[16] Typical pre-exponential factors (A) for electron exchange lie in the region of 10^{13} s^{-1} (see ref [3]) and should not be significantly affected by changes in temperature, chemical structure, or solvent polarity.
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The Distinct Effect of the *o*-Carboranyl Fragment: Its Influence on the I–I Distance in R_3PI_2 Complexes**

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Although compounds of stoichiometry R_3PX_2 (R = organic substituent, X = halogen) have been known for over 100 years, their solid-state structure remains largely unexplored. This is surprising considering that some of these species have found significant use as reagents in synthetic organic and inorganic chemistry and are commercially available.[1] Interest in their solid-state structure has increased in the last decade since the structure of tBu_3PI_2 was disclosed.[2] The existence of significant iodine–iodine interaction in this compound and the four-coordinate molecular structure, novel in phosphane chemistry, stimulated the interest of researchers in the area.[3, 4] Du Mont et al.[2] upon the observation that the I–I bond in tBu_3PI_2 (3.326(1) Å) was longer than in Ph_3AsI_2 (3.005(1) Å),[5] suggested that it could be interpreted either as an iodophosphonium salt or as an iodine charge-transfer complex. With the incorporation of new data it was later considered as a charge-transfer complex.[6] The interpretation of the I–I interaction in R_3PI_2 molecules is, however, still a point of controversy as has been stated recently.[7] We shall consider the I···I Van der Waals distance to be 4.3 Å, thus any distance smaller than this suggests an I–I bond interaction.

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The structures of halophosphoranes in the solid-state depend largely on the starting phosphane R_nPX_{3-n}, the solvent used, the halogen, and the phosphane:halogen ratio.[8] In the solid-state structures of R_3PX_2 three basic structural motifs are found: trigonal bipyramidal in Ph_3PF_2,[9] $(C_6F_5)_3PCl_2$, $Ph_2(C_6F_5)PCl_2$,[10] and Ph_3PCl_2;[11] the molecular charge-transfer "spoke" structure for tBu_3PI_2,[2] Ph_3PI_2,[3a] $PhMe_2PI_2$,[3b] Ph_3PBr_2,[12] iPr_3PI_2[13] and Ph_3PIBr,[14] and the ionic form, for example, in $[nPr_3PCl]Cl$,[10] and $[Ph_3PCl]Cl$.[4a] In the last two types of structure the P center is tetracoordinate. For this coordination, the distinction between molecular charge-transfer "spoke" structure and the ionic form is very tenuous, and there seems to be a continuum in the X–X bond strength. If attention is focused solely on R_3PI_2 compounds, a few examples exist which bring information on the I–I and P–I distances: in $PhMe_2PI_2$,[3b] iPr_3PI_2,[13] tBu_3PI_2[2] and Ph_3PI_2,[3a] the observed I–I bond lengths [Å], P–I bond lengths are in parenthesis, are 3.408(2) [2.410(2)], 3.383(1) [2.409(2)] and 3.372(1) [2.420(2)], 3.326(2) [2.461(2)], and 3.161(2) [2.481(4)], respectively. The shortening of the I–I bond implies that elongation of the P–I bond takes place. In no case has an I–I bond been found that is as short as that in Ph_3AsI_2 (3.005(1) Å).[5] For comparison, the I–I bond in I_2 is 2.660 Å.[15] The elongation of the I–I bond is expected since electron density is transferred into the σ* orbital of the diiodine by the electron donor. As a consequence the more basic the phosphanes are the longer the I–I bond will be and thus the shorter the P–I bond.

The *o*-carborane, 1,2-$C_2B_{10}H_{12}$, is an icosahedral cluster in which the two carbon atoms are in adjacent positions. One way to build the orbital set of *o*-carborane is to consider that each participating atom has as its valence orbital set two sp, and two p orbitals. This situation is very similar to the molecular orbitals in acetylene. Consequently, the C–H group of *o*-carborane is acidic and may be removed by strong bases. Moreover, the *o*-carborane cage through substitution at carbon is extremely electron-withdrawing. During our research on *o*-carboranylmonophosphane derivatives, 1-PR_2-2-R′-1,2-$C_2B_{10}H_{10}$[16] (Figure 1), we considered the possibility that a molecular charge-transfer "spoke" structure could be obtained. This would provide data on the electron-withdrawing capacity of the *o*-carboranyl cluster through the influence on the I–I distance, and also allow new data concerning the R_3P-I-I continuum to be obtained. There are several *o*-carboranylmonophosphanes of the type (*o*-carboranyl)R_2P available, but we decided to look for one with the highest basicity. The R′ radical in 1-PR_2-2-R′-1,2-$C_2B_{10}H_{10}$ can be varied and although its influence on the basicity is not considerable it is adequate to improve crystallization; the R radicals influence on the phosphorous center is important. Thus, a basic carboranylphosphane was chosen to compensate for the –I (inductive effect) influence of the *o*-carboranyl cluster on the phosphorus center.

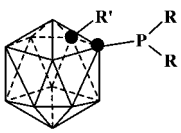

Figure 1. *closo*-Carboraylmonophosphane (● = C, other vertices are BH).

