A Concise Ex Chiral Pool Approach to Novel Bidentate Camphane Phosphane Ligands

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Dedicated to Professor Henning Hopf on the occasion of his 60th birthday

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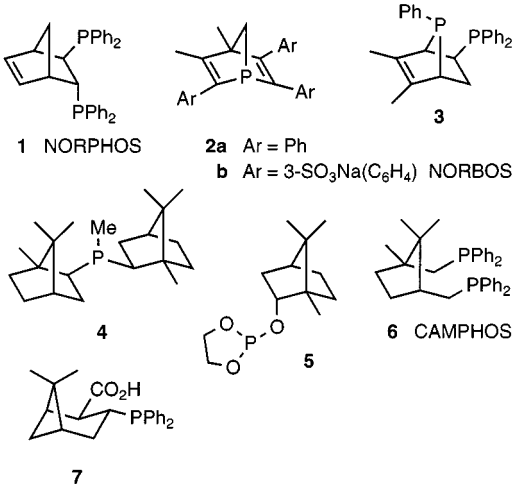
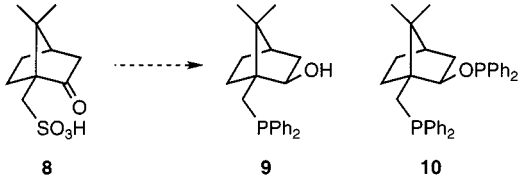
The bidentate hydroxy phosphane **20** and the phosphane phosphinite **21**, each bearing a camphane skeleton, were prepared in five and six steps (52% and 28% yield), respectively, from (1*S*)-(+)-camphorsulfonic acid **8** via the triethylsilyl-protected iodide **17** as a key intermediate. An X-ray crystal structure was obtained for **21**.

Introduction

Since the first use of a chiral phosphane ligand for asymmetric catalysis in 1968,[1] several hundred different phosphanes have been synthesized.[2] This is because a few phosphanes, in particular bidentate ones such as BINAP,[3] DIOP,[4] and ferrocenyl phosphanes,[2d,2e,5] are of general use and give high enantioselectivities in different reaction types. Mono- and diphosphanes derived from norbornane or norbornene such as NORPHOS **(1)**, have been widely used for catalytic reactions (Scheme 1).[2a,6] In addition, phosphanorbornadienes **2**[7] and phosphanorbornenes **3**[8] are easily available by [4 + 2] cycloaddition of 2*H*-phospholes to alkynes or alkenes. Compounds **2a** display significant activities in hydrogenation and hydroformylation.[7] Water-soluble derivatives of **2** such as NORBOS **(2b)** have proved to be superior ligands in biphasic hydroformylation.[9,10] Surprisingly, the corresponding camphane skeleton has only rarely been used for the synthesis of chiral phosphane ligands. Among the few examples are the ligands **4**,[11] **5**[12] and **6**.[13] Recently, a chiral phosphane **7** derived from pinene was employed for Pd-catalyzed allylic substitutions.[14] We were thus interested in developing a route towards the chiral, bidentate hydroxyphosphane **9** and phosphane phosphinite **10**, starting from commercially available (1*S*)-(+)-camphorsulfonic acid **(8)** (Scheme 2). It was anticipated that both ligands **9**, **10** should allow favorable formation of six- and seven-membered chelate rings with metal ions.[15,16] The results concerning the synthesis and structural properties of **9** and **10** are reported below.



Scheme 1



Scheme 2

Results and Discussion

Following a procedure by Lipp et al.[17] and Proth,[18] camphorsulfonic acid **8** was treated with aqueous KOH to give the potassium salt **11** in 96% yield, which was subsequently converted into the sulfobromide **12** by reaction with PBr_5 (Scheme 3). Although compound **12** could be obtained in 93% yield, its preparation turned out to be highly capricious and the yields were not reproducible. Thermal extrusion of sulfur dioxide was achieved upon heating **12** in xylene for 5 h to give bromide **13** in 80% yield. Due to the difficulties in the synthesis of **12** we sought an alternative route. Fortunately, the corresponding camphor iodide **14** was available in one step in 85% by direct nucleophilic dis-

