DOI: 10.1002/ejic.201100428

Through-Space *J*(P,P) and *J*(P,F) Spin–Spin Coupling in C_1-Symmetric Biaryl Diphosphanes

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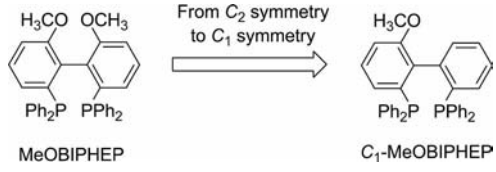
Keywords: Biphenyl / Coupling / Phosphanes / Fluorine / NMR spectroscopy

The first simultaneous $^{31}P,^{31}P$ and $^{31}P,^{19}F$ solution-phase through-space nuclear spin–spin coupling in biphenyl derivatives is reported. The magnitudes of the coupling constants are in the range 5.3–28.7 and 2.3–5.1 Hz, respectively. Their observation became possible through access to a recently developed class of C_1-symmetric biphenyl diphosphanes. We used this to prepare a series of model compounds for the study of the through-space couplings. Various 1D and 2D techniques [COSY, NOESY, heteronuclear single quantum coherence (HSQC), HMBC, HSCQ-TOCSY, selective $^1H\{^{31}P\}$-decoupling and iterative bandshape analysis] were applied to assign the ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra as completely as possible. X-ray structure determinations confirmed the structural assignments and afforded P···P distances and torsion angles in the solid state. No simple correlation was found between the experimental $J(^{31}P,^{31}P)$ values in solution and the relevant geometric parameters (P···P distance and torsional angle between the phosphorus lone pairs) in the solid state.

Introduction

Phosphane-based ligand research for catalysis is one of the most fascinating and prolific areas of chemistry. Over the last 60 years, intensive efforts have been devoted to the synthesis of new phosphanes and to their application in coordination chemistry.[1] Particular attention has been paid to their use in catalysis and especially in asymmetric hydrogenation.[2] In this context, an increasingly large number of phosphane ligands has been developed and tested in transition metal-catalyzed reactions. In particular, the role of the ligand backbone is one of the cornerstones of investigations in the field of ligand design. Thus, phosphorus substituents have been successively attached to various building blocks, such as tartaric acid derivatives, binaphthyl, biphenyl, ferrocenyl and heteroaromatic scaffolds, providing great structural diversity and leading to powerful ligands including DIOP,[3] BINAP,[4] MeO-BIPHEP[5] and Josiphos.[6] Among these phosphanes, our group has recently reported the synthesis and catalytic properties of new C_1-symmetric biaryl diphosphane ligands.[7] These studies have highlighted their efficiency in benchmark asymmetric hydrogenation reactions in comparison to classical C_2-symmetric biaryl diphosphanes, such as BINAP and MeO-BIPHEP (Scheme 1).



Scheme 1. From C_2-symmetry to C_1-symmetry in biaryl diphosphane ligands as exemplified for MeO-BIPHEP.

In the course of our NMR studies on these diphosphanes, an unexpected variety of *J*(P,P) and, in some cases, *J*(P,F) through-space nuclear spin–spin couplings was observed, which have not been previously reported. To date, the observation of scalar through-space interactions has been limited mainly to fluorine containing organic species,[8] with the through-space $^{19}F,^1H$ coupling observed by Davis et al. in 1961 being the first example.[9] Through-space coupling with at least one fluorine atom is quite common. More recent experimental studies have been published by Ernst and Mallory et al.,[8a,8i] and theoretical investigations by Peralta and Arnold et al.[8j,8k]

Although through-space coupling involving one phosphorus nucleus is described in the literature, this phenomenon has been less systematically studied and has phosphorus exclusively in the +III oxidation state.[10] For example, Odorisio et al.[11] and Goddard et al.[12] reported the $^{31}P,^1H$ coupling through space in 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocinenes. In 1990, Pascal Jr. et al.[13] observed the first $^{31}P,^{13}C$ spin–spin coupling through space in cyclophanes. Pye et al. reported an analogous through-space coupling in 4,12-bis(diphenylphosphanyl)[2.2]paracyclophane.[14] Pastor et al. studied numerous bis(phosphites)

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100428.

and observed $^{31}P,^{31}P$ coupling through space.[15] Sawamura et al. also observed a large $^{31}P,^{31}P$ coupling of 22.0 Hz in chiral bis[1-(diarylphosphanyl)ethyl]-1,1′′-biferrocene between the two P nuclei separated by seven bonds.[16] On the other hand, Hillebrand et al. claimed a $^{31}P,^{31}P$ coupling of 27.3 Hz to be present in 4,5-bis(diphenylphosphanyl)-xanthene.[17] Similarly, Hierso et al. reported $^{31}P,^{31}P$ coupling through space in tetraphosphane ferrocenyl derivatives[18] and suggested, in analogy to Mallory's theory, a lone-pair overlap model for this type of coupling. Matt et al. reported $^{31}P,^{31}P$ coupling through space in diphosphane calixarenes where the phosphorus atoms are ten bonds apart,[19] and, finally, extremely large through-space $^{31}P,^{31}P$ couplings of about 240 Hz were observed in a series of di-bridged calix[4]arene bisphosphites.[20]

In contrast, $^{31}P,^{19}F$ coupling through space is less often described in the literature than $^{31}P,^{1}H$ or $^{31}P,^{13}C$ couplings.[21] $^{31}P,^{19}F$ coupling through space has been mainly observed in 2-(trifluoromethyl)phenylphosphanes.[22]

Results and Discussion

$^{31}P^{31}P$ Coupling in Bis(diphenylphosphanyl)biphenyls

We synthesized the first C_1-MeO-BIPHEP analogue (**1**) and showed its efficiency in asymmetric hydrogenation in 2007 (Figure 1).[7b–7f] In this molecule, the two phosphorus groups are nonequivalent due to the C_1-symmetry of the biphenyl backbone. When we analyzed its proton-decoupled ^{31}P NMR spectrum, instead of observing two singlets as expected, we were surprised to see that the nonequivalent phosphorus nuclei appeared as doublets with a coupling constant of $^{5}J(P,P)$ = 18.3 Hz. First we assumed that through-bond coupling was responsible for this multiplicity as five bonds separate the phosphorus atoms.

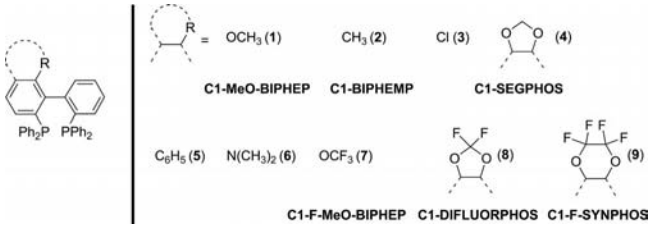


Figure 1. C_1-symmetric bis(diphenylphosphanyl)biphenyls.

However, we recently prepared a series of analogues carrying various substituents at the *ortho* position instead of a methoxy group. Our goal was to modify the steric and electronic properties of the biaryl backbone and to investigate the influence of these parameters on the catalytic activity. Thus, eight new bis(diphenylphosphanyl)biphenyl compounds with R = CH_3 (**2**), Cl (**3**), OCH_2O (**4**), Ph (**5**), $N(CH_3)_2$ (**6**), OCF_3 (**7**), OCF_2O (**8**) and OCF_2CF_2O (**9**) were synthesized (Figure 1).

In most of these compounds, the phosphorus groups also appear as two doublets in the ^{31}P NMR spectra measured from $CDCl_3$ solutions at room temperature. We noticed that the value of $J(P,P)$ is strongly dependent on the nature of the *ortho*-substituent R and varies from 11.4 when R = Ph (**5**) to 28.7 Hz when R = –OCF_2O– (**8**). The most reasonable explanation for these NMR patterns is the existence of a through-space coupling (nuclear spin–spin coupling through nonbonded interactions) of the phosphorus atoms. But surprisingly, for bis(diphenylphosphanyl)biphenyls substituted by an $N(CH_3)_2$ (**6**) or OCF_3 (**7**) group, the phosphorus nuclei appear as one singlet in the ^{31}P NMR spectrum, see below for an explanation.

Requirements for Through-Space Nuclear Spin–Spin Coupling

Most notably, this phenomenon was studied and analyzed by Mallory et al. who established a qualitative model to explain through-space coupling.[8b,8c] Some prerequisites are necessary to observe through-space coupling in NMR: (i) Two lone-pair atomic orbitals of crowded elements (phosphorus, nitrogen or fluorine) must be available. (ii) They have to be in close proximity to permit overlap, which can be achieved by rigid backbone architecture. (iii) Homonuclear through-space coupling can only be observed between anisochronous nuclei, i.e. in an unsymmetrical system or by making use of the ^{13}C satellites in an otherwise symmetrical system. Due to the large one-bond $^{19}F,^{13}C$ coupling constants, the observation of $J(F,F)$ in the latter case is relatively easy but it is difficult to observe $J(P,P)$ in symmetrical cases containing isochronous P^{III} nuclei because one-bond $^{31}P^{III},^{13}C$ couplings are relatively small (generally < 15 Hz) and of similar magnitude as the corresponding two- and three-bond couplings. Additional difficulty arises when the P^{III} nucleus is connected to three nonequivalent ^{13}C nuclei and experiences three $^{1}J(P,C)$ couplings of a similar size. Hence, the observation of through-space coupling involving two phosphorus(III) atoms is rare.[15–20] Particularly in the field of biaryl-based diphosphanes, no through-space P,P coupling has been reported so far. In this context, it is of note that attempts to extract $J(P,P)$ solely from the splitting patterns of ^{13}C NMR signals of diphosphanes [i.e. extracting $J(A,A')$ or $J(A,B)$ from the X parts of AA′X or ABX spin systems] give unreliable results because the desired coupling constant is insufficiently correlated with the X frequencies.[17]

In 2000, Mallory et al. quantified the through-space coupling interaction for a family of 1,8-difluoronaphthalenes through an exponential relationship between ab initio calculated intramolecular F···F distances and the observed $J(F,F)$ values.[8a] Earlier, for difluorinated cyclophanes, Ernst and Ibrom derived a similar exponential correlation between through-space $J(F,F)$ and nonbonded F···F distances calculated by molecular mechanical methods.[8i] The key feature of Mallory's theory is that the magnitude of the through-space coupling constant depends on the degree of lone-pair orbital overlap.[10c] For a series of fluoro-substituted aromatic ^{15}N-enriched oximes the authors also demonstrated that changing the angle between the two orbitals

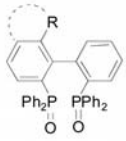
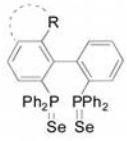
involved in the proximate $J(^{19}F,^{15}N)$ coupling affects its size.[8b] In 2004, Hierso et al. successfully extended Mallory's model to $^{31}P,^{31}P$ through-space spin–spin interactions in organometallic species.[18,23]

Discussion of the $^{31}P,^{31}P$ Coupling in Bis(diphenylphosphanyl)biphenyls

In order to prove that the spin information from ^{31}P to ^{31}P is transmitted through space and not through the five bonds of the biaryl backbone in the molecules mentioned above several investigations were carried out.

