Supplementary material

Tracking Reactive Intermediates in Phosphine–Promoted Reactions with Ambiphilic Phosphino-Boranes

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Computational details

Phosphorus was treated with a Stuttgart–Dresden pseudopotential in combination with its adapted basis set.[1] The basis set has been augmented by a set of polarization function (d for P). Carbon, boron, oxygen, nitrogen and hydrogen atoms have been described with a 6–31G(d,p) double–ζ basis set.[2] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[3,4] Geometry optimisations were carried out without any symmetry restrictions, the nature of the *extrema* (*minimum*) was verified with analytical frequency calculations. All these computations have been performed with the Gaussian 03[5] suite of programs.

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Model compound $Me_2P(o\text{–}C_6H_4)BMe_2$

28
E = -421.993856 a.u.

C	-0.034394	0.000390	-0.328130
C	-0.030579	0.000122	1.076288
C	1.212890	0.000193	1.735839
C	2.408868	0.000525	1.010781
C	2.383941	0.000801	-0.381513
C	1.157888	0.000732	-1.048984
B	-1.356228	-0.000230	1.947284
P	1.070090	-0.000212	3.586114
C	2.174911	-1.433445	4.067910
C	2.174417	1.433203	4.068487
C	-2.075324	-1.370970	2.254708
C	-2.075531	1.370158	2.255761
H	3.364565	0.000572	1.530886
H	3.313310	0.001066	-0.945026
H	1.132940	0.000944	-2.135919
H	-0.978427	0.000341	-0.869941
H	-2.731955	-1.336638	3.129750
H	-2.720213	-1.590190	1.387402
H	-1.394030	-2.222389	2.345645
H	-2.730746	1.335335	3.131848
H	-1.394705	2.222058	2.345594
H	-2.722083	1.588825	1.389549
H	2.261518	-1.465482	5.157986
H	1.713488	-2.365163	3.731453
H	3.175573	-1.353887	3.632627
H	2.261079	1.464788	5.158572
H	3.175079	1.354198	3.633103
H	1.712632	2.364901	3.732471

Model isocyanate MeNCO

7
E= -207.907241 a.u.

C	-0.155433	0.000000	0.722361
O	-0.666791	0.000000	1.786056
N	0.492543	0.000000	-0.292017
C	0.324868	0.000000	-1.714644
H	1.307503	0.000000	-2.191289
H	-0.218791	-0.890023	-2.049672
H	-0.218791	0.890023	-2.049672

1:1 adduct of $Me_2P(o–C_6H_4)BMe_2$ with MeNCO: isomer 3^*_N

35
E= -629.919477 a.u.

C	1.097404	-0.374562	-0.713508
C	-0.130481	-0.178130	-0.048483
C	-0.033573	-0.148836	1.359236
C	1.172435	-0.310870	2.062486
C	2.351147	-0.499186	1.357435
C	2.303919	-0.526317	-0.040159
B	-1.494480	0.061909	-0.923188
O	-2.759453	-0.437874	-0.114022
C	-2.990500	-0.264167	1.142043
N	-4.076601	-0.347865	1.815263
P	-1.563691	0.120445	2.266503
C	-1.693310	-0.965635	3.733400
C	-1.726298	1.844745	2.867271
C	-1.534893	-0.821145	-2.279102
C	-1.705754	1.654178	-1.200463
H	1.190664	-0.293151	3.150418
H	3.292533	-0.626502	1.883972
H	3.220790	-0.676580	-0.605263
H	1.094439	-0.415118	-1.798952
H	-2.521103	-0.736870	-2.752390
H	-0.806649	-0.478938	-3.025652
H	-1.348255	-1.889527	-2.109325
H	-2.626634	1.832867	-1.770225
H	-1.772830	2.266355	-0.287943
H	-0.876926	2.069750	-1.787654
H	-2.721652	-0.891770	4.092339
H	-1.483735	-1.992223	3.427782
H	-0.989095	-0.657436	4.509396
H	-2.714048	1.954224	3.320200
H	-0.942175	2.059339	3.597259
H	-1.631210	2.521005	2.016071
C	-5.292759	-0.643764	1.074348
H	-6.153537	-0.263823	1.631971
H	-5.292371	-0.215103	0.065153
H	-5.418761	-1.729424	0.969010