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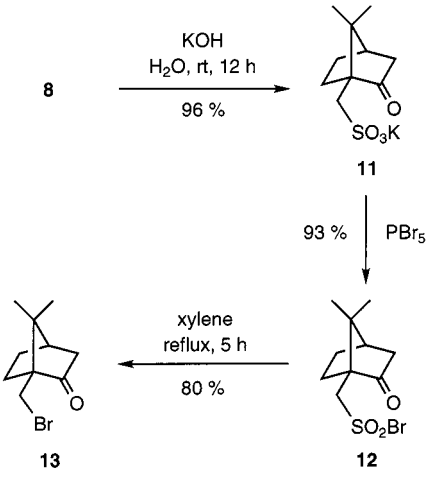
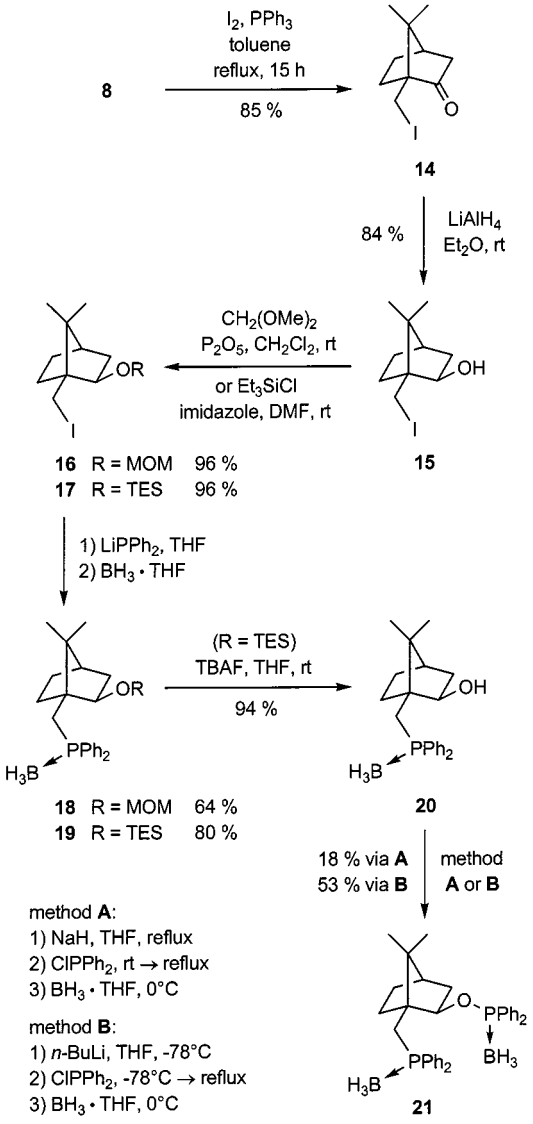


Scheme 3

placement of the sulfonic acid moiety with iodine in the presence of PPh_3 (Scheme 4).[19] Reduction of the carbonyl group in **14** with $LiAlH_4$ proceeded exclusively from the *endo*-face to give 84% of the iodo alcohol **15**. All attempts to achieve direct coupling of the alcohol moiety with chlorodiphenylphosphane after deprotonation with various bases (DMAP, triethylamine, sodium hydride) failed. Therefore we decided to introduce a protecting group prior to conversion of the iodide to the diphenylphosphane moiety. This strategy would allow access to both hydroxy phosphane **9** and phosphane phosphinite **10**. Introduction of the MOM group with formaldehyde dimethylacetal and P_2O_5 proceeded uneventfully in high yield. The MOM ether **16** was then treated with lithiumdiphenylphosphane, and subsequent trapping with BH_3·THF gave the phosphane borane adduct **18** in 64% yield. However, upon attempted deprotection of **18** with BBr_3·SMe_2 an inseparable mixture of the desired hydroxyphosphane **20** and another compound was obtained. The latter compound is presumably formed via Wagner−Meerwein rearrangement of an intermediate secondary cation/carbenium ion.[20] As a consequence we switched to silyl protecting groups. Whereas *tert*-butyldimethylsilyl chloride (TBSCl) was sterically too bulky, the corresponding triethylsilyl chloride (TESCl) reacted smoothly with **15** to give the triethylsilyl-protected iodide **17** in 96% yield. After subsequent iodide-phosphane exchange, the phosphane borane adduct **19** was obtained in high yield (80%). Compound **19** underwent clean desilylation with TBAF to give hydroxyphosphane **20** in excellent yield. Introduction of the second phosphane moiety was achieved by deprotonation in THF, treatment with chlorodiphenylphosphane and subsequent trapping with BH_3·THF. When NaH was used for the deprotonation (method A), compound **21** was obtained in only 18% yield. However, by using *n*BuLi (method B), the yield could be increased to 53%.