First, the existence of coupling between the two phosphorus nuclei follows from the identical coupling constant in the two ^{31}P signals and from the fact that no other ^{31}P resonances are present. Confirmation was obtained from 2D $^{31}P,^{31}P$ COSY experiments, which showed the expected cross peaks between the two ^{31}P chemical shifts. The P,P coupling of 22.5 Hz in **3**, for example, might in principle arise from through-bond interactions but its magnitude is abnormally large for a five-bond coupling, particularly as the biphenyl system is expected to be twisted about the C1–C1′ bond, which severely dampens the conjugation between the phenyl rings. When we converted the diphosphanes **1**–**5** into their corresponding bis(phosphane oxides) and bis(phosphane selenides), the P,P couplings disappeared as the lone pair electrons are no longer available for through-space interactions but are involved in P–O or P–Se "double" bonds (Table 1).

Table 1. ^{31}P NMR signals of the corresponding selenides and oxides.

	^{31}P NMR signal	
R		
OCH_3	32.6(s), 32.4(s)	35.4(s), 35.1(s)
CH_3	34.4(s), 34.3(s)	36.3(s), 34.2(s)
Cl	31.8(s), 31.7(s)	35.1(s), 33.7(s)
$-OCH_2O-$	33.6(s), 32.9(s)	35.9(s), 34.8(s)
C_6H_5	31.1(s), 31.0(s)	35.3(s), 31.9(s)

We have thus proved that the observed $^{31}P,^{31}P$ coupling is transmitted through space in **1**–**5**. This also applies to the remaining compounds. However, we still need to explain why the two chemically nonequivalent phosphorus nuclei appear as a unique singlet in the bis(diphenylphosphanyl)biphenyls **6** [R = $N(CH_3)_2$] and **7** (R = OCF_3). When we lowered the temperature, the ^{31}P signals of both **6** and **7** decoalesced and became AB spectra. At first glance, this gave the impression of slowing some conformational process. However, little line broadening occurred and it transpired that we were only dealing with slightly temperature dependent chemical shifts, which are equal at room temperature and therefore prevent signal splitting. In fact, when the solvent was changed from $CDCl_3$ to CD_2Cl_2, both compounds showed anisochronous ^{31}P nuclei at room temperature, albeit with small chemical shift differences of 0.1 for **6** and 0.2 ppm for **7**. The *J*(P,P) values were found to be 5.3 and 22.4 Hz for **6** and **7**, respectively.

Through-Space $^{31}P,^{19}F$ Coupling in Fluorinated Bis(diphenylphosphanyl)biphenyls

In diphosphane **7** (R = OCF_3) only a barely resolved $^{31}P,^{19}F$ coupling of 1.4 Hz could be observed between the trifluoromethoxy group and the phosphorus nucleus of the PPh_2 substituent at C2′. The OCF_3 group probably prefers a conformation in which it can avoid the region of steric hindrance. In order to enforce $^{31}P,^{19}F$ interactions we devised the bis(diphenylphosphanyl)biphenyls **8** and **9**, substituted with rigid, cyclic fluorinated ether substituents (Figure 2). One would expect that there is at least one fluorine atom that cannot evade close contact with the P2′ atom due to the restricted mobility about the C6–O bond in these compounds (Figure 2).

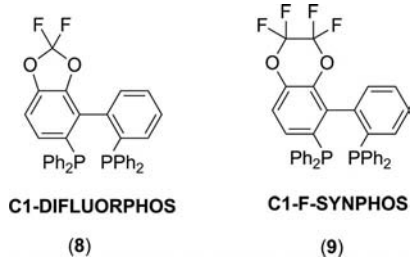
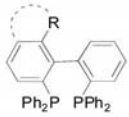
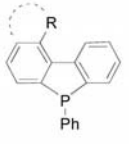


Figure 2. C_1-symmetric bis(diphenylphosphanyl)biphenyls carrying a fluorinated ether substituent.

Indeed, the presumed $^{31}P,^{19}F$ through-space coupling in **8** was larger than that in **7** (2.3 vs. 1.4 Hz). In compound **9** the more deshielded phosphorus atom is coupled to two fluorine nuclei (5.1 and 2.5 Hz, see Table 2). This is discussed further below. In the corresponding bis(dicyclohexylphosphanyl)biphenyls, **10** and **11**, no $^{31}P,^{19}F$ coupling was detected because the lines were broad, both in the ^{31}P and ^{19}F spectra.

In order to further substantiate the notion that the $^{31}P,^{19}F$ coupling is transmitted through space, we prepared two cyclic compounds with only one phosphorus atom each in which through-space coupling cannot occur, namely the phosphafluorene derivatives **12** and **13**. In these compounds the phosphorus appears as a singlet at δ = –5.2 (**12**) and –7.8 ppm (**13**), see Table 2. The systems **8/9** and **12/13** are comparable with respect to the arrangement of the F_2C–O–C6–C1–C2–P sequence of atoms (apart from the nonrotational C2–P bonds in **12/13**). Hence, the absence of P,F coupling in **12/13** as opposed to **8/9** gives support to our hypothesis that the P,F couplings observed in **8/9** are through-space couplings involving P2′ and not through-bond cou-

Table 2. ^{31}P NMR of **8**, **9**, **12** and **13** in $CDCl_3$ at room temperature.

	R	δ_P [ppm]	multiplicities and couplings involving ^{31}P [Hz]
	OCF_2O (**8**)	–12.7	dd, J = 28.7, 2.3
		–14.1	d, J = 28.7
	OCF_2CF_2O (**9**)	–13.9	ddd, J = 24.6, 5.1, 2.5
		–14.7	d, J = 24.6
	OCF_2O (**12**)	–5.2	s
	OCF_2CF_2O (**13**)	–7.8	s

plings involving P2. Experimentally this was proved as described below.

In addition, the ^{31}P NMR spectrum of bis(diphenylphosphanyl)biphenyl **9** (R = OCF_2CF_2O) was recorded in C_6D_6 and in [D_6]DMSO at two different concentrations (c = 0.33 and 3.3 mg/mL) and at 100 °C in $C_2D_2Cl_4$. The multiplicities stayed the same as in $CDCl_3$ solution, which demonstrates that the P,F couplings are not solvent, concentration or temperature dependent.

In order to elucidate the spin coupling pattern of **8** in more detail and to prove that the ^{31}P nucleus involved in spin coupling with ^{19}F is the phosphorus atom bound to C2′ and not that bound to C2, we carried out additional ^{31}P and ^{19}F NMR experiments. The spin system under discussion is of the type AGKQTXZ (A, G = ^{31}P; K, Q = ^{19}F; T, X, Z = ^{1}H, Figure 3).

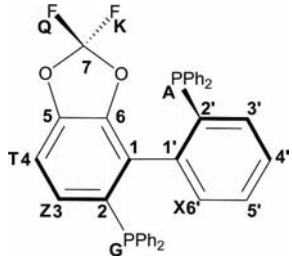


Figure 3. AGKQTXZ spin system in compound **8**.

In the otherwise complicated ^{1}H NMR spectrum, three well resolved and separated signals were observed (Figure 4, Table 3). Protons H_T and H_Z with their common coupling of 8.2 Hz can only be H3 and H4 with H_Z being H3 because of its $^3J(P,H_Z)$ = 3.1 Hz coupling to phosphorus and H_T being H4 with $^4J(P,H_T) \approx 0$ Hz. This is more likely than the reverse assignment and was supported by $^{1}H,^{13}C$ HMBC. Selective $^{1}H\{^{31}P\}$ continuous wave decoupling showed that the 3.1 Hz coupling in the dd of H_Z originates from P_G, $J(P_G,H_Z)$ = 3.1 Hz, δ_P = –14.1 ppm, and P_G is the phosphorus atom bound to C2. On the other hand, the 4.1 Hz coupling of H_X is J(P2′,H6′), which follows from selective decoupling of the signal at δ_P = –12.7 ppm.

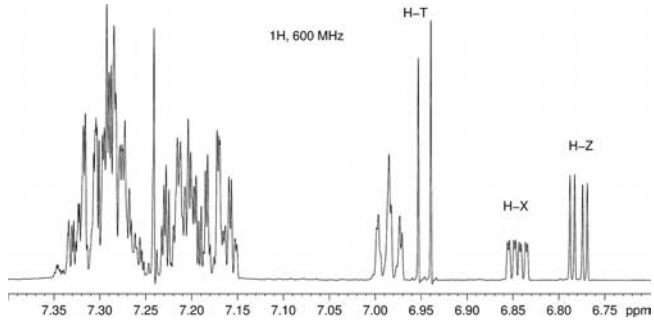


Figure 4. ^{1}H NMR spectrum of **8** (600 MHz, $CDCl_3$).

Table 3. NMR data of **8**.

Signal	Assignment	δ [ppm]	Multiplicity[a]	J [Hz]
P_A	P2′	–12.7	dd	28.7, 2.3
P_G	P2	–14.1	d	28.7
F_K	$F_{anti}7$	–49.73	d	95.4
F_Q	$F_{syn}7$	–50.14	dd	95.4, 2.3
H_T	H4	6.95	d	8.2
H_X	H6′	6.85	ddd	7.6, 4.1, 1.3
H_Z	H3	6.78	dd	8.2, 3.1

[a] Multiplicities of ^{19}F and ^{31}P signals refer to ^{1}H-decoupled spectra.

In the $^{31}P\{^{1}H\}_{cpd}$ spectrum of **8**, P_A (δ_P = –12.7 ppm) and P_G (δ_P = –14.1 ppm) have a mutual coupling constant J(P,P) of 28.7 Hz. The signal of P_A shows a doublet splitting of 2.3 Hz (Figure 5a) caused by one of the fluorine nuclei, F_Q. P_A is P2′ as shown above, so the observed $J(P_A,F_Q)$ coupling of 2.3 Hz involves P2′ and not P2. It can be taken for granted that this coupling operates more or less exclusively through space because the intervening seven chemical bonds have neither suitable geometry nor suitable electronic characteristics (two consecutive saturated centres, C7 and O6) for long-range through-bond coupling. Furthermore, it is likely that P2′ couples to the fluorine atom on the same side of the benzodioxole plane, F_Q in **8**, which is the fluorine atom in front of the plane in the diagram (Figure 3). If the J(P,F) coupling under discussion involved P2 instead of P2′, one would expect very similar couplings between P2 and *both* ^{19}F nuclei because of the planar nature of the benzodioxole ring system.

