DOI: 10.1002/ejoc.200700538

Ambiphilic Compounds: Synthesis and Structure of a Phosphane–Borane with a Flexible Diphenyl Ether Tether

Magnus W. P. Bebbington,[a] Ghenwa Bouhadir,[a] and Didier Bourissou*[a]

Keywords: Ambiphilic derivatives / Phosphanes / Boranes / Tethered compounds / Lithiation / Solvent effects

The preparation of desired phosphane–borane **1** involves selective lithiation trapping of 2-bromo-2′-iododiphenyl ether **3** to give bromophosphane **4** followed by a second lithiation/electrophilic trapping to install the boron fragment. The structure of the new phosphane–borane was verified by single-crystal X-ray diffraction studies. A problematic intramolecular cyclization of lithiated intermediate **7** in THF was prevented by the use of toluene as the solvent. This result will also be of interest to chemists seeking to prepare related unsymmetrical diphosphanes.

Introduction

Diphosphane ligands have played a key role in the development of transition-metal-catalyzed reactions, including in many industrially important processes.[1] Recently, we initiated a research program aimed at exploring the use of phosphane–boranes (PB) **A** as so-called *ambiphilic ligands* for transition metals (Figure 1).[2] The resultant metal complexes possess in some cases novel coordination modes involving P→M→B and P→M–X→B[3] bridging interactions. Besides the synthetic challenges and fundamental questions raised by such transition metal→borane interactions,[4,5] new insights might also be expected for the use of such ambiphilic ligands in organometallic catalysis. Indeed, ligands featuring pendant Lewis acid moieties open promising ways to activate M–X bonds[6,7] and to anchor substrates in the coordination sphere.[8] In addition, PB derivatives **A**–**C** have recently become of major interest as metal-free systems capable of dihydrogen activation,[9] as readily tunable fluorescent systems[10] and as direct precursors for photoisomerizable heterodienes.[11] It is most likely that further developments will emerge in the near future that take advantage of the high structural modularity of ambiphilic compounds. In this regard, essentially rigid spacer groups (such as the *ortho*- or *para*-phenyl group in **A**–**C**) have so far been used to assemble PB derivatives.[12] With the aim to extend the structural variety of PBs to flexible systems, we thus became interested in using the diphenyl ether tether that has been extensively employed for diphosphanes.[13] In this communication, we detail the preparation and X-ray structure of POB compound **1**, which is related to the more rigid PSB derivative **D** of Emslie et al.[14] The synthesis of **1** includes a lithiation protocol of more general interest to those working in phosphane ligand development, as illustrated by the synthesis of an unsymmetrical diphosphane POP′.

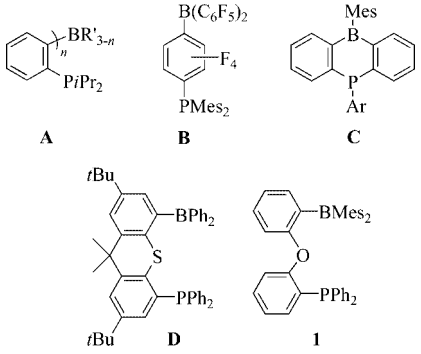


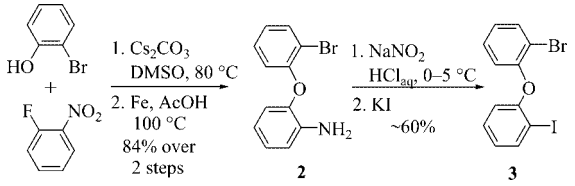
Figure 1. Representative PB ambiphilic compounds **A**–**D** with rigid spacers and target phosphane–borane **1** containing a flexible diphenyl ether tether.

Results and Discussion

DPEphos and related diphosphanes are usually prepared directly and efficiently by metallation of diphenyl ether with *n*BuLi·TMEDA followed by trapping with the appropriate P electrophiles.[13a,13b] All our attempts to extrapolate this strategy to related PBs and even unsymmetrical diphosphanes only led to intractable mixtures. The preparation of target **1** was therefore envisaged from sequential lithiation of 2-bromo-2′-iododiphenyl ether (**3**) (Scheme 1) by analogy with the synthetic route developed to obtain PBs **A**.[2] Compound **3** was to be accessed in one step from known aniline **2**.[15] Thus, the synthesis begins with a S_NAr reaction of commercially available 2-bromophenol and 1-fluoro-2-