The relative configuration of the isoborneol skeleton of **20**, **21** was unambiguously established from 1D and 2D ^1H and ^{13}C NMR spectroscopic data. In the IR spectra, compound **20** displays a strong $P-C_{Phenyl}$ stretching frequency at 1434 cm^{-1} and the corresponding IR spectrum of **21**



Scheme 4

contains two signals at 1483 and 1437 cm^{-1}, respectively, indicating P−C bonds of different strengths. The ^{31}P NMR spectrum of compound **20** displays a doublet ($^1J_{P,B}$ = 70.6 Hz) at δ = 10.4 due to the $^{31}P/^{11}B$ coupling. The corresponding ^{31}P NMR spectrum of **21** contains a doublet ($^1J_{P,B}$ = 69.6 Hz) at δ = 102.6 indicating the presence of the phosphinite P-1. The signal for phosphane P-2 appears as a broad singlet at δ = 12.6 without any noticeable coupling. In the ^{13}C NMR spectra the signal for C-2 is shifted upfield from δ = 76.0 to 85.2 when comparing **20** with **21**. The signal for C-10 displays only a small downfield shift from δ = 24.1 (d, $^1J_{P,C}$ = 33.1 Hz) to δ = 22.8 (d, $^1J_{P,C}$ = 34.6 Hz).

Fortunately, we were able to determine an X-ray crystal structure of **21**. As shown in Figure 1, the phosphorus atoms are almost tetrahedrally surrounded by the four substituents. The observed P−B and P−C distances are in good agreement with other phosphane borane adducts.[21] The P−O distance of **21** is 161.3(2) pm, which is typical for phosphinites.[22]

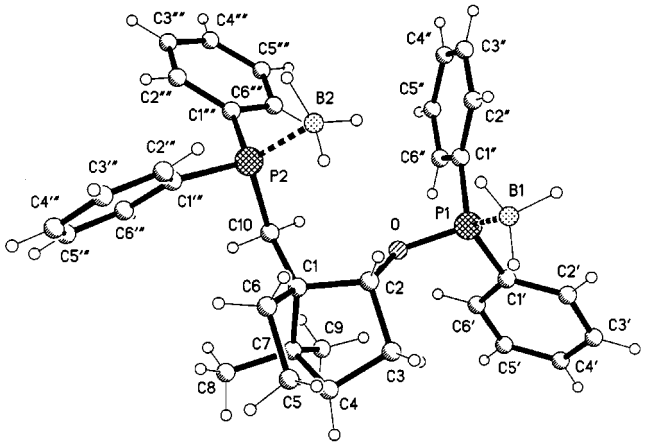


Figure 1. X-ray crystal structure of phosphane phosphinite **21** (see ref.[25]); ellipsoids correspond to 50% probability; selected bond lengths [Å] and angles [°]: P(1)−O 1.613(2), P(1)−C(1′′) 1.809(3), P(1)−C(1′) 1.826(3), P(1)−B(1) 1.909(4), P(2)−C(1′′′) 1.818(3), P(2)−C(1′′′′) 1.822(3), P(2)−C(10) 1.841(3), P(2)−B(2) 1.929(3), O−C(2) 1.464(3); O−P(1)−C(1′′) 101.08(12), O−P(1)−C(1′) 103.47(13), C(1′′)−P(1)−C(1′) 107.29(14), O−P(1)−B(1) 116.36(14), C(1′′)−P(1)−B(1) 114.52(15), C(1′)−P(1)−B(1) 112.82(17), C(1′′′)−P(2)−C(1′′′′) 107.23(13), C(1′′′)−P(2)−C(10) 103.81(13), C(1′′′′)−P(2)−C(10) 102.28(12), C(1′′′)−P(2)−B(2) 114.63(15), C(1′′′′)−P(2)−B(2) 110.65(14), C(10)−P(2)−B(2) 117.09(14), C(2)−O−P(1) 120.46(16), C(1)−C(10)−P(2) 117.32(18), C(6′)−C(1′)−P(1) 121.1(3), C(2′)−C(1′)−P(1) 119.4(3), C(6′′)−C(1′′)−P(1) 122.9(2), C(2′′)C(1′′)−P(1) 118.9(2), C(6′′′)−C(1′′′)−P(2) 121.7(2), C(2′′′)−C(1′′′)−P(2) 118.8(2), C(2′′′′)−C(1′′′′)−P(2) 122.1(2), C(6′′′′)−C(1′′′′)−P(2) 119.1(2)

Conclusions

As shown above, the novel chiral hydroxyphosphane **20** and the corresponding phosphane phosphinite **21** are readily available in five and six steps, respectively, from (1*S*)-camphorsulfonic acid **(8)**. Preliminary complexation studies of phosphane phosphinite **21** with the symmetrical cobalt alkyne complex (tolane)$Co_2(CO)_6$ indicated the formation of two different cobalt complexes, presumably a *chelated* and a *bridged* complex.[23−27] However detailed spectroscopic data are required to confirm these assignments and to further elucidate the synthetic utility of such chiral cobalt alkyne complexes. Work towards this goal is currently being pursued in our laboratory.