The ^{19}F nuclei at δ_F = –49.73 (F_K) and –50.14 ppm (F_Q) mutually couple with J(F,F) = 95.4 Hz and F_Q again shows a $J(P_A,F_Q)$ coupling of 2.3 Hz (Figure 5b). The chemical nonequivalence of the two ^{19}F nuclei indicates that internal rotation about the C1–C1′ bond is slow on the NMR time scale at room temperature. Incidentally, slow rotation about C1–C1′ applies to all the bis(diphenylphosphanyl)biphenyls in this study deduced from the appearance of four sets of

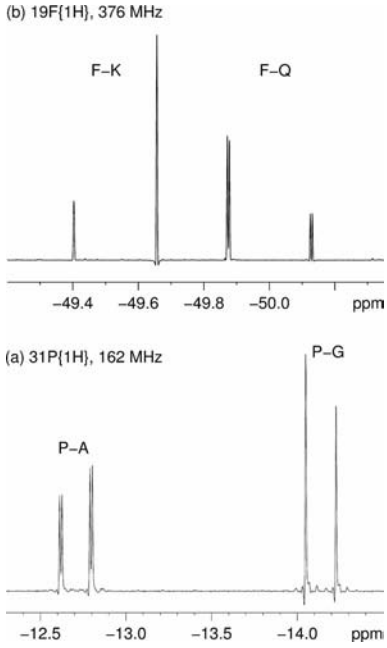


Figure 5. ^{1}H-decoupled NMR spectra of **8** in $CDCl_3$, (a) ^{31}P at 162 MHz, (b) ^{19}F at 376 MHz. The high-frequency ^{31}P signal and the low-frequency ^{19}F signal show a ^{31}P,^{19}F coupling of 2.3 Hz.

phenyl signals in each ^{13}C NMR spectrum, i.e. all PPh_2 groups have diastereotopic phenyl substituents at room temperature.

A similar study was carried out with diphosphane **9**, which was considered as an AGKLMNTXZ spin system (A, G = ^{31}P; K, L, M, N = ^{19}F and T, X, Z = ^{1}H, Figure 6).

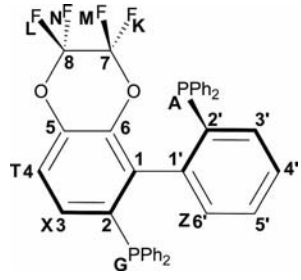


Figure 6. AGKLMNTXZ system in diphosphane **9**.

In the complex ^{1}H NMR spectrum of **9** three signals were assigned (Table 4). Selective $^{1}H\{^{13}P_{cw}\}$ decoupling, as in the case of **8**, allowed the assignment of the ^{31}P resonances: P_A at δ_P = –13.9 ppm corresponds to P2′ and P_G at δ_P = –14.7 ppm to P2; P_A shows *two* couplings to ^{19}F of 5.1 and 2.5 Hz.

In the four-spin ^{19}F subsystem, all fluorine atoms are chemically nonequivalent. Thus, there is a slow rotation about C1–C1′. Two fluorine atoms are coupled to the same phosphorus atom, namely P2′ (δ_P = –13.9 ppm), with J = 5.1 and 2.5 Hz, respectively. The ^{19}F spin system was analyzed by iterative full line-shape fitting. The mutual coupling of the fluorine atoms coupled to ^{31}P is 18.9 Hz. It is likely that both are *syn* with respect to P2′, i.e. *cis* to each other. They are both oriented towards the front of the plane

Table 4. NMR data of **9**.

Signal	Assignment	δ [ppm]	Multiplicity	J [Hz]
P_A	P2′	–13.9	ddd	24.6, 5.1, 2.5
P_G	P2	–14.7	d	24.6
F_K	$F_{anti}7$	–90.44	ddd	148.5, 18.4, 10.1
F_L	$F_{syn}8$	–91.26	dddd	147.3, 18.9, 10.1, 2.5
F_M	$F_{syn}7$	–92.72	dddd	148.5, 18.9, 5.1, 3.8
F_N	$F_{anti}8$	–93.07	ddd	147.3, 18.4, 3.8
H_T	H4	7.05	d	8.5
H_X	H3	6.86	dd	8.5, 2.6
H_Z	H6′	6.73	ddd	7.6, 4.1, 1.3

of the drawing of **9** in Figure 6 and are bound to C7 and C8, respectively (Figure 7, Table 4). We assign the fluorine atom with the 5.1 Hz coupling to F_M (closer to P2′) and that with the 2.5 Hz coupling to F_L (further from P2′). The dihedral angle dependence of ^{3}J(F,F) is complex.[24] Hence, the *cis* orientation of F_L and F_M cannot be derived simply from the size of ^{3}J(F,F).

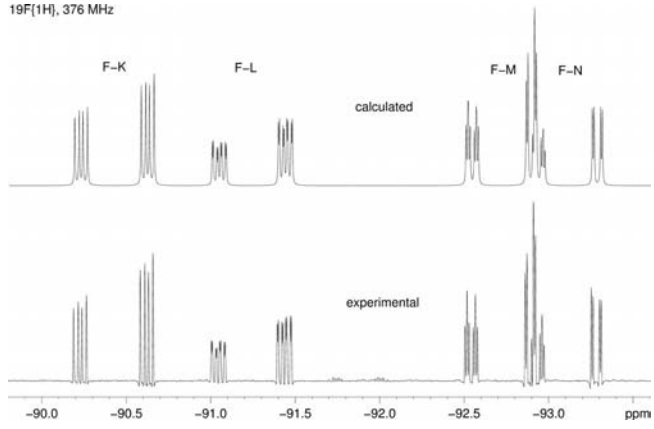


Figure 7. Experimental (bottom) and calculated (top) 376.5 MHz ^{19}F NMR spectra of **9**. Fluorine signals F–L and F–M show ^{31}P-^{19}F couplings of 2.5 and 5.1 Hz, respectively.

As far as the size of our through-space coupling constants is concerned, a J(P,P) of up to 28.7 Hz may not seem overly large when compared, for example, with the biggest through-space J(F,F) of 110.1 Hz that we reported previously.[8i] A proper comparison, however, should refer to the reduced coupling constants $K(X,Y) = 4\pi^2 J(X,Y)/(h\gamma_X\gamma_Y)$, which take into account the magnetogyric ratios of the coupled nuclei. A J(P,P) value of 28.7 Hz thus translates to a K(P,P) value of 1.46×10^{20} $T^2 J^{-1}$ (or $kg A^{-2} s^{-2} m^{-2}$), whereas a J(F,F) value of 110.1 Hz corresponds to K(F,F) = 1.03×10^{20} $T^2 J^{-1}$. Hence there is more significance to the J(P,P) than to the J(F,F) value. Our largest J(P,F) coupling of 5.1 Hz corresponds to a K(P,F) value of just 1.11×10^{19} $T^2 J^{-1}$.

There are two very similar chemical shifts of the mutually coupled ^{31}P nuclei in the ^{13}C NMR spectra of bis(phosphanes) **6** and **7**, which makes their ^{13}C NMR spectra second order: each ^{13}C signal represents the X part of an ABX spectrum. When two lines of these X parts are distinctly more intense than the remaining (two or four) lines, their frequency difference is readily recognized as the sum

$|J(A,X) + J(B,X)|$. As the approximate size of $J(A,X)$ and/or $J(B,X)$ can be estimated from the values in the first order spectra of the other bis(diphenylphosphanyl) compounds, this allows the deduction of the relative signs of $J(A,X)$ and $J(B,X)$ in these cases. Consider, for example, the C1 signal in **7** where $|\sum J(P,C)| = |^2J(P2,C1) + {}^3J(P2',C1)| = 39.7$ Hz. The individual magnitudes of $^2J(P2,C1)$ in **1**–**3** are 30.8–32.5 and those of $^3J(P2',C1)$ are 6.5–7.1 Hz. Hence these two types of coupling must be of equal sign in order to give a sum of ca. 40 Hz. Were they of opposite sign, their sum would be 24–26 Hz. From the literature $^2J(P,C\text{-}ortho)$ is positive in triphenylphosphane.[25] Hence $^3J(P2',C1)$ in this series of compounds must also be positive. From the C6′ signal of **7**, $|\sum J(P,C)| = 9.6$ Hz with $^3J(P2',C6') = 6.2$–6.3 and $^4J(P2,C6') = 3.1$–3.8 Hz in **1**–**3**. These two couplings must therefore also have the same sign. With $^3J(P,C\text{-}meta)$ being positive in triphenylphosphane,[25] $^4J(P2,C6')$ is also positive in our compounds. The situation is less clear cut for the P,C couplings involved in C2 and C2′ because of the varying magnitude of $^1J(P,C)$ and the small size of $^4J(P,C)$.

Applying Mallory's model of the transmission of through-space coupling by overlap of the lone-pair electron orbitals to our biphenyl diphosphanes, we searched for a simple correlation between the observed $^{31}P,^{31}P$ coupling constants and the geometries of those compounds for which X-ray structure determinations had been carried out (**4**, **6**, **8**, **9**). A simple exponential of the type $J(P,P) = a \times \exp[-b \times d(P\cdots P)]$, where the P···P distance, $d(P\cdots P)$, is the only geometric parameter on which the coupling depends, was far from successful in reproducing the experimental findings, in contrast to our previously derived exponential dependence of $J(F,F)$ on $d(F\cdots F)$.[25] Multiplying the exponential by an angular function such as $\cos\Theta$(lp–P–P–lp) or the square thereof, where Θ is the dihedral angle between the phosphorus lone pairs, did not improve the result. Thus, for the time being, we tentatively conclude that the X-ray geometries do not reflect the geometries well, particularly the conformations, of the biphenyl diphosphanes in solution.

Crystallographic Studies

Single-crystal X-ray analyses have been carried out for **4**, **6**, **8** and **9**.[26] Perspective ORTEP diagrams including the atomic numbering schemes are provided in Figures 8, 9, 10 and 11. The torsion angles P–C–C–P between the planes of the two Ph ring of the biphenyl system, Θ, are 110.35 (**4**), 111.03 (**6**), 110.36 (**8**) and 102.28° (**9**). Thus, due to trisubstitution, the two phosphane substituents show an increased distance compared to a typical C_2-symmetric bis(diphenylphosphanyl)biphenyl molecule, such as BIPHEMP (88.7°).[27] The P···P distance in the OCH_2O derivative **4** is 4.574, for NMe_2 (**6**) 4.696, OCF_2O (**8**) 4.414 and OCF_2CF_2O (**9**) 4.455 Å. Although no correlation between the solid-state structures and the $J(P,P)$ coupling constants in solution was found, we note that the smallest coupling constant of 5.3 Hz in the NMe_2 derivative **6** coincides with the largest P···P distance.

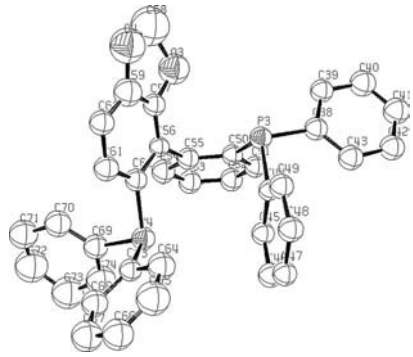


Figure 8. Molecular structure of compound **4** in the solid state.

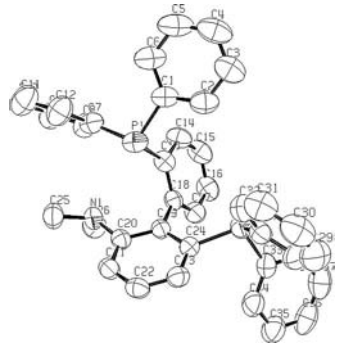


Figure 9. Molecular structure of compound **6** in the solid state.

