ray diffraction analysis of **2** demonstrated the presence of this structural motif in the solid state, and a variety of experimental techniques and computational methods suggest that it also exists when **2** is dissolved in halogenated solvents. Furthermore, we have shown that the ^{31}P NMR spectra of phosphane–I_2 adducts are greatly influenced by weak interactions between the adducts and I-containing species. This observation is of great relevance to the calculation of theoretical ^{31}P NMR spectra.

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