First assays with 1-P*i*Pr_2-2-Me-1,2-$C_2B_{10}H_{10}$ (**1**) were titrations with I_2 in dry $CHCl_3$. This has been a standard experiment in the development of this R_3PI_2 chemistry, and

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provides information on the complex equilibrium established. The ^{31}P NMR results are shown in Table 1. A nice point is the continuous upfield shift from the plain *closo*-carboranylmonophosphane up to the 1:1 stoichiometry (δ33.0 to 15.2), from

Table 1. Titration study of **1** with I_2 in $CDCl_3$.

1:I_2 ratio	^{31}P NMR (δ)
1:0	33.0
1:0.25	24.7
1:0.50	15.4
1:1	15.2
1:1.25	21.1
1:1.50	28.8
1:2	30.7

that point on there is a continuous downfield shift (δ15.2 to 30.7 ppm), after the addition of further amounts of iodine. This behavior is not abnormal for triorganophosphanes, and can be interpreted considering the formation of $R_2R'PI$-I followed by the formation of $[R_2R'PI]I_3$.[17] The formation of the latter is corroborated by UV/Vis spectra in which the electronic absorption bands at 241, 302 and 363 nm are indicative of I_3^- ions.[3a, 6] The I_3^- ion is less nucleophilic than I^- ions, thus facilitating the formation of the cationic $[R_2R'PI]^+$ species. However, contrary to previous studies, no formation of solid phases was observed during the titration. These results suggested that *o*-carboranylphosphanes could produce the sought after $R_2R'PI_2$ molecular "spoke" charge-transfer complexes, and that the *o*-carboranylphosphanes do not behave like phosphorus triiodide (PI_3) or alkyldiiodophosphanes (RPI_2) which cannot compete in solution with iodide anions for coordination to the I^+ unit of the $[R_2R'PI]^+$ ion.[17a]

The compound (1-P*i*Pr$_2$-2-Me-1,2-$C_2B_{10}H_{10}$)$\cdot I_2$ (**2**) is isolated as a red brown crystalline solid from the reaction of stoichiometric quantities of **1** and I_2 in toluene at $+4\,^\circ$C. The spectroscopic data indicated a minor discrepancy between the $^{31}P\{^1H\}$ NMR of the $CDCl_3$ solution of **2** and the 1:1 ratio I_2 titration of **1** in $CDCl_3$ ($\delta = 14.0$ versus 15.2). At present we do not have further data to see if this variation has structural consequences or if it is because of a kinetic effect. The $^{11}B\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ demonstrated that changes had taken place at the P atom that affected the ^{11}B NMR resonance signals of the cluster. This was to be expected since increasing or decreasing the electron density of the P atom alters the electron density distribution of the cluster, a result of the good cluster–phosphorous communication that we have described.[16a]

Crystals suitable for X-ray analysis were obtained directly from the toluene solution used for the synthesis of **2**. The crystal structure of **2** confirmed our expectations[18] (Figure 2) and has a structure similar to that of the charge-transfer "spoke" R_3PI_2 and Ph_3AsI_2 complexes. However, it has a particular characteristic that makes it notable: its I–I bond (3.021(1) Å) is practically equal to that found in Ph_3AsI_2 (3.005(1) Å) and represents the shortest reported I–I interaction in organophosphane–diiodine chemistry. This short bond length also implies that the As atom of the Ph_3As group behaves electronically like the P atom of 1-P*i*Pr$_2$-2-Me-1,2-$C_2B_{10}H_{10}$.

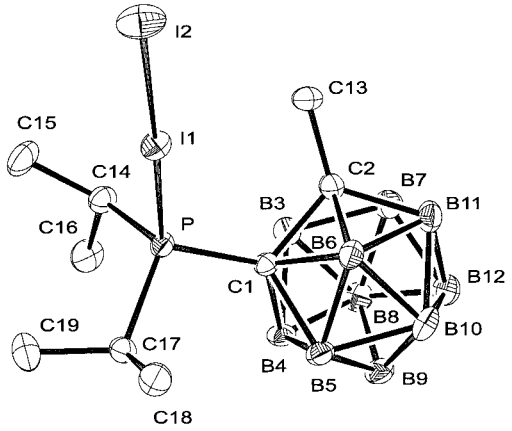

Figure 2. Molecular structure of **2** showing the atom labeling scheme. The thermal ellipsoids are set at the 30% probability level and the hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: I1-P 2.5978(14), I1-I2 3.021(1), P-C14 1.851(4), P-C17 1.855(4), P-C1 1.871(4), C1-C2 1.690(6); P-I1-I2 177.49(3), C14-P-C17 112.6(2), C14-P-C1 107.3(2), C17-P-C1 105.0(2), C14-P-I1 109.75(15), C17-P-I1 107.17(15), C1-P-I1 115.11(14).