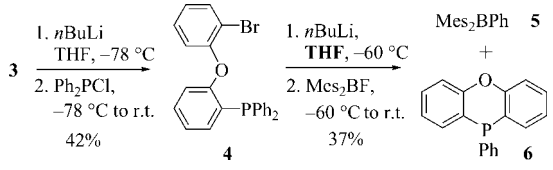
[a] Laboratoire Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069), Université Paul Sabatier
118, Route de Narbonne, 31062 Toulouse Cedex 04, France
Fax: +33-5-61558204
E-mail: dbouriss@chimie.ups-tlse.fr

nitrobenzene.[16] Reduction of the nitro group under standard conditions[15] gave aniline **2** quantitatively. Diazotization of the aniline and subsequent treatment with KI[17] gave a mixture of iodobromo compound **3** and an unidentified aromatic impurity (ca. 20% by GC–MS) in moderate yield. Repeated chromatographic attempts to further purify this compound were unsuccessful.



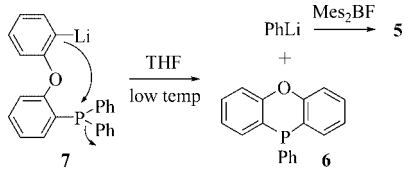
Scheme 1. Preparation of 2-bromo-2′-iododiphenyl ether (**3**).

Pleasingly however, lithium–halogen exchange with *n*BuLi at low temperature in THF, followed by trapping with chlorodiphenylphosphane gave the desired bromophosphane **4** as a stable white solid amenable to chromatographic purification (37% isolated yield). Spectroscopic data were consistent with the structure, notably including a single peak in the ^{31}P NMR spectrum at δ = –16 ppm and a molecular ion at m/z = 433 in the EI mass spectrum. Our initial attempts to prepare the target **1** by a second low-temperature lithium–halogen exchange in THF were unsuccessful. In THF, the ^{31}P NMR spectrum showed a major product with δ = –54 ppm, and the desired molecular ion (at m/z = 602) was not detected by mass spectrometry. An apparent molecular ion at m/z = 276, and crystallization from the crude reaction mixture of a second product shown to be phenyl dimesitylborane **5** by an X-ray diffraction study suggested the concomitant formation of cyclic phosphane **6**, a structure consistent with the ^{31}P NMR chemical shift (Scheme 2).[18] Product **6** is thought to arise from an intramolecular cyclization of the first-formed aryllithium **7** with expulsion of phenyllithium (Scheme 3). The PhLi is then trapped by Mes_2BF to give borane **5**. An analogous reaction was reported for the related biphenyl system, in which rotation about the aryl–aryl C–C bond and hence variation of the torsion angle between the aromatic rings is also unimpeded.[19]



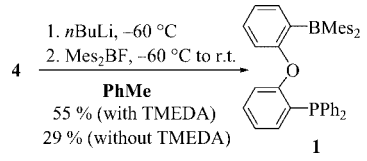
Scheme 2. Preparation and lithiation in THF of bromophosphane **4**.

Some experimentation was therefore required to prevent this undesired process. Prior addition of TMEDA to a solution of *n*BuLi in hexanes/THF and then inverse addition of bromophosphane **4** did not significantly alter the product profile. However, a change to toluene as the solvent brought about a significant breakthrough (Scheme 4),[20] as only a trace amount of the cyclized product was observed by ^{31}P



Scheme 3. Postulated mechanism for the formation of cyclic phosphane **6** and borane **5** from lithiated phosphane **7**.

NMR of the reaction mixture following the addition of Mes_2BF. Instead, the major product had δ = –17 ppm, only a slight shift relative to the starting material ($\Delta\delta$ = –1 ppm). The ^{11}B NMR spectrum showed a broad signal at δ = +80 ppm, consistent with a triarylborane,[21] and the EI mass spectrum had the expected molecular ion at m/z = 602. Crystallization of the product from Et_2O gave analytically pure PB **1** (55% isolated yield) and allowed unambiguous confirmation of its structure by X-ray diffraction analysis (Figure 2). The torsion angle between the two phenyl rings of the spacer is about 60°, and the absence of intramolecular P→B interaction, suggested by the NMR spectroscopic data, is clear from the large separation of the P and B atoms (5.37 Å). This is not unexpected given the steric bulk surrounding the boron atom.[22] Presumably the change in product profile results from a difference in the aggregation state of the intermediate aryllithium in the two solvents. The extent to which the *ortho* oxygen serves to stabilize the aryllithium may also be important.[23]



Scheme 4. Preparation of phosphane–borane **1**.