1:1 adduct of $Me_2P(o\text{–}C_6H_4)BMe_2$ with MeNCO: isomer 3^*_O

35
E= -629.933296 a.u.

C	1.049785	-0.000237	-0.733055
C	-0.176410	0.000006	-0.027684
C	-0.028530	-0.000080	1.373081
C	1.213198	-0.000384	2.036733
C	2.380214	-0.000615	1.293272
C	2.286286	-0.000539	-0.104310
B	-1.548057	0.000451	-0.924833
N	-2.904904	0.000409	-0.048768
C	-3.076788	0.000161	1.258862
O	-4.115175	-0.000016	1.932573
P	-1.546508	0.000200	2.324049
C	-1.710256	-1.467693	3.408403
C	-1.709990	1.468434	3.407993
C	-1.565188	-1.362887	-1.834681
C	-1.564657	1.364326	-1.833894
H	1.262641	-0.000440	3.124185
H	3.348463	-0.000853	1.785288
H	3.193912	-0.000719	-0.703154
H	1.018585	-0.000185	-1.818962
H	-2.429443	-1.411513	-2.509992
H	-0.679029	-1.428548	-2.478225
H	-1.582039	-2.278536	-1.227586
H	-2.428799	1.413633	-2.509300
H	-1.581284	2.279635	-1.226279
H	-0.678384	1.430056	-2.477274
H	-2.729948	-1.469864	3.799814
H	-1.540684	-2.364965	2.810298
H	-0.986275	-1.426735	4.224851
H	-2.729618	1.470829	3.799568
H	-0.985888	1.427646	4.224344
H	-1.540413	2.365511	2.809597
C	-4.176993	0.000454	-0.776655
H	-3.977428	0.002002	-1.845498
H	-4.768972	-0.883403	-0.517839
H	-4.770224	0.882751	-0.515444

Compound *i*$Pr_2P(o–C_6H_4)BMes_2$

72
E= -1198.3356642 a.u.
C 3.9643100074 8.7827557169 -1.5945365532
C 3.2460412408 8.3609791639 -0.4460981465
C 1.884739809 8.7080370223 -0.3506110633
H 1.3129092413 8.352790767 0.5038161857
C 1.2514991167 9.4909949686 -1.3128507839
H 0.2023334196 9.7521581524 -1.2015415713
C 1.9686981727 9.9132422096 -2.4280427357
H 1.4882043815 10.5121447963 -3.1976230147
C 3.3066645011 9.5433292912 -2.5698043465
H 3.834746384 9.8478513923 -3.4689066423
P 5.7248895317 8.1663239718 -1.8106891658
C 5.8317367234 7.9506917661 -3.6981216303
H 5.5641533529 8.8912425448 -4.1950347899
C 4.8563039293 6.8580951684 -4.1420338403
H 4.9201266625 6.708674523 -5.2269272961
H 3.8197749469 7.1058494791 -3.8978257298
H 5.0954046719 5.9018214945 -3.6628584045
C 7.2624691195 7.5824242066 -4.0997960701
H 7.6112563881 6.6965426329 -3.5566548103
H 7.9706703683 8.3928696213 -3.9084496873
H 7.3076204682 7.3530562883 -5.1715658941
C 6.7193394212 9.760373751 -1.4525034189
H 6.2492042022 10.0982516988 -0.5214494525
C 8.1761002478 9.4229674991 -1.1190906942
H 8.7283377986 9.0587926894 -1.9914017607
H 8.2377851276 8.6612063306 -0.3372344418
H 8.6957091979 10.318601737 -0.7568150532
C 6.6077852992 10.8800780942 -2.4837882034
H 7.137486254 11.7738283341 -2.129986121
H 5.5677782256 11.1669591286 -2.6636428131
H 7.0563069905 10.6010330475 -3.4437256284
B 3.850904986 7.5874630903 0.7966982477
C 3.0098605977 6.3769743592 1.375502373
C 2.6381153015 6.3137119941 2.7447509415
C 1.84729781 5.2584447936 3.2075139518
H 1.5605157036 5.240304892 4.2577063067
C 1.4259300956 4.2240104476 2.3726889312
C 1.8162865677 4.2727115249 1.0345827117
H 1.5195584439 3.4667886576 0.3651883109
C 2.5753446049 5.327171254 0.5237220712
C 3.0479156874 7.3635531166 3.7514286715
H 2.7788341957 8.374918863 3.4313868757
H 4.128606616 7.3622386876 3.919738449
H 2.5562859059 7.184053029 4.7119130178
C 0.5624787709 3.1059149433 2.8917758917
H 0.7398070021 2.9224152827 3.9557608711
H 0.7455329797 2.1731547877 2.3497085816
H -0.5021383678 3.3450786504 2.7756748361
C 2.9393294389 5.2799231689 -0.9413162449
H 2.7866629068 4.2737962918 -1.3431259586