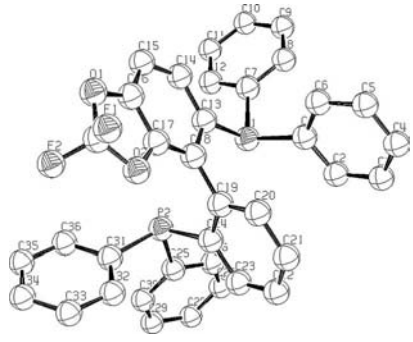


Figure 10. Molecular structure of compound **8** in the solid state.

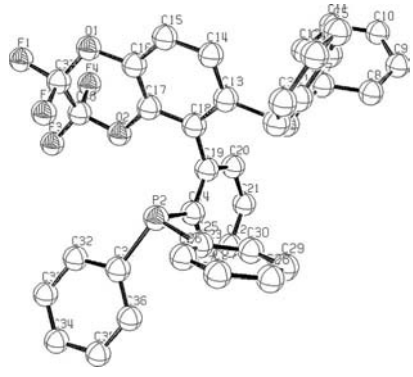


Figure 11. Molecular structure of compound **9** in the solid state.

Conclusions

So far, studies of the transmission of nuclear spin–spin coupling through space have focused on fluorine- and nitrogen-containing organic compounds. In this work, we provide experimental evidence for and numerical values of through-space *J*(P,P) and *J*(P,F) coupling constants. We have identified the first simultaneous through-space P,P- and P,F-coupling in biphenyl derivatives and analyzed this phenomenon by accurate NMR studies and X-ray crystallographic analysis. The study of this uncommon NMR coupling pattern became possible due to access to a new class of C_1-symmetric bis(diphenylphosphanyl)biphenyls. Attempts to correlate the experimental through-space *J*(P,P) coupling constants in solution with the geometries of the compounds in the solid state were unsuccessful.

Experimental Section

General Consideration: All reactions and workup procedures were performed under an inert atmosphere of argon using conventional vacuum line and Schlenk techniques. Toluene and THF were distilled by heating with sodium benzophenone under argon. Starting materials, if commercial, were purchased and used as received, provided that adequate checks (melting ranges, refractive indices and gas chromatography) had confirmed the purity. Air- and moisture-sensitive materials were stored in Schlenk tubes and were protected by and handled under an atmosphere of argon, using appropriate glassware. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 600 and at 101 and 151 MHz, respectively. The instruments used were a Bruker Avance II 600 with a TCI (^{1}H, ^{13}C, ^{15}N) cryo probe head, a Bruker DRX 400 with a QNP (^{1}H, ^{13}C, ^{19}F, ^{31}P) probe head and a Bruker Avance III 400 spectrometer with a BBFO+ (^{1}H, ^{19}F, ^{15}N–^{31}P) probe head. Chemical shifts are reported in δ units (ppm) and were measured relative to tetramethylsilane (δ_H = 0.00 ppm) and $CDCl_3$ (δ_C = 77.01 ppm). ^{19}F and ^{31}P chemical shifts were referenced to the frequencies previously determined for CCl_3F (δ_F = 0.00 ppm) and ext. 85% H_3PO_4 (δ_P = 0.00 ppm), respectively, in $CDCl_3$. Assignment techniques used were DEPT-135, H,H-COSY, H,H-NOESY, H,C-HSQC, H,C-HMBC, HSQC-TOCSY and selective ^{1}H{^{31}P}-decoupling. In order to distinguish ^{31}P,^{13}C coupling constants from small chemical differences in the ^{13}C NMR spectra, these spectra were recorded both at 151 and at 101 MHz. Abbreviations: *i*-dpp, *o*-dpp, *m*-dpp and *p*-dpp refer to the *ipso*-, *ortho*-, *meta*-, and *para*-positions, respectively, of the diphenylphosphanyl substituents. Iterative analysis of the ^{19}F NMR spectrum of **9** was carried out with Bruker's WIN-DAISY software.[28]

General Synthetic Procedure: At 25 °C, butyllithium (2 equiv. for dibromobiaryls or 3 equiv. for bromoiodobiaryls) in hexanes was added dropwise to a solution of dihalobiaryl (1 equiv.) in toluene (5 mmol/mL). The reaction mixture was heated at 100 °C. After 1 h, it was cooled to 50 °C and a 1.0 M solution of chlorodiphenylphosphane (2 or 3 equiv. for dibromobiaryls and bromoiodobiaryls, respectively) in toluene (1 mmol/mL) was quickly added. The solution was heated for 2.5 hours and then cooled to room temperature. Water was immediately added followed by extraction into dichloromethane. The combined organic layers were dried with sodium sulfate and the solvents were removed under reduced pressure.

(6-Methoxybiphenyl-2,2′-diyl)-bis(diphenylphosphane) (1): Prepared from 2,2′-dibromo-6-methoxybiphenyl. The crude product was purified by column chromatography on silica gel using cyclohexane as the eluent to separate phosphafluorene and diphosphane from triphenylphosphane. Triturating from dichloromethane afforded pure (6-methoxybiphenyl-2,2′-diyl)bis(diphenylphosphane) (**1**; 17%) as a colourless powder. M.p. 227–228 °C (dec.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33–7.19 (m, 18 H), 7.18–7.14 (m, 4 H), 7.08–7.03 (m, 2 H, *o*-dpp), 6.82 (ddm, $J \approx$ 7.5, 4.3, 1.4 Hz, 1 H, H6′), 6.77 (dd, J = 8.3, 1.0 Hz, 1 H, H5), 6.66 (ddd, J = 7.7, 3.2, 1.0 Hz, 1 H, H3), 3.22 (s, 3 H, OCH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.1 (C_q, dd, J = 9.6, 2.0 Hz, C6), 143.9 (C_q, dd, J = 33.3, 7.9 Hz, C1′), 138.39 (C_q, dd, J = 10.4, 1.3 Hz, C2), 138.38 (C_q, d, J = 13.1 Hz, *i*-dpp), 138.32 (C_q, d, J = 13.8 Hz, *i*-dpp), 137.57 (C_q, dd, J = 13.1, 0.8 Hz, *i*-dpp), 137.44 (C_q, dd, J = 13.0, 0.8 Hz, *i*-dpp), 137.2 (C_q, dd, J = 9.1, 1.3 Hz, C2′), 136.2 (C_q, dd, J = 32.5, 7.1 Hz, C1), 134.6 (d, J = 2.4 Hz, C3′), 134.1 (CH, d, J = 20.1 Hz, 2 C, *o*-dpp), 133.9 (CH, d, J = 19.9 Hz, 2 C, *o*-dpp), 133.349 (CH, dd, J = 18.8, 2.3 Hz, 2 C, *o*-dpp), 133.346 (CH, dd, J = 18.9, 1.2 Hz, 2 C, *o*-dpp), 131.2 (CH, dd, J = 6.2, 3.8 Hz, C6′), 128.8 (CH, d, J = 1.1 Hz, C4), 128.18 (CH, d, J = 6.8 Hz, 2 C, *m*-dpp), 128.15 (CH, d, J = 6.0 Hz, 2 C, *m*-dpp), 128.14 (CH, d, J = 5.6 Hz, 2 C, *m*-dpp), 127.97 (CH, d, J = 6.7 Hz, 2 C, *m*-dpp), 128.4, 128.3 (br.), 128.00, 127.92, 127.86 (CH, C5′ and 4 *p*-dpp), 127.6 (CH, C4′), 126.0 (CH, d, J = 1.6 Hz, C3), 110.5 (CH, C5), 54.7 (OCH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ = –13.6 (d), –14.0 (d, J = 18.3 Hz). MS(EI): *m*/*z* (%) = 535.1 (< 1) [M^+], 459.1 (1) [M^+ – Ph], 351.1 (100) [M^+ – PPh_2], 337.1 (6) [M^+ – PPh_2–Me], 183.1 (42) [M^+ – PPh_2–Me–2 Ph]. HRMS for $C_{37}H_{30}OP_2$ [M + H]: calcd. 553.1845; found 553.1886.

(6-Methylbiphenyl-2,2′-diyl)bis(diphenylphosphane) (2): Prepared from 2,2′-dibromo-6-methylbiphenyl. The crude product was purified by column chromatography on silica gel using cyclohexane as the eluent to separate phosphafluorene and diphosphane from triphenylphosphane. Crystallization from methanol afforded pure (6-methylbiphenyl-2,2′-diyl)bis(diphenylphosphane) (**2**, 30%) as colourless crystals. M.p. 181–182 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37–7.32 (m, 2 H, *o*-dpp), 7.31–7.12 (m, 20 H), 7.07 (m, 1 H, H5′), 6.96 (tm, $J \approx$ 7 Hz, 2 H, *o*-dpp), 6.86 (ddd, J = 7.5, 3.5, 1.4 Hz, 1 H, H3), 6.61 (*ca* dddd, J = 7.6, 4.4, 1.3, 0.6 Hz, 1 H, H6′), 1.68 ppm (s, 3 H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.41 (C_q, dd, J = 30.8, 6.5 Hz, C1 or C1′), 146.37 (C_q, dd, J = 32.4, 7.0 Hz, C1′ or C1), 138.75 (C_q, d, J = 14.2 Hz, *i*-dpp), 137.63 (C_q, d, J = 13.0 Hz, *i*-dpp), 137.36 (C_q, dd, J = 9.8, 2.1 Hz, C2), 137.26 (C_q, dd, J = 13.4, 1.3 Hz, *i*-dpp), 137.08 (C_q, dd, J = 13.5, 1.5 Hz, *i*-dpp), 136.92 (C_q, dd, J = 10.0, 1.8 Hz, C2′), 136.92 (C_q, dd, J = 6.0, 2.1 Hz, C6), 134.44 (CH, d, J = 21.0 Hz, 2 C, *o*-dpp), 134.43 (CH, d, J = 2.3 Hz, C3′), 134.24 (CH, d, J = 20.5 Hz, 2 C, *o*-dpp), 133.40 (CH, dd, J = 18.4, 3.1 Hz, 2 C, *o*-dpp), 133.18 (CH, dd, J = 18.6, 1.4 Hz, 2 C, *o*-dpp), 131.30 (CH, d, J = 1.4 Hz, C3), 130.65 (CH, dd, J = 6.2, 3.1 Hz, C6′), 130.39 (CH, C5), 128.55 (CH, *p*-dpp), 128.36 (CH, *p*-dpp), 128.32 (CH, C5′), 128.23 (CH, d, J = 7.1 Hz, 2 C, *m*-dpp), 128.21 (CH, d, J = 5.9 Hz, 2 C, *m*-dpp), 128.07 (CH, d, J = 5.7 Hz, 2 C, *m*-dpp), 128.06 (CH, d, J = 7.1 Hz, 2 C, *m*-dpp), 127.98 (CH, *p*-dpp), 127.72 (CH, *p*-dpp), 127.67 (CH, C4), 127.47 (CH, C4′), 20.58 ppm (t, J = 2.7 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): –12.8 (d), –14.6 ppm (d, J = 27.1 Hz). MS(EI): *m*/*z* (%) = 535.1 (< 1) [M^+], 459.1 (1) [M^+ – Ph], 351.1 (100) [M^+ – PPh_2], 337.1 (6) [M^+ – PPh_2–Me], 183.1 (42) [M^+ – PPh_2–Me–2 Ph]. $C_{32}H_{30}P_2$ (536.58): calcd. (%) C 82.82, H 5.64; found C 82.53, H 5.92.