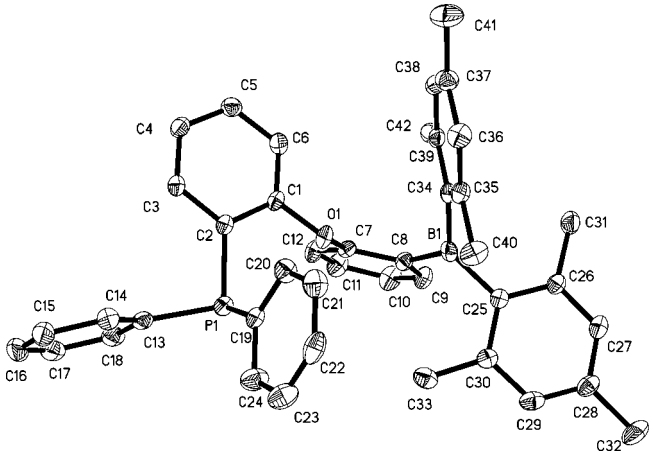
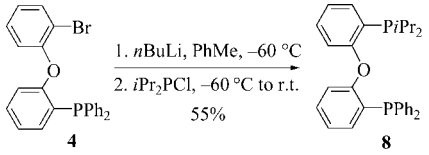


Figure 2. Thermal ellipsoid diagram (50% probability) of **1**.

In view of the widespread use of diphosphanes as ligands,[1] we elected to examine the possibility of preparing unsymmetrical DPEphos[13] derivatives by this route, none of which appear in the literature to the best of our knowl-

edge[24] and which would be of general interest to those working in the field of diphosphane chemistry. We first conducted control experiments to check that the cyclization reaction observed above was also problematic in the reaction of P electrophiles. Accordingly, the addition of iPr$_2$PCl following lithium–halogen exchange with **4**/nBuLi in THF gave a large proportion (ca. 70% by ^{31}P NMR) of cyclic product **6**, together with some starting material (ca. 20%) and some unidentified products. However, upon employing toluene as solvent, we observed clean conversion to diphosphane **8** (^{31}P NMR signals at δ = –16.5 and + 9.9 ppm, Scheme 5). An analytical sample was recrystallized from Et$_2$O/pentane. Despite the presence of an electron-rich dialkylphosphane group, compound **8** is somewhat surprisingly quite stable to aerobic oxidation (no oxidation observed by ^{31}P NMR after 3 d standing in air, <5% oxidation overnight in a solution of undistilled $CDCl_3$).[25] Notably, formation of cyclized product **6** in toluene in the absence of any electrophile was very slow (<5% after 1 h) even at room temperature.



Scheme 5. Preparation of unsymmetrical diphosphane **8**.

Conclusions

We developed a synthesis of a phosphane–borane with a flexible diphenyl ether tether, thus extending the structural diversity of this potentially useful class of compounds. In doing so, we have circumvented a problematic intramolecular cyclization reaction, thus opening a general route to flexible unsymmetrical diphosphanes.

Experimental Section

General Procedures: All reactions were performed under an inert atmosphere of argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{11}B, ^{13}C and ^{31}P NMR spectra were recorded with Bruker AC200, Avance 300 or AMX 500 instruments. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to Me$_4$Si as external standard, and ^{11}B and ^{31}P chemical shifts are reported in ppm relative to external BF_3·OEt_2 and 85% H_3PO_4, respectively. Mass spectra were recorded with a Hewlett–Packard HP5989 spectrometer. Aniline **2** was prepared in 84% yield over two steps according to literature procedures.[15]