H 3.9828945532 5.5559770888 -1.1191238424
H 2.3225198029 5.9696303162 -1.526880683
C 5.1536915368 8.1085303364 1.5224251791
C 5.2625835399 9.4554224808 1.9586142298
C 6.3886835085 9.8709006665 2.6749266389
H 6.4414300586 10.903469531 3.0164900295
C 7.4433760312 9.0060509686 2.9669012454
C 7.3446804989 7.689401357 2.515373349
H 8.1602305652 6.9967172815 2.7170313476
C 6.2269815742 7.2264341413 1.8173170075
C 4.1819435692 10.4824799275 1.7063353444
H 4.4017524326 11.4096349371 2.243450552
H 3.1933935189 10.1418379998 2.0308651355
H 4.0911620028 10.7248001929 0.6428759013
C 8.6326578294 9.4675372905 3.7658392915
H 8.7933668182 10.5446754284 3.6609671912
H 9.5479932724 8.9547964666 3.4546800673
H 8.4933489019 9.261291704 4.8345587085
C 6.2329393816 5.7985367032 1.3342678968
H 6.3016243292 5.768415703 0.2397555879
H 5.3216907725 5.2661970807 1.6193379025
H 7.0891410539 5.2514670765 1.7392866603

PhNCO

14
E = -399.577822 a.u.

C	-0.265746	0.000000	0.032800
N	-0.897970	0.000000	1.274282
C	-0.646271	0.000000	2.455539
O	-0.539858	0.000000	3.627815
C	-1.064677	0.000000	-1.114878
C	-0.468280	0.000000	-2.372181
C	0.920385	0.000000	-2.495812
C	1.713897	0.000000	-1.348643
C	1.130353	0.000000	-0.085980
H	-2.144018	0.000000	-1.003731
H	-1.094593	0.000000	-3.259672
H	1.382056	0.000000	-3.478628
H	2.796876	0.000000	-1.434286
H	1.746363	0.000000	0.808754

1:1 adduct of *i*$Pr_2P(o–C_6H_4)BMes_2$ with PhNCO: isomer 3_N

86
E= -1597.8920086 a.u.

C	2.095903	1.245898	-0.241419
C	0.850744	1.173847	-0.855781
C	-0.279634	0.564196	-0.268114
C	-0.034801	0.070061	1.031789
C	1.217284	0.121309	1.670479
C	2.298781	0.701022	1.026339
B	-1.691334	0.330481	-1.149871
C	-1.833909	1.476117	-2.333068
P	-1.454007	-0.539314	1.949543
C	-1.640675	0.297885	3.612972
N	-3.011437	0.485186	-0.139417
C	-4.291259	1.042502	-0.560688
C	-1.436905	-1.271663	-1.670144
C	-3.048977	0.029741	1.120544
O	-3.999336	-0.034959	1.906072
C	-1.506346	-2.402599	2.109608
H	1.346008	-0.296119	2.664563
H	3.272103	0.741281	1.506480
H	2.917427	1.735871	-0.758634
H	0.739809	1.630274	-1.831282
H	-1.737190	-2.699879	1.079401
C	-0.146705	-3.008675	2.464547
C	-2.635432	-2.854543	3.039393
H	-2.667858	0.010007	3.866010
C	-0.686342	-0.175933	4.709414
C	-1.593223	1.817369	3.431938
H	-0.987701	0.283783	5.657146
H	-0.704620	-1.258699	4.852839
H	0.345699	0.132082	4.520002
H	-1.784205	2.298484	4.397239
H	-0.613337	2.149657	3.076555
H	-2.356755	2.168534	2.733324
H	-2.764002	-3.937879	2.942901
H	-2.406118	-2.645254	4.089329
H	-3.585749	-2.372752	2.796819
H	-0.228250	-4.099548	2.409879
H	0.631415	-2.700640	1.761980
H	0.177919	-2.756530	3.478702
C	-2.342224	1.182128	-3.629466
C	-2.318388	2.139781	-4.649219
C	-1.826781	3.428700	-4.455377
C	-1.423384	3.757424	-3.165513
C	-1.439976	2.827645	-2.118459
C	-2.972186	-0.143017	-3.989086
H	-2.711718	1.867613	-5.627768
C	-1.743894	-3.718607	-1.464571
C	-0.514593	-4.008094	-2.046349
C	0.174289	-2.920939	-2.568485
C	-0.264553	-1.598766	-2.420552
C	-3.663252	-2.336706	-0.858769