(6-Chlorobiphenyl-2,2′-diyl)bis(diphenylphosphane) (3): Prepared from 2,2′-dibromo-6-chlorobiphenyl. The crude product was purified by column chromatography on silica gel using cyclohexane as the eluent. Crystallization from acetonitrile afforded (6-chlorobi-

phenyl-2,2′-diyl)bis(diphenylphosphane) (**3**; 23%) as colourless crystals. M.p. 158–159 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.37 (m, 3 H, H5 and *o*-dpp), 7.34–7.20 (m, 15 H), 7.18–7.09 (m, 5 H), 6.91 (ddd, J = 7.7, 3.0, 1.2 Hz, 1 H, H3), 6.81 (dt, J = 6.9, 1.4 Hz, 2 H, *o*-dpp), 6.65 ppm (dddd, J = 7.6, 4.3, 1.3, 0.5 Hz, 1 H, H6′). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 145.15 (C_q, dd, J = 32.5, 6.5 Hz, C1), 144.68 (C_q, dd, J = 32.8, 6.6 Hz, C1′), 140.65 (C_q, dd, J = 14.2, 2.3 Hz, C2), 137.89 (C_q, d, J = 14.5 Hz, *i*-dpp), 137.41 (C_q, dd, J = 12.5, 1.2 Hz, *i*-dpp), 136.76 (C_q, d, J = 12.5, *i*-dpp), 136.75 (C_q, dd, J = 10.1, 1.7 Hz, C2′), 136.40 (C_q, dd, J = 13.1, 1.2 Hz, *i*-dpp), 134.80 (C_q, dd, J = 7.3, 2.6 Hz, C6), 134.78 (CH, d, J = 2.3 Hz, C3′), 134.19 (CH, d, J = 20.8 Hz, 2 C, *o*-dpp), 133.86 (CH, dd, J = 19.0, 3.1 Hz, 2 C, *o*-dpp), 133.83 (CH, d, J = 20.0 Hz, 2 C, *o*-dpp), 133.11 (CH, dd, J = 18.9, 1.0 Hz, 2 C, *o*-dpp), 132.20 (CH, d, J = 1.3 Hz, C3), 130.71 (CH, dd, J = 6.3, 3.3 Hz, C6′), 129.68 (CH, C5), 128.85 (CH, C4), 128.34 (CH, d, J = 0.8 Hz, C5′), 128.27 (CH, d, J = 6.1 Hz, 2 C, *m*-dpp), 128.27 (CH, d, J = 7.5 Hz, 2 C, *m*-dpp), 128.19 (CH, d, J = 7.3 Hz, 2 C, *m*-dpp), 128.15 (CH, d, J = 6.6 Hz, 2 C, *m*-dpp), 128.72, 128.29, 128.26, 128.18, 128.05 ppm (CH, 4 *p*-dpp and C4′). ^{31}P NMR (162 MHz, $CDCl_3$): –12.0 (d), –14.1 ppm (d, J = 22.5 Hz). MS(EI): *m*/*z* (%) = 555.3 (< 1) [M^+], 521.1 [M^+ – Cl], 479.1 (1) [M^+ – Ph], 443.1 (< 1) [M^+ – Cl–Ph], 371.1 (100) [M^+ – PPh_2], 336 (6) [M^+ – PPh_2–Cl], 257.1 [M^+ – PPh_2– Cl–Ph], 183 (34) [M^+ – PPh_2–Cl–2 Ph]. $C_{36}H_{27}ClP_2$·H_3CCN (598.05): calcd. (%) C 76.32, H 5.06; found C 76.44, H 5.06.

[2-{5-(Diphenylphosphanyl)benzo[*d*][1,3]dioxol-4-yl}phenyl]diphenylphosphane (4): Prepared from 5-bromo-4-(2-bromophenyl)-benzo[1,3]dioxole. The crude product was purified by column chromatography on silica gel using cyclohexane as the eluent to separate phosphafluorene and diphosphane from triphenylphosphane. Crystallization from methanol afforded pure [2-{5-(diphenylphosphanyl)benzo[*d*][1,3]dioxol-4-yl}phenyl]diphenylphosphane (**4**, 18%) as colourless crystals. M.p. 160–161 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32–7.12 (m, 22 H), 7.11 (dddd, J = 7.7, 3.6, 1.4, 0.5 Hz, 1 H, H3′), 6.89 (ddd, J = 7.5, 4.1, 1.2 Hz, 1 H, H6′), 6.72 (d, J = 8.0 Hz, 1 H, H4), 6.57 (dd, J = 8.0, 3.5 Hz, 1 H, H3), 5.71 and 5.12 ppm (both d, J = 1.5, 1 H each, OCH_2O). ^{13}C NMR (151 MHz, $CDCl_3$; numbering of carbon atoms as for a 2,2′-bisphosphane): δ = 147.69 (C_q, C5), 146.05 (C_q, dd, J = 11.7, 1.9 Hz, C6), 140.84 (C_q, dd, J = 31.7, 6.7 Hz, C1′), 138.46 (C_q, d, J = 13.3 Hz, *i*-dpp), 137.70 (C_q, dd, J = 11.0, 1.2 Hz, C2′), 137.67 (C_q, dd, J = 13.2, 1.4 Hz, *i*-dpp), 137.52 (C_q, d, J = 13.3 Hz, *i*-dpp), 136.97 (C_q, dd, J = 13.1, 1.1 Hz, *i*-dpp), 134.19 (CH, d, J = 20.7 Hz, 2 C, *o*-dpp), 134.01 (CH, d, J = 1.7 Hz, C3′), 133.82 (CH, d, J = 20.1 Hz, 2 C, *o*-dpp), 133.46 (CH, dd, J = 19.1, 1.6 Hz, 2 C, *o*-dpp), 133.30 (CH, dd, J = 18.8, 1.9 Hz, 2 C, *o*-dpp), 130.69 (CH, dd, J = 5.6, 3.1 Hz, C6′), 129.93 (C_q, dd, J = 10.1, 1.4 Hz, C2), 128.44 (CH, C5′), 128.40 (CH, d, J = 1.9 Hz, C3), 128.38–128.29 (CH, overlapped, *p*-dpp), 128.33 (CH, d, J = 2.4 Hz, C4′), 128.31 (CH, *p*-dpp), 128.28 (CH, d, J = 6.1 Hz, 2 C, *m*-dpp), 128.18 (CH, d, J = 6.8 Hz, 2 C, *m*-dpp), 128.14 (CH, d, J = 6.1 Hz, 2 C, *m*-dpp), 128.12 (CH, *p*-dpp), ≈128.1 (C_q, dd, $J \approx 37$, 7 Hz, C1; signal partially hidden), 128.06 (CH, d, J = 7.0 Hz, 2 C, *m*-dpp), 127.95 (CH, *p*-dpp), 108.25 (CH, d, J = 1.0 Hz, C4), 100.85 ppm (CH_2, OCH_2O). ^{31}P NMR (162 MHz, $CDCl_3$): –12.4 (d), –14.2 ppm (d, J = 27.6 Hz). MS(EI): *m*/*z* (%) = 565.1 (1) [M^+], 489.1 (5) [M^+ – Ph], 381 (100) [M^+ – PPh_2], 353 (6) [M^+ – PPh_2–OCH_2], 183.1 (25) [M^+ – PPh_2–2 Ph–OCH_2O]. $C_{37}H_{28}O_2P_2$·0.5 H_3COH (582.17): calcd. (%) C 77.31, H 5.19; found C 77.36, H 5.11.

2,2′-Bis(diphenylphosphanyl)-6-phenylbiphenyl (5): Prepared from 2,2′-dibromo-6-phenylbiphenyl. Purification by chromatography using cyclohexane as the eluent followed by triturating from methanol afforded 2,2′-bisdiphenylphosphanyl-6-phenylbiphenyl (**5**; 24%) as a colourless powder. **M**.p. 85–86 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.24 (m, 12 H), 7.18–7.14 (m, 3 H), 7.12–7.03 (m, 10 H), 7.01 (ddd, J = 7.6, 3.2, 1.4 Hz, 1 H, H3), 6.95 (ddd, J = 7.6, 3.7, 1.0 Hz, 1 H, H3′), 6.89 (ddm, J = 7.6, 4.5 Hz, 1 H, H6′), 6.60–6.56 (m, 2 H, *o*-dpp), 6.53–6.49 ppm (m, 2 H, *o*-dpp). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.54 (C_q, dd, J = 33.2, 7.8 Hz, C1′), 145.55 (C_q, dd, J = 32.5, 6.3 Hz, C1), 142.00 (C_q, dd, J = 6.0, 2.6 Hz, C6), 141.53 (C_q, t, J = 1.8 Hz, *i*-ph), 139.02 (C_q, d, J = 14.6 Hz, *i*-dpp), 138.47 (C_q, dd, J = 14.1, 0.9 Hz, *i*-dpp), 138.26 (C_q, dd, J = 11.7, 1.9 Hz, C2), 137.38 (C_q, dd, J = 13.6, 0.7 Hz, *i*-dpp), 136.58 (C_q, d, J = 13.9 Hz, *i*-dpp), 135.77 (C_q, dd, J = 11.0, 1.3 Hz, *i*-dpp), 135.36 (CH, d, J = 2.6 Hz, C3′), 134.19 (CH, d, J = 20.4 Hz, 2 C, *o*-dpp), 134.18 (CH, dd, J = 19.7, 3.4 Hz, 2 C, *o*-dpp), 133.54 (CH, d, J = 1.6 Hz, C3), 132.94 (CH, d, J = 18.7 Hz, 2 C, *o*-dpp), 132.82 (CH, d, J = 18.6 Hz, 2 C, *o*-dpp), 132.80 (CH, dd, J = 4.6, 1.7 Hz, C6′), 130.88 (CH, d, J = 0.7 Hz, C5), 130.53 (d, J = 1.3 Hz, 2 C), 127.37 (2 C, *o*-, *m*-ph), 128.50, 128.26, 127.92, 127.59, 127.48, 126.07 (CH, 4 *p*-dpp, *p*-ph and C4), 128.28 (d, J = 7.1 Hz, 2 C, *m*-dpp), 128.19 (d, J = 6.6 Hz, 2 C, *m*-dpp), 127.97 (d, J = 5.6 Hz, 2 C, *m*-dpp), 127.91 (d, J = 5.8 Hz, 2 C, *m*-dpp), 127.65 (CH, C4′), 127.38 (CH, d, J = 0.9 Hz, C5′). ^{31}P NMR (162 MHz, $CDCl_3$): –13.9 (d), –15.1 ppm (d, J = 11.4 Hz). MS(EI): *m*/*z* (%) = 598.2 (< 1) [M^+], 413.2 (100) [M^+ – PPh_2], 183.1 (22) [M^+ – PPh_2–3 Ph]. $C_{42}H_{32}P_2$ (598.65): calcd. (%) C 84.26, H 5.39; found C 83.40, H 5.66.

