Primary phosphanes (RPH$_2$) have a reputation as noxious compounds which are spontaneously flammable in air.$^{[1]}$ We have recently demonstrated, however, that they can be stabilized to air oxidation without any need for steric protection, providing sufficient π conjugation is incorporated into the organic R group; thus we were able to prepare the first air-stable chiral primary phosphanes.$^{[3]}$ Since then, we have been developing a working model based on DFT, which indicates that, contrary to popular belief, many primary phosphanes will be air-stable if the molecule contains a high degree of conjugation (see below).$^{[3]}$ As such, the model predicted that the incorporation of the phosphino group onto a boron dipyrromethene (Bodipy)$^{[4]}$ skeleton would also produce air-stable primary phosphanes. These phosphanes should provide a highly versatile gateway into a vast range of fluorescent phosphanes, which are currently sorely underrepresented, despite the importance of phosphanes in catalytic and biomedical applications. To explore this exciting possibility, we commenced a synthetic study based on the strategy shown below.$^{[2]}$

**Scheme 1.** Synthetic procedure for the novel compounds 2a/2b, 3a/3b, and 4a/b. $^*$DPPB = 1,4-bis(diphenylphosphino)butane, DMSO = dimethyl sulfoxide.

Table 1: Photochemical data of compounds 2a/b, 3a/b, and 4a/b.$^{[1,4]}$

|      | $\lambda_{	ext{abs}}$ [nm] | $\lambda_{	ext{em}}$ [nm] | $\epsilon$ [M$^{-1}$ cm$^{-1}$] | $\Phi$         |
|------|-----------------|-----------------|----------------|---------------|
| 1    | 526             | 540             | 78000          | 0.65          |
| 2a   | 519             | 531             | 80000          | 0.079         |
| 2b   | 514             | 524             | 87000          | 0.36          |
| 3a   | 518             | 534             | 83000          | 0.039         |
| 3b   | 513             | 527             | 91000          | 0.29          |
| 4a   | 518             | 532             | 79000          | 0.042         |
| 4b   | 512             | 526             | 79000          | 0.33          |
| 5b   | 513             | 528             | 90000          | 0.34          |
| 6b   | 513             | 527             | 64000          | 0.28          |

[a] Determined in THF at room temperature.

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sponding phosphonate 3b and the primary phosphane 4b, which also retain generally better quantum yields and molar absorption coefficients (Φ and ε and Table 1).[7] The primary phosphane 4b is air-stable as a solid and in solution over seven days; Figure 1 depicts its crystallographically determined molecular structure.

Figure 1. View of the molecular structure of 4b with 50% probability displacement ellipsoids. Hydrogen atoms bound to carbon atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: P1–H1A 1.42(4), P1–H1B 1.23(4), P1–C21 1.8289(17), C5–C18 1.493(2), C5–C6 1.397(2), N2–C6 1.400(2), B1–N1 1.591(2), B1–N2 1.593(2), B1–C24 1.615(3); H1A-P1-H1B 87(2), C4-C5-C6 122.60(15), N1-B1-C24 110.61(15), N1-B1-N2 104.89(12).

Again this air stability is in accord with that predicted by the model; the high degree of π conjugation raises the orbital energies of both the neutral molecule and the associated radical cation, which was found to correlate with a higher resistance to air oxidation.[5] For 4b, the phosphino group is not incorporated in any orbital above HOMO-3 (Figure S7 in the Supporting Information). The two methyl groups on the boron of 4b are involved in the HOMO-1, but in contrast to the diphenyl substitution on 4a, the dimethyl substitution has a much lower impact on the quantum yield of 4b (see above, Table 1), which has a value almost eight times that of 4a.