H	-2.388434	-4.542093	-1.157595
C	0.007322	-5.414869	-2.157326
H	1.086392	-3.096515	-3.138757
C	0.564009	-0.607543	-3.211608
C	-5.483574	0.310071	-0.454844
C	-6.700476	0.861670	-0.846099
C	-6.765579	2.164722	-1.331886
C	-5.596443	2.915964	-1.392953
C	-4.377281	2.366215	-1.001092
H	-5.477758	-0.683766	-0.032653
H	-7.603886	0.264455	-0.755622
H	-7.715526	2.593300	-1.639127
H	-5.621804	3.944551	-1.742059
H	-3.492191	2.979232	-1.039099
H	-1.445641	2.771126	0.067648
H	-0.046052	3.590710	-0.613250
H	-1.618411	4.379660	-0.642359
H	-3.557089	-0.041257	-4.908693
H	-2.232425	-0.932611	-4.148716
H	-3.648232	-0.494689	-3.206781
H	-1.802042	5.453050	-5.214106
H	-0.824450	4.319473	-6.148540
H	-2.581552	4.283096	-6.292139
H	0.061738	0.346172	-3.359947
H	1.538135	-0.421198	-2.747296
H	0.761909	-1.028104	-4.204232
H	0.587785	-5.556033	-3.074709
H	0.668629	-5.663594	-1.317178
H	-0.806708	-6.146698	-2.156623
H	-4.151667	-3.297247	-1.050339
H	-3.813198	-2.117862	0.203748
H	-4.207367	-1.581078	-1.423893
C	-1.759316	4.423472	-5.583107
H	-1.108314	4.778804	-2.952014
C	-1.117303	3.410338	-0.752696
C	-2.219982	-2.408245	-1.303791