2′,6-Bis(diphenylphosphanyl)-*N*,*N*-dimethylbiphenyl-2-amine (6): Prepared from (6,2′-dibromobiphenyl-2-yl)dimethylamine. The crude product was purified by column chromatography on silica gel using cyclohexane as the eluent to separate phosphafluorene, diphosphane and triphenylphosphane. Crystallization from acetonitrile afforded pure 2′,6-bis(diphenylphosphanyl)-*N*,*N*-dimethylbiphenyl-2-amine (**6**, 44%) as colourless needles. M.p. 150–152 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35–7.25 (m, 13 H), 7.22–7.15 (m, 7 H), 7.07–7.04 (m, 2 H), 7.02 (dd, J = 8.0, 1.1 Hz, 1 H), 7.00–6.97 (m, 1 H), 6.91–6.88 (m, 2 H), 6.76 (ddd, J = 7.7, 3.2, 1.1 Hz, 1 H), 2.13 ppm (s, 6 H, NMe_2). ^{13}C NMR (151 MHz, $CDCl_3$; numbering of carbon atoms as for a 2,2′-bisphosphane): δ = 152.68 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 10.3 Hz, C6), 146.62 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 43.4 Hz, C1′), 142.38 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 38.2 Hz, C1), 139.65 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 14.0 Hz, *i*-dpp), 138.77 (C_q, d, $|\Sigma J_{PC}|$ = 13.7 Hz, *i*-dpp), 138.63 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 13.1 Hz, *i*-dpp), 138.09 (C_q, d, $|\Sigma J_{PC}|$ = 12.8 Hz, *i*-dpp), 137.67 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 10.9 or 9.5 Hz, C2), 136.61 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 8.4 Hz, C2′), 136.18 (CH, d, $|\Sigma J_{PC}|$ = 2.9 Hz, C3′), 133.96 (CH, AB*X*, $|\Sigma J_{PC}|$ = 19.9 Hz, 2 C, *o*-dpp), 133.25 (CH, AB*X*, $|\Sigma J_{PC}|$ = 19.9 Hz, 2 C, *o*-dpp), 133.19 (CH, AB*X*, $|\Sigma J_{PC}|$ = 21.0 Hz, 2 C, *o*-dpp), 132.93 (CH, AB*X*, $|\Sigma J_{PC}|$ = 18.8 Hz, 2 C, *o*-dpp), 132.73 [CH, AB*X* ("t"), $|\Sigma J_{PC}|$ = 12.9 Hz, C6′], 128.63 (CH, d, $|\Sigma J_{PC}|$ = 1.5 Hz, C3), 128.40 (CH, br., C4), 128.33 (CH, *p*-dpp), 128.31 (CH, $|\Sigma J_{PC}|$ = 6.4 Hz, 2 C, *m*-dpp), 128.10 (CH, $|\Sigma J_{PC}|$ = 5.6 Hz, 2 C, *m*-dpp), 128.03 (d, $|\Sigma J_{PC}|$ = 1.6 Hz, C5′), 128.02 (CH, $|\Sigma J_{PC}|$ = 5.4 Hz, 2 C, *m*-dpp), 127.92 (CH, $|\Sigma J_{PC}|$ = 5.8 Hz, 2 C, *m*-dpp), 127.77 (CH, *p*-dpp), 127.56 (CH, *p*-dpp), 127.50 (CH, *p*-dpp), 127.27 (CH, C4′), 119.18 (CH, C5), 43.19 (CH_3, NMe_2). ^{31}P NMR (162 MHz, $CDCl_3$): –14.0 (s); (CD_2Cl_2): –14.4 (d), –14.5 ppm (d, J = 5.3 Hz). MS(EI): *m*/*z* (%) = 564.2 (< 2) [M^+], 521.0 (< 2) [M^+ – NMe_2], 488.2 (3) [M^+ – Ph], 380.1 (100) [M^+ – PPh_2], 364.1 (25) [M^+ – Me–PPh_2], 336.1 (6) [M^+ – NMe_2–PPh_2]. $C_{38}H_{33}NP_2$ (565.62): calcd. (%) C 80.69, H 5.88, N 2.46; found C 80.80, H 6.17, N 2.29.

[6-(Trifluoromethoxy)biphenyl-2,2′-diyl]bis(diphenylphosphane) (7): Prepared from 2,2′-dibromo-6-trifluoromethoxybiphenyl. Purification by chromatography on silica gel using cyclohexane as the elu-

ent followed by triturating from acetonitrile afforded [6-(trifluoromethoxy)biphenyl-2,2′-diyl]bis(diphenylphosphane) (**7**, 10%). M.p. 179–180. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36–7.26 (m, 13 H), 7.26–7.15 (m, 9 H), 7.11 (td, J = 7.5, 1.3 Hz, 1 H, H5′), 6.95 ("ddd", $J \approx$ 7.7, 2.7, 1.1 Hz, 1 H, H3), 6.90 (m, 2 H, *o*-dpp), 6.70 ppm (br. dd, J = 7.6, 3.2 Hz, 1 H, H6′). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.11 (C_q, qm, J_{FC} = 7.8 Hz, C6), 141.71 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 40.1 Hz, C1′), 140.88 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 11.5 Hz, C2), 139.59 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 39.7 Hz, C1), 137.68 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 14.0 Hz, *i*-dpp), 137.103 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 11.0 Hz, *i*-dpp), 137.099 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 12.4 Hz, *i*-dpp), 136.88 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 9.0 Hz, C2′), 136.39 (C_q, AB*X*, $|\Sigma J_{PC}|$ = 11.7 Hz, *i*-dpp), 134.57 (CH, AB*X*, $|\Sigma J_{PC}|$ = 1.8 Hz, C3′), 134.16 (CH, AB*X*, $|\Sigma J_{PC}|$ = 21.1 Hz, 2 C, *o*-dpp), 133.71 (CH, AB*X*, $|\Sigma J_{PC}|$ = 21.7 Hz, 2 C, *o*-dpp), 133.61 (CH, AB*X*, $|\Sigma J_{PC}|$ = 20.1 Hz, 2 C, *o*-dpp), 133.18 (CH, AB*X*, $|\Sigma J_{PC}|$ = 20.1 Hz, 2 C, *o*-dpp), 131.84 (CH, AB*X*, $|\Sigma J_{PC}|$ = 1.3 Hz, C3), 131.22 (CH, AB*X*, $|\Sigma J_{PC}|$ = 5.5 or 4.1 Hz, C6′), 128.88 (CH, C4), 128.77–128.13 (CH, several m + s, 13 C, 4 *m*-dpp, 4 *p*-dpp, C4′), 128.11 (CH, C5′), 120.11 (C_q, q, J_{FC} = 258.0 Hz, CF_3), 119.63 (CH, q, J = 1.7 Hz, C5). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –13.7 ppm (s); (CD_2Cl_2): δ = –13.90 (d), –14.15 ppm [dq, J(P,P) = 22.3, J(P,F) = 1.4 Hz]. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –56.9 ppm [d, J(P,F) = 1.4 Hz]. MS(EI): *m*/*z* (%) = 606.1 (< 2) [M^+], 529.2 (6) [M^+ – Ph], 421.1 (100) [M^+ – PPh_2], 353.2 (3) [M^+ – PPh_2–3 F], 336.2 (8) [M^+ – PPh_2–OCF_3], 260.3 (11) [M^+ – PPh_2–OCF_3–Ph], 183.1 (51) [M^+ – PPh_2–OCF_3–2 Ph]. $C_{37}H_{27}F_3OP_2$ (606.55): calcd. (%) C 73.27, H 4.49; found C 72.91, H 4.63.

[2-{5-(Diphenylphosphanyl)-2,2-difluorobenzo[*d*][1,3]dioxol-4-yl]-phenyl]diphenylphosphane (8): Prepared from 5-bromo-2,2-difluoro-4-(2-iodophenyl)benzo[1,3]dioxole. The crude product was purified by chromatography on silica gel using cyclohexane as the eluent. Triturating from methanol afforded pure [2-{5-(diphenylphosphanyl)-2,2-difluorobenzo[*d*][1,3]dioxol-4-yl}phenyl]diphenylphosphane (**8**; 47%) as a colourless solid. M.p. 153–154 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35–7.14 (m, 21 H), 7.00–6.97 (m, 2 H, *o*-dpp), 6.95 (d, J = 8.2 Hz, 1 H, H4), 6.85 (ddd, J = 7.6, 4.1, 1.3 Hz, 1 H, H6′), 6.78 ppm (dd, J = 8.2, 3.1 Hz, 1 H, H3). ^{13}C NMR (151 MHz, $CDCl_3$; numbering of carbon atoms as for a 2,2′-bisphosphane): δ = 143.70 (C_q, C5), 142.33 (C_q, dd, J = 11.6, 1.7 Hz, C6), 139.13 (Cq, dd, J = 32.2, 6.5 Hz, C1′), 137.69 (C_q, d, J = 13.6 Hz, *i*-dpp), 137.43 (C_q, d, J = 11.8, 1.1 Hz, C2′), 136.83 (C_q, d, J = 12.5 Hz, *i*-dpp), 136.69 (C_q, dd, J = 13.0, 1.6 Hz, *i*-dpp), 136.56 (C_q, dd, J = 12.2, 1.3 Hz, *i*-dpp), 134.43 (CH, d, J = 2.0 Hz, C3′), 133.87 (CH, d, J = 20.6 Hz, 2 C, *o*-dpp), 133.68 (CH, d, J = 20.4 Hz, 2 C, *o*-dpp), 133.61 (CH, dd, J = 19.1, 2.2 Hz, 2 C, *o*-dpp), 133.52 (C_q, dd, J = 14.0, 1.6 Hz, C2), 133.15 (CH, dd, J = 18.8, 1.6 Hz, 2 C, *o*-dpp), 131.24 (C_q, dd, J = 257.1, 255.2 Hz, CF_2), 130.72 (CH, dd, J = 5.7, 3.1 Hz, C6′), 129.79 (CH, d, J = 1.7 Hz, C3), 129.31 (C_q, dd, J = 36.9, 6.9 Hz, C1), 128.95 (CH, C4′), 128.72 (CH, *p*-dpp), 128.58 (CH, C5′), 128.57 (CH, *p*-dpp), 128.38 (CH, d, J = 7.0 Hz, 2 C, *m*-dpp), 128.34 (CH, d, J = 6.1 Hz, 2 C, *m*-dpp), 128.31 (CH, d, J = 6.9 Hz, 2 C, *m*-dpp), 128.32 (CH, *p*-dpp), 128.30 (CH, d, J = 6.2 Hz, 2 C, *m*-dpp), 128.23 (CH, *p*-dpp), 108.97 ppm (CH, C4). ^{19}F NMR (376 MHz, $CDCl_3$): –49.57 (d, J = 95.4 Hz), –49.96 ppm (dd, J = 95.4, 2.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): –12.72 (dd, J = 28.7, 2.3 Hz), –14.15 ppm (d, J = 28.7 Hz). MS(EI): *m*/*z* (%) = 602.1 (< 1) [M^+], 525.2 (8) [M^+ – Ph], 417.1 (100) [M^+ – PPh_2], 183.1 (51) [M^+ – 2 PPh_2–CF_2]. HRMS for $C_{37}H_{26}F_2O_2P_2$ [M + H]: calcd. 603.1449; found 603.1378.