This was one of our objectives, to show that the R_3P-I-I bond could be modulated and that there is a continuum in the I–I bond; compound **2** has provided one of the limits. Research is underway to find out if this I–I bond can be made even shorter by adequately combining carboranyl/alkyl or aryl substituents in phosphane chemistry. The second objective was to show the distinct properties of the *o*-carborane cage, the electron-pulling capacity, lipophilicity, B–H bonds, bulkiness, and the capacity for substitution on boron atoms should make this species a distinct fragment that can provide a new chemistry.[19]

Experimental Section

2: I_2 (13.9 mg, 5.5×10^{-2} mmol) was added to a solution of **1** (15 mg, 5.5×10^{-2} mmol) in toluene (5 mL). The solution was stirred at room temperature for 1 h and left for two months at $+4\,^\circ$C. After this time red brown crystals were obtained, yield: 91%; $^1H\{^{11}B\}$ NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS):$\delta = 1.48$ (dd, $^3J(H,H) = 7.0$ Hz, $^3J(P,H) = 17.4$ Hz, 6H; CH_3), 1.54 (dd, $^3J(H,H) = 6.8$ Hz, $^3J(P,H) = 18.8$ Hz, 6H; CH_3), 2.33 (s, 3H; CH_3), 2.52 (ddq, $^2J(P,H) = 2.3$ Hz, $^3J(H,H) = 6.8$ Hz, $^3J(P,H) = 7.0$ Hz, 2H; CH); ^{11}B NMR (96.29 MHz, $CDCl_3$, 25 °C, $Et_2O\cdot BF_3$):$\delta = 2.6$ (d, $^1J(B,H) = 144$ Hz; 1B), −3.9 (d, $^1J(B,H) = 154$ Hz, 1B), −7.7 (d, $^1J(B,H) = 154$ Hz, 5B), −9.5 (d, $^1J(B,H) = 176$ Hz, 3B); $^{31}P\{^1H\}$ NMR (121.48 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4):$\delta = 14.0$ (s); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS):$\delta = 18.9$ (s), 21.9 (s), 26.3 (s), 30.6 (s), 67.7 (d, $^1J(P,C) = 48.1$ Hz), 79.2 (s); elemental analysis calcd (%) for $C_9H_{27}B_{10}I_2P$: C 20.46, H 5.12; found: C 20.35, H 5.19.

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[18] The X-ray diffraction data were collected at 294 K with a Rigaku AFC-5S four-circle diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Crystal data for **2**: Formula $C_9H_{27}B_{10}I_2P$, $M_r = 528.18$, crystal size: $0.36 \times 0.34 \times 0.30$ mm, monoclinic, space group $P2_1/a$ (No. 14), $a = 14.087(4)$, $b = 10.358(2)$, $c = 15.230(3)$ Å, $\beta = 110.33(2)^\circ$, $V = 2083.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.684$ g cm^{-3}, $\mu = 3.082$ mm^{-1}, $F(000) = 1008$, reflections collected 3835, unique 3673 [$R_{int} = 0.0187$]. An empirical absorption correction with ψ-scan data was applied. The structure was solved using SIR92 and was refined against $|F^2|$ using program SHELXL-97 (230 parameters). R indices were (all data): $R_1 = 0.0524$, $wR_2 = 0.0727$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144823. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Remote Enantioselection Transmitted by an Achiral Peptide Nucleic Acid Backbone**

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Peptide nucleic acid (PNA; Figure 1b) is an achiral DNA (or RNA) mimic with an amide (pseudopeptide) backbone. PNA oligomers form double helices with complementary DNA or RNA through Watson–Crick base pairing.[1] Complementary strands of PNA form DNA-like double helices but the left-handed and right-handed duplexes have equal stability in the absence of chiral influences.[2]

The RNA-world hypothesis which states that our biological life was preceded by a prebiotic system in which RNA oligomers functioned both as genetic materials and as enzyme-like catalysts is widely accepted.[3] This hypothesis raises the problem of the origin of RNA and, in particular, emphasizes the difficulty of forming and replicating a homochiral nucleic acid in a solution of racemic nucleotides.[4] One possible solution to this problem involves a gradual transition from an achiral genetic material (for example, one resembling PNA) to RNA.

Although there are now claims that PNA could have been a prebiotic molecule,[5] this is highly speculative. We have used PNA extensively as a model for the type of achiral polymer that could have preceded RNA.[6] The influence of chiral substituents on the distribution of left- and right-handed PNA helices has been reported at some length.[2, 7] Here we continue to explore the possibility of a transition from an achiral nucleic acid analogue to RNA, and show that as few as two D-deoxynucleotides incorporated at one end of a decameric PNA double helix can control the handedness of the helix. Furthermore, we show that this can result in enantioselective chemistry both remote from and at residues not covalently connected to the inducing chiral dinucleotide. Remote enantioselection of this kind could overcome the problem of enantiomeric cross-inhibition, and thus greatly simplify a stepwise evolutionary transition from a prebiotic achiral to a biological homochiral genetic material.

We prepared a series of PNA-containing duplexes (Figure 1a): DS is an achiral PNA double helix, while D1 is the corresponding duplex in which the N-terminus cytosine

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