1:1 adduct of *i*$Pr_2P(o–C_6H_4)BMes_2$ with PhNCO: isomer 3_O

86
E= -1597.9122962 a.u.
C 2.0495696082 -1.3496783339 0.3043558736
C 0.9620666559 -1.0195910564 -0.4954943369
C -0.2217271326 -0.4554483078 0.0173062229
C -0.2679144064 -0.3161971275 1.4238009547
C 0.8399611157 -0.6080510784 2.2397895669
C 2.0050638136 -1.1150846307 1.679011534
B -1.3869570729 0.05521119 -1.0235332729
C -1.437359738 1.7104590407 -1.1851018936
P -1.8272183235 0.2884841589 2.1503217553
C -1.6839781649 2.137909801 2.417744168
O -2.7779045451 -0.291648456 -0.3551910164
C -3.1396819873 -0.0872310349 0.8646542161
N -4.3005332991 -0.1653662935 1.4157975009
C -5.493282945 -0.5347607678 0.7744287191
C -1.3646754527 -0.8679840389 -2.3886102153
C -2.3865208513 -0.7007186582 3.6621102598
H 0.8033965781 -0.4367980518 3.3094400875
H 2.860656769 -1.3371027449 2.3103503296
H 2.9424451881 -1.7771487815 -0.145059027
H 1.0192773687 -1.1891768966 -1.5673666091
C -3.40344556 0.0737436796 4.504874568
H -2.9228471568 -1.5146007339 3.1609940555
C -1.2888622769 -1.3049682315 4.5380548874
C -3.018027199 2.8617389776 2.6050552681
C -0.6648063338 2.4659436596 3.5109621423
H -1.271775362 2.4381987305 1.4455183641
H -0.5019472651 3.5487879416 3.5306376117
H -1.0173933413 2.1707048112 4.5044644699
H 0.3048095958 1.9940846991 3.3285919503
H -2.843453194 3.9357664686 2.4817910469
H -3.7591907543 2.5574044452 1.8635056042
H -3.4397112918 2.704862679 3.6003441181
H -3.8356162353 -0.6115831186 5.2425296329
H -2.9355553161 0.8939675407 5.0583237396
H -4.2138053073 0.4609772328 3.8865689218
H -1.7732142807 -1.9024967937 5.3185873961
H -0.6223677037 -1.9677301797 3.983723369
H -0.6899425628 -0.5419919827 5.0461176293
C -5.6067686533 -1.0878474378 -0.5152968186
C -6.8557886799 -1.4538115875 -1.0114921317
C -8.0106175981 -1.271934809 -0.2522212006
C -7.9082914034 -0.7205810647 1.0253419373
C -6.6647890125 -0.3638623233 1.5328400471
H -4.7215955364 -1.2219800609 -1.1232733974
H -6.9228826565 -1.8819980423 -2.0082013015
H -8.9800148615 -1.5571894405 -0.6511776957
H -8.7992278748 -0.5737324025 1.630249894
H -6.5719795497 0.0554292404 2.5304491962
C -2.6437016901 2.3091460205 -1.6511298934
C -2.8074655934 3.6991207332 -1.6680930006

C	-1.8041286195	4.5735889236	-1.2616295713
C	-0.5906095838	4.0014690953	-0.8907574088
C	-0.3845857573	2.6139261896	-0.8616654342
C	-3.7996022205	1.5146122936	-2.2175784627
H	-3.7502240252	4.1060224831	-2.0328525951
C	-2.0126536067	6.0646197347	-1.2499136024
H	0.2417740227	4.6558931759	-0.6343611531
C	1.0342226655	2.19329244	-0.534581556
C	-1.7243069087	-2.2446979711	-2.3083428908
C	-1.7410688184	-3.0550438022	-3.4490070747
C	-1.3914721097	-2.5754747558	-4.7080098059
C	-0.9825345444	-1.2479778152	-4.7839119028
C	-0.9568345612	-0.4013150651	-3.6675032687
C	-2.0824054123	-2.9458880483	-1.0142651579
H	-2.0250301303	-4.1015774798	-3.3419101838
C	-1.4513531938	-3.4534278376	-5.92977739
H	-0.6633085978	-0.8492248733	-5.7460040716
C	-0.4573142912	1.0019211536	-3.9315846761
H	-1.940993995	-4.0259832174	-1.1231743931
H	-1.4619682106	-2.613840683	-0.1792013319
H	-3.1250962616	-2.7799924481	-0.726995933
H	-1.2583525499	1.7447748016	-3.8804540339
H	0.3031837883	1.317807198	-3.2142619421
H	-0.0142031718	1.0596760952	-4.9308525811
H	-0.7274732871	-3.1368704253	-6.6873271265
H	-1.2473409371	-4.5002872737	-5.6826271442
H	-2.4443651391	-3.4189459032	-6.3959131942
H	-1.0613029601	6.6029971574	-1.3016057195
H	-2.6308410422	6.389262015	-2.0931898575
H	-2.5228239693	6.3908355037	-0.3344458746
H	1.1390815013	1.7295747743	0.4510264511
H	1.426079547	1.4738433494	-1.2577156742
H	1.6928053321	3.0670681884	-0.5550085173
H	-4.3055885205	2.101199995	-2.9918106428
H	-3.4728657236	0.5737386523	-2.6629640198
H	-4.5467772323	1.2716647968	-1.456193487

Table 1. Energetic data computed for the formation of the PB / isocyanate adducts (in kcal/mol, total energies ΔE including ZPVE correction, ΔH and ΔG computed at 25°C).