Figure 2 plots absorption coefficient ε and fluorescence intensity versus wavelength λ to illustrate the absorption and emission maxima of 4a and 4b in THF; Stokes’ shifts of 14 nm are evident. A sample of 6b was analyzed by X-ray crystallography, and the molecular structure is depicted in Figure 3. This structure shows that the tripodal phosphane adopts a mer configuration about the rhenium center, with the central phosphorus atom trans to a carbonyl ligand and the terminal phosphorus atoms of the ligand 5b trans to each other. Of particular note is the elongated metal–carbon bond length of the carbonyl ligand trans to the phosphorus atom, relative to that of the carbonyl ligand trans to the chlorine atom (1.943(5) versus 1.904(6) Å) and the wider bond angle present for the rhenium–phosphorus–Bodipy carbon junction (122.08(18)°) when compared to the corresponding angles when the carbon atoms form part of a metallocyclic ring (110.61(18)° and 109.18(19)°). The parameters compare well with the only other known tripodal phosphane rhenium spectrum in [D]chloroform gave a doublet at δ = −12.2 ppm and a triplet at δ = −16.4 ppm in a 2:1 ratio (JPP = 27.3 Hz). The phosphane also retains the photophysical characteristics of its precursor 4b (Table 1); modification at the phosphorus center is not detrimental. Having established that the air stability of 4b does not impede on the reactivity of its phosphino group, we sought to study some preliminary coordination chemistry of the tripodal phosphane 5b. Reaction of 5b with [ReCl(CO)_3(PPh_3)_2] in mesitylene generated the octahedral rhenium complex 6b (Scheme 2).
complexes, [ReCl(CO)3(triphos)] (triphos = bis(2-diphenylphosphanoethyl)phenylphosphine). The complex 6b retains a similar absorption–emission profile ($\lambda_{\text{em}}$ 513 nm; $\lambda_{\text{em}}$ 527 nm) to that of the uncomplexed tripodal phosphane 5b and, although the molar absorption coefficient and quantum yield are lowered relative to 5b, these values are not dramatically affected; thus the molar absorption coefficient $\varepsilon$ is lowered from 90000 to 64000 M$^{-1}$ cm$^{-1}$, and the quantum yield is reduced from 0.34 to 0.28. The high quantum yield value is of significance; the aforementioned rhenium tripodal nitrogen complexes give quantum yields of 0.015 to 0.003 (depending on the solvent), as do many other transition-metal fluorescence probes.\(^{[10]}\) Therefore the results indicate that the rhenium phosphane core is straightforward to prepare and retains a highly desirable photophysical profile. Because of the similar coordination chemistry, rhenium is a frequently used mimic of $^{99m}$Tc, which is the most widely used radionuclide in medicinal diagnoses.\(^{[8,11]}\) Thus cores such as 6b offer the potential for correlating fluorescence studies with radioimaging data to better understand and improve the imaging and targeting of diseases. Fluorescence microscopy would facilitate an understanding of cellular activity in vitro, which could then be used in conjunction with information garnered from living specimens that had been subjected to nuclear imaging techniques after treatment with the gamma-emitting $^{99m}$Tc analogues. Our studies are now focused in this area.

**Experimental Section**

Apart from the air stability studies, reactions were carried out using standard Schlenk-line techniques in anhydrous solvents. Full characterization data for compounds 1–6 are given in the Supporting Information.

**Figure 3.** View of the molecular structure of 6b with 50% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: Re–P1 2.3890(14), Re–P2 2.4068(13), Re–P3 2.3877(13), Re–C24 1.904(6), C24–O1 1.128(6), Re–C25 1.943(5), C25–O2 1.338(6), Re–Cl 2.5220(13), P2–C21 1.827(5), C5–C6 1.379(9), C6–N2 1.402(6), N2–B 1.591(9), B–C54 1.630(13); Cl–Re–P1 184.53(4), P1–Re–P3 155.18(5), C24–Re–C25 86.3(2), Re–C25–O2 178.0(5), Re–P2–C21 122.08(18), C4–C5–C6 122.5(5), N1–B–N2 105.5(5).\(^{[7]}\)

1a: Phenyllithium (4.57 mL, 9.15 mmol, 2.0 mol solution in dibutyl ether) was added dropwise to a tetrahydrofuran solution (100 mL) of 1 (2.00 g, 4.36 mmol). The solution was stirred at room temperature until complete consumption of the starting material was observed by TLC. The reaction was quenched with water (20 mL), extracted with dichloromethane (2 × 100 mL), and the combined organic fractions were washed with water (40 mL) and brine (40 mL) and dried over magnesium sulfate. Column chromatography on silica (petroleum ether/toluene, 4:1) gave an orange solid (1.10 g, 44%).

2b: The compound was synthesized in a similar fashion to the above procedure from 1 (2.00 g, 4.36 mmol) and methyl lithium (5.72 mL, 9.15 mmol, 1.6 mol solution in diethyl ether). Column chromatography on silica (petroleum ether/toluene, 9:1) gave an orange solid (0.79 g, 40%).

3a: Compound 2a (1.00 g, 1.74 mmol) was dissolving in dimethyl sulfoxide (40 mL), and palladium acetate (0.117 g, 0.17 mmol), diethyl phosphite (0.25 mL, 1.91 mmol), N,N-diisopropylethylamine (0.91 mL, 5.21 mmol), and 1,4-bis(diphenylphosphino)butane (0.074 g, 0.17 mmol) were added. The mixture was degassed for 20 min, before being heated at 90°C for three days. The reaction was diluted with dichloromethane (100 mL) and washed with water (40 mL) and brine (40 mL) and dried over magnesium sulfate. Column chromatography on silica (ethyl acetate/petroleum ether, 2:1) gave an orange solid (0.96 g, 87%).