Synthesis of Phosphane–Borane 1: A solution of bromophosphane **4** (186 mg, 0.43 mmol) in toluene (1 mL) was added dropwise to a solution of nBuLi (1.6 M in hexanes, 0.27 mL, 0.43 mmol) and TMEDA (50 mg, 0.43 mmol) in toluene (2 mL) at –60 °C. After stirring for 15 min, a solution of dimesityl boron fluoride (116 mg, 0.43 mmol) in toluene (1 mL) was added dropwise. The mixture was brought to r.t. over 30 min, and after 1 h at r.t. the mixture was filtered to remove the Li salts. The solvent was evaporated and crystallization from pentane gave colourless crystals of ligand **1** suitable for X-ray diffraction analysis (143 mg, 55%). M.p. 171–173 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.31–7.04 (m, 14 H, CH-Ar), 6.96–6.86 (m, 2 H), 6.65 (s, 4 H, Mes), 6.48 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H), 6.45–6.40 (m, 1 H), 2.19 (s, 6 H, 2×Me), 1.93 (s, 12 H, 4×Me) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.5 (C-O), 159.1 (d, $^2J_{C,P}$ = 18 Hz, C-O), 142.6 (C_{quat}), 140.4 (C_{quat}), 138.9 (C_{quat}), 138.3 (C_{quat}), 136.9 (d, $J_{C,P}$ = 13 Hz, C_{quat}), 134.7 (CH-Ar), 133.9 (d, J_{CP} = 20 Hz, CH-Ar), 133.4 (CH-Ar), 131.8 (CH-Ar), 130.2 (CH-Ar), 129.9 (d, $J_{C,P}$ = 15 Hz, C_{quat}), 128.8 (CH-Ar), 128.5 (d, $J_{C,P}$ = 7 Hz, CH-Ar), 128.0 (CH-Ar), 123.7 (CH-Ar), 122.5 (CH-Ar), 119.1 (d, $J_{C,P}$ = 2 Hz, CH-Ar), 116.4 (d, $J_{C,P}$ = 1 Hz, CH-Ar), 23.0 (2×Me), 21.2 (4×Me) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = –17.3 ppm. ^{11}B NMR (96.3 MHz, C_6D_6): δ = +80 ppm. MS (EI): m/z (%) = 602 (7) $[M]^+$, 587 (15), 278 (100), 185 (50), 77 (10). HRMS (EI): calcd. for $C_{42}H_{40}BOP$ 602.2910; found 602.2915.

Synthesis of Unsymmetrical Diphosphane 8: A solution of nBuLi (1.4 M in hexanes, 0.33 mL, 0.46 mmol) was added dropwise to a solution of bromophosphane **4** (200 mg, 0.46 mmol) in toluene (2 mL) at – 60 °C. After stirring for 1 h, iPr$_2$PCl (71 mg, 0.46 mmol) was added dropwise. After 2 h at –60 °C, the mixture was brought to r.t. over 30 min, and after 1 h at r.t., water (2 mL) was added. Toluene (10 mL) was added, and the organic layer was separated and dried (Na_2SO_4). The solvent was evaporated, and the crude product was purified by column chromatography (Et$_2$O/pentane, 3:97) to afford diphosphane **8** as a white powder (120 mg, 55%). M.p. 147–148 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.40 (td, $^3J_{H,H}$ = 7.8 Hz, $^3J_{P,H}$ = 1.8 Hz, 1 H, CH-Ar), 7.30–7.08 (m, 12 H, CH-Ar), 7.00–6.90 (m, 2 H, CH-Ar), 6.74–6.66 (m, 2 H, CH-Ar), 6.61 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, CH-Ar), 1.99 (septd, $^2J_{P,H}$ = 1.5 Hz, $^3J_{H,H}$ = 7.0 Hz, 2 H, CHiPr), 0.89 (dd, $^3J_{P,H}$ = 15.0 Hz, $^3J_{H,H}$ = 7.0 Hz, 6 H, 2×Me), 0.79 (dd, $^3J_{P,H}$ = 15 Hz, $^3J_{H,H}$ = 7.0 Hz, 6 H, 2×Me) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.5 (d, $^2J_{C,P}$ = 6 Hz, C_{ipso}-O), 159.6 (d, $^2J_{C,P}$ = 17 Hz, C_{ipso}-O), 136.9 (CH-Ar), 136.7 (CH-Ar), 136.5 (C_{quat}), 134.2 (CH-Ar), 133.9 (CH-Ar), 130.3 (CH-Ar), 129.1 (C_{quat}), 128.8 (CH-Ar), 128.4 (d, $J_{C,P}$ = 7 Hz, CH-Ar), 127.3 (d, $J_{C,P}$ = 23 Hz, C_{quat}), 123.6 (CH-Ar), 122.8 (d, $J_{C,P}$ = 8 Hz, CH-Ar), 118.6 (CH-Ar), 118.2 (CH-Ar), 23.2 (d, $^1J_{C,P}$ = 11 Hz, CHiPr) 20.7 (d, $^2J_{C,P}$ = 21 Hz, CH$_3i$Pr), 20.3 (d, $^2J_{C,P}$ = 11 Hz, CH$_3i$Pr) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = +9.9 (PiPr$_2$), –17.0 (PPh$_2$) ppm. MS (EI+): m/z (%) = 471 (<1) $[M]^+$, 427 (100), 199 (35), 43 (40) ppm. HRMS (ES): calcd. for $C_{30}H_{33}OP_2$ 471.2007; found 471.2018.