adduct	regioisomer	ΔE	ΔH	ΔG
$Me_2P(o–C_6H_4)BMe_2$ / MeNCO	**3*$_O$**	-11.9	-9.8	6.3
$Me_2P(o–C_6H_4)BMe_2$ / MeNCO	**3*$_N$**	-20.2	-17.8	-1.3
$iPr_2P(o–C_6H_4)BMes_2$ / PhNCO	**3$_O$**	0.7	0.7	18.9
$iPr_2P(o–C_6H_4)BMes_2$ / PhNCO	**3$_N$**	13.5	13.8	32.4

Experimental details and spectroscopic data

All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Dry, oxygen–free solvents were employed. Toluene was dried over sodium, diethyl ether was dried over sodium/benzophenone and pentane was dried over CaH_2 and distilled prior to use. ^{1}H, ^{13}C, ^{11}B and ^{31}P NMR spectra were recorded on AMX 500 spectrometer. Chemical shifts are expressed with a positive sign, in parts per million, relative to residual ^{1}H and ^{13}C solvent signals, and external $BF_3.OEt_2$ and 85% H_3PO_4 respectively. Unless otherwise stated, NMR was recorded at 27°C. Mass spectra were recorded on Hewlett Packard 5989A. Infrared spectra were recorded on a FT–IR Perkin–Elmer 1600 spectrometer. The phosphino–borane **1** was prepared as previously described.[6]