[2-{6-(Diphenylphosphanyl)-2,2,3,3-tetrafluoro-2,3-dihydrobenzo[*b*]-[1,4]dioxin-5-yl}phenyl]diphenylphosphane (9): Prepared from 5-bromo-2,2-difluoro-4-(2-iodophenyl)benzo[*b*][1,3]dioxole. The crude product was purified by chromatography on silica gel using cyclohexane as the eluent. Triturating from methanol afforded pure [2-{6-(diphenylphosphanyl)-2,2,3,3-tetrafluoro-2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl}phenyl]diphenylphosphane (**9**; 34%) as a colourless solid. M.p. 169–170 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36–7.14 (m, 21 H), 7.05 (d, J = 8.5 Hz, 1 H, H4), 6.97–6.94 (m, 2 H, *o*-dpp), 6.86 (dd, J = 8.5, 2.6 Hz, 1 H, H3), 6.73 ppm (ddd, J = 7.6, 4.1, 1.3 Hz, 1 H, H6′). ^{13}C NMR (151 MHz, $CDCl_3$; numbering of carbon atoms as for a 2,2′-bisphosphane): δ = 139.99 (C_q, dd, J = 33.3, 6.7 Hz, C1′), 137.56 (C_q, br. m, C5), 137.36 (C_q, d, J = 13.5 Hz, *i*-dpp), 137.17 (C_q, d, J = 12.4 Hz, *i*-dpp), 137.11 (C_q, dd, J = 10.9, 1.4 Hz, C2′), 136.84 (C_q, dd, J = 35.0, 6.7 Hz, C1), 136.50 (C_q, dd, J = 12.0, 1.2 Hz, *i*-dpp), 136.10 (C_q, dd, J = 12.8, 1.2 Hz, *i*-dpp), 135.95 (C_q, dd, J = 13.5, 1.9 Hz, C2), 135.33 (C_q, v.br. d, $J \approx$ 10.2 Hz, C6), 134.90 (CH, d, J = 2.4 Hz, C3′), 134.03 (CH, dd, J = 20.8, 0.5 Hz, 2 C, *o*-dpp), 133.58 (CH, br. d, J = 19.8 Hz, 2 C, *o*-dpp), 133.54 (CH, dd, J = 18.8, 2.7 Hz, 2 C, *o*-dpp), 133.09 (CH, dd, J = 18.8, 1.4 Hz, 2 C, *o*-dpp), 130.94 (CH, dd, J = 6.2, 3.2 Hz, C6′), 130.52 (CH, d, J = 1.5 Hz, C3), 128.88 (CH, d, J = 0.5 Hz, *p*-dpp), 128.78 (CH, C4′), 128.56 (CH, d, J = 0.9 Hz, C5′), 128.42 (CH, d, J = 7.2 Hz, 2 C, *m*-dpp), 128.41 (CH, *p*-dpp), 128.38 (CH, d, J = 6.1 Hz, 2 C, *m*-dpp), 128.31 (CH, d, J = 6.2 Hz, 2 C, *m*-dpp), 128.30 (CH, *p*-dpp), 128.27 (CH, *p*-dpp), 128.26 (CH, d, J = 6.2 Hz, 2 C, *m*-dpp), 116.95 ppm (CH, br., C4), 111.99 (C_q, tt, J = 267.0, 40.2 Hz, CF_2CF_2). ^{19}F NMR (376 MHz, $CDCl_3$): –90.4 (ddd, J = 148.4, 18.4, 10.1 Hz), –91.3 (dddd, J = 147.3, 18.9, 10.1, 2.5 Hz), –92.2 (dddd, J = 148.4, 18.9, 5.1, 3.8 Hz), –93.7 ppm (ddd, J = 147.3, 18.4, 3.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): –13.9 (ddd, J = 24.6, 5.1, 2.5 Hz), –14.7 ppm (d, J = 24.6 Hz). MS(EI): *m*/*z* (%) = 652.6 (< 1) [M^+], 575.1 (2) [M^+ – Ph], 467.1 (100) [M^+ – PPh_2], 183.1 [M^+ – 2 PPh_2–C_2F_4]. $C_{38}H_{26}F_4O_2P_2$ (652.55): calcd. (%) C 69.94, H 4.02; found C 69.56, H 4.37.

Dicyclohexyl[2-{5-(dicyclohexylphosphanyl)-2,2-difluorobenzo[*d*]-[1,3]dioxol-4-yl}phenyl]phosphane (10): At 25 °C, butyllithium (27.3 mmol, 3 equiv.) in hexanes (17.5 mL) was added dropwise to a solution of 5-bromo-2,2-difluoro-4-(2-iodophenyl)benzo[*d*][1,3]-dioxole (4.00 g, 9.11 mmol, 1 equiv.) in toluene (46.0 mL). After 1 h, a solution of chlorodicyclohexylphosphane (6.36 g, 6.00 mL, 27.3 mmol, 3 equiv.) in toluene (30.0 mL) was added. After 2 h, water (70.0 mL) was added followed by extraction into dichloromethane (3× 70.0 mL). The combined organic layers were dried with sodium sulfate, filtered and the solvents evaporated. The crude product was purified by chromatography on silica gel. Triturating from ethyl acetate afforded pure dicyclohexyl[2-{5-(dicyclohexylphosphanyl)-2,2-difluorobenzo[*d*][1,3]dioxol-4-yl}phenyl]phosphane (**10**; 3.00 g, 5.25 mmol, 53%) as a colourless solid. M.p. 194–195 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 (m, 1 H, H3′), 7.42–7.36 (m, 2 H, H4′, H5′), 7.24 (dd, J = 8.3, 1.5 Hz, 1 H, H3), 7.14 (m, 1 H, H6′), 7.06 (d, J = 8.2 Hz, 1 H, H4), 2.00–1.92 (m, 2 H), 1.85–1.48 (m, 20 H), 1.34–0.88 ppm (m, 22 H). ^{13}C NMR (151 MHz, $CDCl_3$; numbering of carbon atoms as for a 2,2′-bisphosphane): δ = 143.09 (C_q, br., C5), 142.26 (C_q, br. d, J = 11.5 Hz, C6), 141.30 (C_q, dd, J = 31.0, 5.2 Hz, C1′), 135.98 (C_q, dd, J = 20.0, 1.4 Hz, C2′), 132.88 (CH, d, J = 3.1 Hz, C3′), 132.26 (C_q, dd, J = 35.2, 5.6 Hz, C1), 131.90 (CH, dd, J = 6.1, 1.9 Hz, C6′), 131.44 (C_q, dd, J = 22.6, 1.9 Hz, C2), 131.30 (C_q, dd, J = 255.2, 253.9 Hz, CF_2), 127.89 (CH, d, J = 3.0 Hz, C3), 127.69 (CH, br., C5′), 127.45 (CH, C4′), 107.69 (CH, br., C4); C1 of cyclohexyl: 36.68 (CH, dd, J = 16.8, 1.3 Hz), 35.43 (CH, dd, J = 15.4, 1.2 Hz), 33.87 (CH, d, J = 14.5), 33.66 (CH, d, J = 14.0 Hz); C2,6 and C3,5 of cyclohexyl: 30.88 (CH_2, dd, J = 11.7, 5.8 Hz), 30.78 (CH_2, d, J = 14.2 Hz), 30.66 (CH_2, dd, J = 11.6, 5.7 Hz), 30.32 (CH_2, d, J = 19.7 Hz), 30.19 (CH_2, d, J = 14.5 Hz), 30.14 (CH_2, d, J = 17.8 Hz), 29.10

(CH_2, d, J = 7.7 Hz), 28.94 (CH_2, d, J = 5.9 Hz), 27.58 (CH_2, d, J = 11.3 Hz), 27.56 (CH_2, d, J = 6.4 Hz), 27.49 (CH_2, d, J = 7.7 Hz), 27.48 (CH_2, d, J = 11.1 Hz), 27.31 (CH_2, d, J = 9.3 Hz), 27.25 (CH_2, d, J = 9.0 Hz), 27.19 (CH_2, d, J = 11.1 Hz), 27.14 (CH_2, d, J = 11.8 Hz); C4 of cyclohexyl: 26.71 ppm (CH_2, m, 2 C), 26.34 (CH_2, br., 2 C). ^{19}F NMR (376 MHz, $CDCl_3$): –49.20 (d, J = 98.4 Hz), –49.89 ppm (d, J = 98.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): –11.0 (d), –12.9 ppm (d, J = 22.7 Hz). MS(EI): m/z (%) = 626.3 (< 1) [M^+], 543.3 (100) [M^+ – Cy], 461.2 (17) [M^+ – 2 Cy], 295.1 (14) [M^+ – 4 Cy], 263 (63) [M^+ – PCy_2–2 Cy]. $C_{37}H_{50}F_2O_2P_2$ (626.74): calcd. (%) C 70.91, H 8.04; found C 71.12, H 8.11.