X-ray Crystallography: Data for **1** were collected at low temperatures by using an oil-coated shock-cooled crystal with a Bruker-AXS CCD 1000 diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. The structure was solved by direct methods using SHELXS-97[26] and refined with all data on F^2 using SHELXL-97.[27] All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were geometrically idealized and refined by using a riding model.

1: monoclinic, space group $P2_1/n$; T = 173 K; a = 9.1254(7) Å, b = 18.5458(13) Å, c = 20.7458(15) Å; β = 101.865(2)°; V = 3436.0(4) Å^3; Z = 4; R [I > 2σ(I)] = 0.0475, wR_2 (all data) = 0.1062 for 5230 unique reflections, 412 parameters, GooF = 1.006.

CCDC-650271 contains 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.

Acknowledgments

The Centre National de la Recherche Scientifique, Université Paul Sabatier and Agence Nationale de la Recherche (project BILI) are warmly acknowledged for financial support of this work. M. W. P. B. thanks the European Union for a Marie Curie Intraeuropean Postdoctoral Fellowship. We also thank Dr. H. Gornitzka for his assistance with the X-ray diffraction analysis.

[1] For example, see: *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**, vols. I–III.

[2] a) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu, D. Bourissou, *Angew. Chem. Int. Ed.* **2006**, *45*, 1611–1614; *Angew. Chem.* **2006**, *118*, 1641–1644; b) S. Bontemps, G. Bouhadir, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2006**, *128*, 12056–12057; c) S. Bontemps, G. Bouhadir, P. W. Dyer, K. Miqueu, D. Bourissou, *Inorg. Chem.* **2007**, *46*, 5149–5151.

[3] a) A related P→Ru–H→B interaction was obtained by borane insertion into a Ru–C bond: R. T. Baker, J. C. Calabrese, S. A. Westcott, T. B. Marder, *J. Am. Chem. Soc.* **1995**, *117*, 8777–8784; b) A related N→Ru–Cl→B bridging coordination was observed from the NB system (2-picolyl)BCy_2: J. Vergnaud, T. Ayed, K. Hussein, L. Vendier, M. Grellier, G. Bouhadir, J.-C. Barthelat, S. Sabo-Etienne, D. Bourissou, *Dalton Trans.* **2007**, 2370–2372.

[4] Transition metal→borane interactions were first structurally authenticated within metallaboratranes: A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, *Angew. Chem. Int. Ed.* **1999**, *38*, 2759–2761; *Angew. Chem.* **1999**, *111*, 2920–2923.

[5] For recent discussions on the precise nature of such interactions, see: a) A. F. Hill, *Organometallics* **2006**, *25*, 4741–4743; b) G. Parkin, *Organometallics* **2006**, *25*, 4744–4747.

[6] For Cp complexes featuring boryl bridges or pendant boryl groups, see: a) W. E. Piers, *Chem. Eur. J.* **1998**, *4*, 13–18; b) S. J. Lancaster, S. Al-Benna, M. Thornton-Pett, M. Bochmann, *Organometallics* **2000**, *19*, 1599–1608; c) H. Braunschweig, F. M. Breitling, E. Gullo, M. Kraft, *J. Organomet. Chem.* **2003**, *680*, 31–42; d) M. Hill, G. Kehr, R. Fröhlich, G. Erker, *Eur. J. Inorg. Chem.* **2003**, 3583–3589; e) S. Aldridge, C. Bresner, *Coord. Chem. Rev.* **2003**, *244*, 71–92; f) M. Hill, G. Erker, G. Kehr, R. Fröhlich, O. Kataeva, *J. Am. Chem. Soc.* **2004**, *126*, 11046–11057.

[7] The activation of a Ni-methyl bond with a phosphanylalane was reported in the context of silane polymerization: F.-G. Fontaine, D. Zargarian, *J. Am. Chem. Soc.* **2004**, *126*, 8786–8794.

[8] Boron analogues of DIOP were simultaneously and independently investigated by Kagan and Jacobsen: a) A. Börner, J. Ward, K. Kortus, H. B. Kagan, *Tetrahedron: Asymmetry* **1993**, *4*, 2219–2228; b) L. B. Fields, E. N. Jacobsen, *Tetrahedron: Asymmetry* **1993**, *4*, 2229–2240.

[9] a) G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126; b) G. J. Kubas, *Science* **2006**, *314*, 1096–1097.