6 M. W. P. Bebbigton, S. Bontemps, G. Bouhadir and D. Bourissou, *Angew. Chem. Int. Ed.,* 2007, **46**, 3333.

2: Diethyl azodicarboxylate (1.6 mL, 10 mmol) was added at room temperature to a solution of phosphinoborane **1** (880 mg, 2 mmol) in toluene (4.5 mL). After 24 h the volatiles were removed under vacuo. The white residue was washed with pentane. Crystals were obtained from a saturated Et_2O solution at room temperature (800 mg, 65%); m.p. 208 °C (from Et_2O). NMR ^{31}P ($CDCl_3$, 202.5 MHz): δ = 60.4. NMR ^{11}B ($CDCl_3$, 160.5MHz): δ = -0.8. ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 173.7 (s broad, *C*O_2Et), 160.9 (s, *C*O_2Et), 156.8 (broad, B-C_{ipso}), 149.5 (broad, B-C_{ipso}), 146.4 (C_{arom}), 144.2 (C_{arom}), 142.7 (C_{arom}), 141.6 (C_{arom}), 141.3 (d, $J_{C\text{-}P}$ = 13 Hz, CH_{arom}), 132.9 (C_{arom}), 132.6 (C_{arom}), 130.8 (d, $J_{C\text{-}P}$ = 3 Hz, CH_{arom}), 128.9 (d, $J_{C\text{-}P}$ = 18 Hz, CH_{arom}), 128.6 (CH_{Mes}), 128.4 (CH_{Mes}), 128.2 (CH_{Mes}), 128.0 (CH_{Mes}), 123.7 (d, $J_{C\text{-}P}$ = 15 Hz, CH_{arom}), 114.4 (d, $^1J_{C\text{-}P}$ = 93 Hz, P-C_{ipso}), 63.3 (CH_2), 60.7 (CH_2), 29.5 (CH_{3Mes}), 27.6 (d, $^1J_{C\text{-}P}$ = 42 Hz, $CH_{i\text{Pr}}$), 26.8 (d, $^1J_{C\text{-}P}$ = 50 Hz, $CH_{i\text{Pr}}$), 26.5 (CH_{3Mes}), 25.0 (CH_{3Mes}), 24.3 (CH_{3Mes}), 20.7 (2xCH_{3Mes}), 17.9 (s, $CH_{3i\text{Pr}}$), 17.2 (s broad, $CH_{3i\text{Pr}}$), 16.5 (d, $^2J_{C\text{-}P}$ = 2 Hz, $CH_{3i\text{Pr}}$), 15.9 (d, $^2J_{C\text{-}P}$ = 4 Hz, $CH_{3i\text{Pr}}$), 14.0 (s, CH_{3Et}), 13.9 (s, CH_{3Et}). NMR ^1H ($CDCl_3$, 500 MHz): δ = 7.54 (ddd, 1H, $J_{P\text{-}H}$ = 8 Hz, $^3J_{H\text{-}H}$ = 5 Hz, $^4J_{H\text{-}H}$ = 1.25 Hz, H_{arom}), 7.21 (m, 3H, H_{arom}), 6.65 (broad, 2H, H_{Mes}), 6.51 (broad, 1H, H_{Mes}), 6.35 (broad, 1H, H_{Mes}), 4.07 (dq, 1H, $^2J_{H\text{-}H}$ = 10 Hz, $^3J_{H\text{-}H}$ = 7 Hz, CH_2), 4.01 (qd, 1H, $^2J_{H\text{-}H}$ = 10 Hz, $^3J_{H\text{-}H}$ = 7 Hz, CH_2), 3.86 (m, 2H, CH_2 and $CH_{i\text{Pr}}$), 3.71 (qd, 1H, $^2J_{H\text{-}H}$ = 10 Hz, $^3J_{H\text{-}H}$ = 7 Hz, CH_2), 2.97 (septd, 1H, $^2J_{H\text{-}P}$ = $^3J_{H\text{-}H}$ = 7 Hz, $CH_{i\text{Pr}}$), 2.34 (s, 3H, CH_{3Mes}), 2.23 (s, 3H, CH_{3Mes}), 2.17 (s, 3H, CH_{3Mes}), 1.98 (s, 3H, CH_{3Mes}), 1.65 (s, 3H, CH_{3Mes}), 1.56 (dd, 3H, $^3J_{H\text{-}P}$ = 18 Hz, $^3J_{H\text{-}H}$ = 7 Hz, $CH_{3i\text{Pr}}$), 1.43 (dd, 3H, $^3J_{H\text{-}P}$ = 18 Hz, $^3J_{H\text{-}H}$ = 7 Hz, $CH_{3i\text{Pr}}$), 1.39 (dd, 3H, $^3J_{H\text{-}P}$ = 18 Hz, $^3J_{H\text{-}H}$ = 7 Hz, $CH_{3i\text{Pr}}$), 1.38 (s, 3H, CH_{3Mes}), 1.19 (t, 3H, $^3J_{H\text{-}H}$ = 7 Hz, CH_{3Et}), 0.90 (dd, 3H, $^3J_{H\text{-}P}$ = 18 Hz, $^3J_{H\text{-}H}$ = 7 Hz, $CH_{3i\text{Pr}}$), 0.89 (t, 3H, $^3J_{H\text{-}H}$ = 7 Hz, CH_{3Et}). MS (ESI^+) *m/z* (%): 617.6 (40) $[MH]^+$, 497.4 (100%) $[M\text{-}Mes]^+$. HRMS (ESI^+) calcd. for $C_{36}H_{51}BN_2O_4P$ $[MH]^+$: 617.3680 found 617.3694.