Dicyclohexyl[2-{6-(dicyclohexylphosphanyl)-2,2,3,3-tetrafluoro-2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl}phenyl]phosphane (11): At 25 °C, butyllithium (12.3 mmol, 3 equiv.) in hexanes (7.87 mL) was added dropwise to a solution of 6-bromo-2,2,3,3-tetrafluoro-5-(2-iodophenyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (2.00 g, 4.09 mmol, 1 equiv.) in toluene (20 mL). After 1 h, a solution of chlorodicyclohexylphosphane (2.86 g, 2.71 mL, 12.27 mmol, 3 equiv.) in toluene (13.0 mL) was added. After 2 h, water (30.0 mL) was added followed by extraction into dichloromethane (3× 30.0 mL). The combined organic layers were dried with sodium sulfate, filtered and the solvents evaporated. The crude product was purified by chromatography on silica gel. Triturating from methanol afforded dicyclohexyl[2-{6-(dicyclohexylphosphanyl)-2,2,3,3-tetrafluoro-2,3-dihydrobenzo[*b*][1,4]dioxin-5-yl}phenyl]phosphane (**11**; 2.00 g, 2.96 mmol, 73%) as colourless crystals. M.p. 97–99 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.56 (m, 1 H, H3′), 7.40 (td, J = 7.4, 1.5 Hz, 1 H, H4′), 7.36 (br. t, J = 7.4 Hz, 1 H, H5′), 7.30 (dd, J = 8.5, 1.0 Hz, 1 H, H3), 7.14 (d, J = 8.5 Hz, 1 H, H4), 7.05 (ddd, J = 7.5, 3.6, 1.5 Hz, 1 H, H6′), 2.02–1.43 (m, 24 H), 1.34–0.87 ppm (m, 20 H). ^{13}C NMR (151 MHz, $CDCl_3$; numbering of carbon atoms as for a 2,2′-bisphosphane): δ = 141.54 (C_q, dd, J = 31.1, 5.4 Hz, C1′), 139.48 (C_q, dd, J = 33.8, 5.1 Hz, C1), 137.21 (C_q, d, J = 2.7 Hz, C5), 136.29 (C_q, dd, J = 19.5, 1.9 Hz, C2′), 135.16 (C_q, dt, J = 10.2, 1.9 Hz, C6), 134.12 (C_q, dd, J = 22.4, 2.2 Hz, C2), 132.72 (CH, d, J = 3.0 Hz, C3′), 132.25 (CH, dd, J = 6.3, 2.0 Hz, C6′), 128.94 (CH, d, J = 2.8 Hz, C3), 127.46 (CH, br., C5′), 127.27 (CH, C4′), 115.53 (CH, C4), CF_2 signals not observed; C1 of cyclohexyl: 36.72 (CH, dd, J = 17.4, 1.3 Hz), 35.54 (CH, dd, J = 15.3, 1.2 Hz), 33.47 (CH, d, J = 14.9), 33.44 (CH, d, J = 14.3 Hz); C2,6 and C3,5 of cyclohexyl: 31.16 (CH_2, dd, J = 12.4, 6.5 Hz), 30.60 (CH_2, dd, J = 11.4, 5.9 Hz), 30.54 (CH_2, d, J = 13.0 Hz), 30.31 (CH_2, d, J = 20.1 Hz), 30.13 (CH_2, d, J = 17.3 Hz), 29.77 (CH_2, br. d, J = 10.3 Hz), 29.73 (CH_2, d, J = 12.9 Hz), 29.31 (CH_2, d, J = 7.2 Hz), 27.64 (CH_2, d, J = 6.9 Hz), 27.59 (CH_2, d, J = 10.8 Hz), 27.50 (CH_2, d, J = 10.4 Hz), 27.48 (CH_2, d, J = 8.7 Hz), 27.34 (CH_2, d, J = 9.8 Hz), 27.21 (CH_2, d, J = 10.5 Hz, 2 C), 27.10 (CH_2, d, J = 11.8 Hz); C4 of cyclohexyl: 26.73 (CH_2, d, J = 1.1 Hz), 26.68 (CH_2, d, J = 1.1 Hz), 26.38 (CH_2, d, J = 0.8 Hz), 26.29 ppm (CH_2, d, J = 0.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): signals 3–4 Hz wide, –88.39 (dt, $J \approx$ 149, 18 Hz), –89.50 (dt, $J \approx$ 148, 18 Hz), –93.94 (dd, $J \approx$ 149, 19 Hz), –95.02 ppm (ddd, $J \approx$ 148, 19, 2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): –10.7 (d), –12.9 ppm (d, J = 22.2 Hz). MS(EI): m/z (%) = 676.74 (< 1) [M^+], 593.3 (100) [M^+ – Cy], 511.2 (16) [M^+ – 2 Cy], 427.1 (10) [M^+ – 3 Cy], 313.1 (69) [M^+ – P – 4 Cy]. $C_{38}H_{50}F_4O_2P_2$ (676.74): calcd. (%) C 67.44, H 7.45; found C 67.61, H 7.53.

2,2-Difluoro-6-phenyl-6*H*-benzo[2,3]phosphindolo[4,5-*d*][1,3]dioxole (12): At –78 °C, butyllithium (4.50 mmol, 3 equiv.) in hexane (2.9 mL) was added slowly to a solution of 5-bromo-2,2-difluoro-4-(2-iodophenyl)benzo[1,3]dioxole (0.66 g, 1.50 mmol, 1 equiv.) in tetrahydrofuran (3.00 mL). After 60 minutes, a solution of dichlorophenylphosphane (0.54 g, 0.41 mL, 3.00 mmol, 2 equiv.) in toluene (3.00 mL) was added slowly. After 15 minutes, the reaction mixture was allowed to reach 25 °C and was treated with a saturated aqueous solution of ammonium chloride (15.0 mL). The mixture was extracted into ethyl acetate (3× 15.0 mL), and the combined organic layers were dried with sodium sulfate. Evaporation of the solvent followed by column chromatography on silica gel using cyclohexane as the eluent gave 2,2-difluoro-6-phenyl-6*H*-benzo[2,3]-phosphindolo[4,5-*d*][1,3]dioxole (**12**; 0.15 g, 0.45 mmol, 30%) as a yellow oil. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.10 (dq, J = 7.8, 0.8 Hz, 1 H, H10), 7.69 (ddt, J = 7.5, 5.1, 0.9 Hz, 1 H, H7), 7.51 (td, J = 7.6, 1.2 Hz, 1 H, H9), 7.38 (tdd, J = 7.5, 2.8, 1.2 Hz, 1 H, H8), 7.37 (dd, J = 8.0, 5.2 Hz, 1 H, H5), 7.31–7.22 (m, 5 H, Ph), 7.02 ppm (dd, J = 8.0, 2.2 Hz, 1 H, H4). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 144.65 (C_q, t, J = 1.1 Hz, C3a), 143.18 (C_q, d, J = 4.6 Hz, C6a), 139.55 (C_q, d, J = 1.1 Hz, C10a), 138.82 (C_q, q, J = 1.3 Hz, C10c), 138.34 (C_q, d, J = 5.1 Hz, C5a), 135.63 (C_q, d, J = 19.5 Hz, *i*-ph), 132.63 (CH, d, J = 20.6 Hz, 2 C, *o*-ph), 131.93 (C_q, t, J = 255.9 Hz, C2), 130.33 (CH, d, J = 21.9 Hz, C7), 129.64 (CH, d, J = 1.2 Hz, *p*-ph), 129.13 (CH, C9), 128.80 (CH, d, J = 7.8 Hz, 2 C, *m*-ph), 128.33 (CH, d, J = 7.8 Hz, C8), 126.90 (C_q, d, J = 4.2 Hz, C10b), 125.45 (CH, d, J = 24.0 Hz, C5), 125.02 (CH, C10), 108.44 ppm (CH, d, J = 8.5 Hz, C4). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = –49.59 (d), –49.82 ppm (d, J = 96.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = –5.2 ppm. MS(EI): m/z (%) = 340.1 (100) [M^+], 308.2 (15) [M^+ – F–O], 273.2 (21) [M^+ – OCF_2], 263.1 (34). [M^+ – Ph], 234.2 (47) [M^+ – PPh], 169.1 (64) [M^+ – PPh–OCF_2], 139.2 (80) [M^+ – PPh–Ph–F].

2,2,3,3-Tetrafluoro-7-phenyl-3,7-dihydro-2*H*-benzo[2,3]phosphindolo[4,5-*b*][1,4]dioxine (13): At –78 °C, butyllithium (4.50 mmol, 3 equiv.) in hexane (2.9 mL) was added slowly to a solution of 6-bromo-2,2,3,3-tetrafluoro-5-(2-iodophenyl)-2,3-dihydrobenzo[*b*]-[1,4]dioxine (0.74 g, 1.50 mmol, 1 equiv.) in tetrahydrofuran (3.00 mL). After 60 minutes, a solution of dichlorophenylphosphane (0.54 g, 0.41 mL, 3.00 mmol, 2 equiv.) in toluene (3.00 mL) was added slowly. After 15 minutes, the reaction mixture was allowed to reach 25 °C and was treated with a saturated aqueous solution of ammonium chloride (15.0 mL). The mixture was extracted into ethyl acetate (3× 15.0 mL), and the combined organic layers were dried with sodium sulfate. Evaporation of the solvent followed by column chromatography on silica gel using cyclohexane as the eluent gave 2,2,3,3-tetrafluoro-7-phenyl-3,7-dihydro-2*H*-benzo[2,3]phosphindolo[4,5-*b*][1,4]dioxine (**13**, 0.27 g, 0.68 mmol, 45%) as an orange solid. M.p. 84–85 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.41 (dq, J = 8.0, 0.8 Hz, 1 H, H11), 7.71 (dddd, J = 7.5, 5.6, 1.2, 0.7 Hz, 1 H, H8), 7.54 (ddd, J = 8.0, 7.4, 1.2 Hz, 1 H, H10), 7.45 (dd, J = 8.2, 4.9 Hz, 1 H, H6), 7.41 (tdd, J = 7.4, 2.8, 1.1 Hz, 1 H, H9), 7.33–7.24 (m, 5 H, *o*-, *m*-, *p*-ph), 7.10 (dd, J = 8.2, 2.3 Hz, 1 H, H5). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 143.4 (C_q, d, J = 2.6 Hz, C7a), 140.8 (C_q, d, J = 4.1 Hz, C6a), 140.7 (C_q, d, J = 1.3 Hz, C11a), 138.0 (C_q, br., C4a), 134.9 (C_q, d, J = 19.1 Hz, *i*-ph), 134.4 (C_q, br. d, J = 1.2 Hz, C11c), 132.9 (CH, d, J = 20.6 Hz, 2 C, *o*-ph), 132.4 (C_q, d, J = 4.4 Hz, C11b), 130.4 (CH, d, J = 22.2 Hz, C8), 129.8 (CH, d, J = 0.9 Hz, *p*-ph), 129.2 (CH, s, C10), 128.9 (CH, d, J = 7.9 Hz, 2 C, *m*-ph), 128.3 (CH, d, J = 8.1 Hz, C9), 126.7 (CH, d, J = 23.3 Hz, C6), 126.3 (CH, s, C11), 116.6 (CH, d, J = 8.5 Hz, C5), 112.3 (C_q, ca. tt, $J \approx$ 268, 40 Hz, C2 or C3), 112.1 ppm (C_q, ca. tt, $J \approx$ 266, 40 Hz, C3 or C2). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = –91.0 ppm –92.3 ppm (m, 4 F). ^{31}P NMR ($CDCl_3$, 161 MHz): δ = –7.8 (s). MS(EI): m/z (%) = 390.1 (100) [M^+], 359.2 (29) [M^+ – O–F], 313.1 (67) [M^+ – Ph], 295.2 (14) [M^+ – Ph–F], 202.2 (12) [M^+ – PPh–CF_2–O–F], 169.1 (24) [M^+ – PPh–Ph–2 F], 157.1 (44) [M^+ – PPh–Ph–CF_2]. $C_{20}H_{11}F_4O_2P{\cdot}H_2O$ (408.28): calcd. (%) C 58.84, H 3.21; found C 58.31, H 3.33.

Supporting Information (see footnote on the first page of this article): NMR spectra of **1**–**13** (^{1}H, ^{13}C, ^{31}P and, where applicable, ^{19}F) are presented.

Acknowledgments

We are grateful to the Ministère de la Recherche (France) and the Centre National de la Recherche Scientifique (CNRS) (France). L. B. thanks LONZA AG (Switzerland) for a PhD grant. We thank Petra Holba-Schulz for carefully recording countless NMR spectra, Dr. Kerstin Ibrom for help with the selective $^{1}H\{^{31}P\}$ experiments and Dr. Lydia Brelot (Service de Radiocristallographie, University of Strasbourg, France) for assistance with single crystal structure elucidation.

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Received: April 20, 2011
Published Online: June 28, 2011