3b: The compound was prepared in a similar fashion to 3a, by using 2b (1.00 g, 2.22 mmol), toluene (40 mL), bis(dibenzylideneacetone)palladium (0.128 g, 0.22 mmol), diethyl phosphite (0.34 mL, 2.66 mmol), N,N-diisopropylethylamine (1.16 mL, 6.66 mmol), and 1,4-bis(diphenylphosphino)butane (0.095 g, 0.22 mmol). Column chromatography on silica (ethyl acetate/n-hexane, 3:1) gave an orange solid (0.60 g, 53%).

4a: Lithium aluminum hydride (3.16 mL, 3.16 mmol, 1.0 mol solution in tetrahydrofuran) was added to a Schlenk flask and cooled to −78°C in a dry ice/acetone bath. Chlorotrimethylsilane (0.40 mL, 3.16 mmol) was added to the resultant white suspension, and the mixture was allowed to warm to room temperature over 30 min. A colorless solution was evident which was then cooled to −40°C in a dry ice/acetonitrile bath, and a solution of 3a (1.00 g, 1.58 mmol) in tetrahydrofuran (100 mL) was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. The solution was concentrated in vacuo and then quenched in an ice-bath with degassed water (20 mL). The product was extracted with diethyl ether (3 × 20 mL) and dried over magnesium sulfate. Column chromatography on silica (dichloromethane/petroleum ether, 1:2) gave 4a as an orange solid (0.77 g, 92%).

4b: The compound was prepared in a similar fashion to 4a, by using lithium aluminum hydride (3.93 mL, 3.93 mmol, 1.0 mol solution in tetrahydrofuran), chlorotrimethylsilane (0.50 mL, 3.93 mmol), and 3b (1.00 g, 1.97 mmol) in tetrahydrofuran (100 mL). Column chromatography on silica (chloroform/n-hexane, 1:4) gave 4b as an orange solid (0.74 g, 93%).\(^{[2]}\)

5b: Vinyldiphenylphosphine (0.16 mL, 0.78 mmol), [Pt(nbd)$_2$Cl] (0.018 g, 0.057 mmol), and 4b (0.150 g, 0.37 mmol) were dissolved in toluene (10 mL), and the reaction was stirred at reflux for five days. Column chromatography on silica (dichloromethane/n-hexane, 1:1) gave 5b as an orange solid (0.21 g, 70%).

6b: 5b (0.050 g, 0.060 mmol), [ReCl(CO)$_3$(PPh$_3$)$_2$] (0.050 g, 0.060 mmol), and mesitylene (2 mL) were heated to reflux for four hours. After passing the mixture through a silica pad, eluting first with n-hexane and then with dichloromethane, an orange solid was obtained (0.051 g, 82%).\(^{[2]}\)
The difluoride analogue of 3a/b was prepared, but reduction of this compound with LiAlH₄ resulted in decomposition of the backbone.

The quantum yield was referenced to 4,4-difluoro-8-phenyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene, \( \Phi = 0.76 \) in THF. Other photophysical properties: \( \lambda_{\text{abs}} = 524 \text{ nm} \), \( \lambda_{\text{em}} = 537 \text{ nm} \), \( \varepsilon = 86 \text{ 000} \text{ M}^{-1} \text{ cm}^{-1} \).

Crystal data for 4b: \( \text{C}_{25}\text{H}_{34}\text{BN}_{2}\text{P}, M = 404.32, \) monoclinic, space group \( P2_1/n \), \( a = 7.9693(6), b = 11.0597(7), c = 26.1232(16) \text{ Å}, \beta = 90.345(6)^\circ \), \( V = 2302.4(3) \text{ Å}^3 \), \( Z = 4, T = 150 \text{ K}, 4902 \) reflections collected, merging of equivalent reflections prevented by twinning, \( R(F, F^2>2\sigma) = 0.0401, R_w(F^2, \text{all data}) = 0.1078, \) goodness of fit = 1.031. Crystal data for 6b: \( \text{C}_{55}\text{H}_{60}\text{BClN}_{2}\text{O}_{2}\text{P}_{3}\text{Re}, M = 1106.42, \) monoclinic, space group \( P2_1, a = 8.1749(4), b = 10.0931(4), c = 33.0892(12) \text{ Å}, \beta = 91.786(4)^\circ \), \( V = 2728.92(2) \text{ Å}^3 \), \( Z = 2, T = 150 \text{ K}, 17360 \) reflections collected, 10027 unique, \( R_{int} = 0.0381, R(F, F^2>2\sigma) = 0.0348, R_w(F^2, \text{all data}) = 0.0749, \) goodness of fit = 1.013. CCDC 849750, 849751, 849752, 849753, 849754 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.