[10] For examples of PB compounds with unusual optical or ion-sensing properties, see: a) Z. Yuan, N. J. Taylor, Y. Sun, T. B. Marder, I. D. Williams, L.-T. Cheng, *J. Organomet. Chem.* **1993**, *449*, 27–37; b) T. Agou, J. Kobayashi, T. Kawashima, *Org. Lett.* **2005**, *7*, 4373–4376; c) T. Agou, J. Kobayashi, T. Kawashima, *Inorg. Chem.* **2006**, *45*, 9137–9144; d) M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima, F. P. Gabbai, *Chem. Commun.* **2007**, 1133–1135.

[11] M. W. P. Bebbington, S. Bontemps, G. Bouhadir, D. Bourissou, *Angew. Chem. Int. Ed.* **2007**, *46*, 3333–3336; *Angew. Chem.* **2007**, *119*, 3397–3400.

[12] H. Braunschweig, R. Dirk, B. Ganter, *J. Organomet. Chem.* **1997**, *545–546*, 257–266.

[13] For selected examples of DPEphos-type ligands, see: a) M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics* **1995**, *14*, 3081–3089; b) M. Caporali, C. Müller, B. B. P. Staal, D. M. Tooke, A. L. Spek, P. W. N. M. van Leeuwen, *Chem. Commun.* **2005**, 3478–3480. For general discussions on the influence of the bite angle of POP ligands, see: c) P. Dierkes, P. W. N. M. van Leeuwen, *J. Chem. Soc. Dalton Trans.* **1999**, 1519–1529; d) Z. Freixa, P. W. N. M. van Leeuwen, *Dalton Trans.* **2003**, 1890–1901.

[14] a) D. J. H. Emslie, J. M. Blackwell, J. F. Britten, L. E. Harrington, *Organometallics* **2006**, *25*, 2412–2414; b) S. R. Oakley, K. D. Parker, D. J. H. Emslie, I. Vargas-Baca, C. M. Robertson, L. E. Harrington, J. F. Britten, *Organometallics* **2006**, *25*, 5835–5838.

[15] M. P. Olmsted, P. N. Craig, J. J. Lafferty, A. M. Pavloff, C. L. Zirkle, *J. Org. Chem.* **1961**, *26*, 1901–1907.

[16] C. J. Dinsmore, C. B. Zartman, *Tetrahedron Lett.* **1999**, *40*, 3989–3990.

[17] For a relevant example, see: D. Clive, A. G. Angoh, S. M. Bennett, *J. Org. Chem.* **1987**, *52*, 1339–1342.

[18] L. A. van der Veen, P. H. Keeven, G. C. Schoemaker, J. N. H. Reek, P. C. J. Kamer, P. W. N. van Leeuwen, M. Lutz, A. L. Spek, *Organometallics* **2000**, *19*, 872–883.

[19] a) O. Desponds, M. Schlosser, *J. Organomet. Chem.* **1996**, *507*, 257–261; b) M. Cereghetti, W. Arnold, E. A. Broger, A. Rageot, *Tetrahedron Lett.* **1996**, *37*, 5347–5350; c) F. Leroux, H. Mettler, *Synlett* **2006**, 766–770.

[20] Coordinating solvents have been shown to accelerate some reactions of organolithiums. For an example in the case of lithium–halogen exchange, see: B. Jedlicka, R. H. Crabtree, P. E. M. Siegbahn, *Organometallics* **1997**, *16*, 6021–6023.

[21] Free triarylboranes typically display 11B chemical shifts around 70 ppm: a) N. M. D. Brown, F. Davidson, J. W. Wilson, *J. Organomet. Chem.* **1981**, *209*, 1–11; b) H. C. Brown, U. S. Racherla, *J. Org. Chem.* **1986**, *51*, 427–432.

[22] Aryldimesitylboranes do not normally bind fragments larger than fluoride, see: C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574–4585.

[23] For a review of directed *ortho*-metallations in the synthesis of biaryls, see: E. J.-G. Anctil, V. Snieckus, *J. Organomet. Chem.* **2002**, *653*, 150–160.

[24] A Scifinder Scholar search revealed only symmetrical derivatives of DPEphos.

[25] Similar behaviour was reported for the widely used dialkyl biarylphosphanes, see: T. E. Barder, S. L. Buchwald, *J. Am. Chem. Soc.* **2007**, *129*, 5096–5101.

[26] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[27] G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen, **1997**.

Received: June 12, 2007
Published Online: August 3, 2007