3_O: PhNCO (0.19 mL, 1.75 mmol) was added at room temperature to a solution of phosphinoborane **1** (155 mg, 0.35 mmol) in toluene (1.5 mL). After 1 h the yellow solution becomes colorless. The volatiles were removed under vacuo. The white residue was washed with 3*1 mL of pentane. Crystals were obtained from a saturated Et_2O solution at room temperature (110 mg, 56%); mp: 74 °C. ^{31}P NMR ($CDCl_3$, 202.5 MHz) δ: 1.2. ^{11}B NMR ($CDCl_3$, 160.5 MHz) δ: 4.7. ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ: 168.0 (broad, C_{ipso}-B), 150.6 (d, $^1J_{C\text{-}P}$ = 120.0 Hz, C=N), 146.3 (d, $J_{C\text{-}P}$ = 21.0 Hz, CH_{arom}), 142.8 (broad, C_{arom}, B_{Mes}), 138.8 (s, C_{arom}), 137.3 (d, $J_{C\text{-}P}$ = 12.0 Hz, CH_{arom}), 133.8 (s, C_{arom}), 131.7 (d, $J_{C\text{-}P}$ = 2.5 Hz, CH_{arom}), 129.9 (d, $J_{C\text{-}P}$ = 8.0 Hz, CH_{arom}), 129.5 (s, C_{arom}), 128.9 (broad, CH_{Mes}), 128.7 (s, C_{arom}), 128.4 (s, CH_{arom}), 128.2 (broad, C_{arom}, B_{Mes}), 127.9 (s, C_{arom}), 125.6 (d, $J_{C\text{-}P}$ = 11.0 Hz, CH_{arom}),124.2 (s, CH_{arom}), 124.0 (s, CH_{arom}), 117.9 (d, $^1J_{C\text{-}P}$ = 72.0 Hz, C_{ipso}-P), 24.8 (s, *o*-CH_{3Mes}), 24.7 (d, $^1J_{C\text{-}P}$ = 41.5 Hz, $CH_{i\text{Pr}}$), 20.8 (s, *p*-CH_{3Mes}), 16.8 (s, $CH_{3i\text{Pr}}$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.57 (m, 2H, H_{arom}), 7.42 (m, 4H, H_{arom}), 7.29 (m, 2H, H_{arom}), 7.14 (m, 1H, H_{arom}), 6.60 (broad, 4H, H_{Mes}), 2.23 (broad, 2H, $CH_{i\text{Pr}}$), 2.18 (s, 6H, *p*-CH_{3Mes}), 1.78 (broad, 12H, *o*-CH_{3Mes}), 1.42 (broad, 3H, $CH_{3i\text{Pr}}$), 1.41 (broad, 3H, $CH_{3i\text{Pr}}$), 1.35 (d, 3H, $^3J_{H\text{-}P}$ = 16.8 Hz, $CH_{3i\text{Pr}}$), 1.33 (d, 3H, $^3J_{H\text{-}P}$ = 19.2 Hz, $CH_{3i\text{Pr}}$). IR (ν cm^{-1}) in toluene solution: 3085(m), 3058(m), 3026(m), 2972(m), 2924(m), 2870(m), 1616(s), 1604(m), 1586 (s). MS (ESI^+) *m/z* (%): 562.5 (100) $[MH]^+$. HRMS (ESI^+) calcd. for $C_{37}H_{46}BNOP$ $[MH]^+$: 562.3410 found 562.3420.

Selected Crystal data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC–682859 (**2**) and 682860 (**3$_O$**). These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

2: $C_{36}H_{50}BN_2O_4P$, M = 616.56, triclinic, space group $P\ \bar{1}$, a = 12.2517(12), b = 16.8989(17), c = 17.0838(17) Å, α = 86.287(2)°, β = 77.074(2)°, γ = 89.524(2)°, V = 3440.1(6) Å^3, Z = 4, crystal size 0.6 x 0.5 x 0.2 mm^3, 17368 reflections collected (11517 independent, R_{int} = 0.0779), 843 parameters, $R1$ [I>2σ(I)] = 0.0569, wR_2 [all data] = 0.1469, GOF = 0.937, largest diff. peak and hole: 0.336 and -0.315 eÅ^{-3}.

3$_O$: $C_{39.50}H_{51}BNOP$, M = 597.59, monoclinic, space group: $P2_1/c$, a = 10.5050(14), b = 18.114(3), c = 18.875(3) Å, α = 90°, β = 101.404(3)°, γ = 90°, V = 3520.7(8) Å^3, Z = 4, crystal size 0.6 x 0.4 x 0.2 mm^3, 17251 reflections collected (5941 independent, R_{int} = 0.0810), 425 parameters, $R1$ [I>2σ(I)] = 0.0693, wR_2 [all data] = 0.1720, GOF = 1.045, largest diff. peak and hole: 0.554 and –0.432 eÅ^{-3}.

Data were collected at 173(2) K using an oil–coated shock–cooled crystal on a Bruker–AXS CCD 1000 diffractometer (λ = 0.71073 Å). Semi-empirical absorption corrections were employed for **3$_O$**.[7] The structure was solved by direct methods (SHELXS–97),[8] and refined using the least–squares method on F^2.[9]

7 SADABS, Program for data correction, Bruker-AXS.

8 G. M. Sheldrick, *Acta Crystallogr.,* 1990, **A46**, 467.

9 SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, 1997.