Experimental Section

General: All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. Analytical TLC was performed on precoated Macherey−Nagel SIL G/UV_{254} plates (0.25 mm thickness) and the products were visualized by UV detection, phosphomolybdic acid (5 wt-% in EtOH) or Vaughn′s reagent.[28] Flash chromatography[29] was carried out with Merck silica gel 60 (230−400 mesh). − NMR spectra: Bruker AM 400 and Bruker DRX 400 (^{1}H: 400 MHz, ^{13}C: 50 MHz, ^{31}P: 162 MHz), Bruker DPX 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz). Multiplets in ^{13}C NMR spectra were assigned with the aid of DEPT experiments. − Optical rotations (1-dm cells, 1-mL capacity, room temp.): Perkin−Elmer Model 241 polarimeter. − Melting points: Rheometric Scientific DSC SP, heating and cooling rate: 10 K min^{-1}. − IR: Nicolet 320 FT-IR spectrometer. − MS: Finnigan Model MAT 8430 (EI). − GC-MS: Carlo Erba HRGC 5160 coupled with a Finnigan MAT 4515 (EI, 40 eV).

(1*S*)-Camphor-10-sulfonic Acid Bromide (12): To a solution of (1*S*)-camphor-10-sulfonic acid **8** (20.0 g, 86.1 mmol) in H_2O (20 mL) was added KOH (5.13 g, 91.4 mmol) and the resulting mixture was stirred for 12 h at room temp. After evaporation of the solvent in vacuo, the colorless solid residue was dried for several days in a vacuum desiccator over P_2O_5. The crude product **11** (22.4 g, 82.8 mmol, 96%) was used without further purification.
To a cooled suspension of **11** (11.5 g, 42.5 mmol) in Et_2O (120 mL) was added portionwise PBr_5 (24.0 g, 55.7 mmol) at 0 °C with vigorous stirring. The cooling bath was removed and the mixture was stirred for 2 h at room temp. and then refluxed for 2 h. After cooling to room temp. the mixture was carefully poured onto a mixture of ice (200 g) and H_2O (200 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 × 200 mL). The combined organic layers were washed with H_2O (3 × 50 mL), dried over Na_2SO_4 and evaporated to give a yellow solid (11.7 g, 93%), which was used without further purification.

(1*S*)-10-Bromocamphor (13): A solution of (1*S*)-camphor-10-sulfonic acid bromide **12** (1.00 g, 3.39 mmol) in xylene (30 mL) was refluxed for 5 h. Then the mixture was concentrated to a final volume of 3 mL and purified by flash chromatography on SiO_2 (hexane/ethyl acetate 20:1) to yield 631 mg (80%) of a colorless solid; m.p. 78 °C; $[\alpha]_D^{23}$ = +25.7 (*c* = 1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1746 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 3 H, 9-H), 1.11 (s, 3 H, 8-H), 1.41 (ddd, *J* = 12.3/9.3/3.4 Hz, 1 H, 5-H_{ax}), 1.64−1.51 (m, 1 H, 6-H), 1.91 (d, *J* = 18.2 Hz, 1 H, 3-H_{ax}), 2.08−1.97 (m, 1 H, 5-H_{eq}), 2.17−2.09 (m, 2 H, 4-H, 6-H), 2.41 (ddd, *J* = 18.2/4.9/2.9 Hz, 1 H, 3-H_{eq}), 3.41 (d, ^2J = 10.8 Hz, 1 H, 10-H_b), 3.62 (d, ^2J = 10.8 Hz, 1 H, 10-H_a). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (C-9), 20.4 (C-8), 26.7 (C-5), 27.6 (C-6), 29.3 (C-10), 42.9 (C-3), 43.9 (C-4), 48.2 (C-7), 60.2 (C-1), 215.4 (C-2). − MS (EI): *m*/*z* (%) = 232 (8) [M$^+$], 230 (8), 151 (100), 133 (7), 123 (37), 109 (77), 107 (22), 95 (27), 93 (30), 91 (26), 81 (92), 79 (32), 77 (19), 69 (16), 67 (45), 55 (18), 53 (21). − $C_{10}H_{15}BrO$ (231.1): calcd. C 51.97, H 6.54; found C 52.04, H 6.48.

(1*S*)-10-Iodocamphor (14): To a solution of **8** (9.30 g, 40.0 mmol) and triphenylphosphane (52.5 g, 0.20 mol) in toluene (400 mL) was added iodine (30.5 g, 120 mmol) and the mixture was refluxed for 15 h. After cooling to room temp. the mixture was washed with H_2O (2 × 200 mL), dried over $MgSO_4$ and evaporated. Purification by flash chromatography on SiO_2 (hexane/ethyl acetate 7:1) yielded 9.42 g (85%) of a colorless solid; m.p. 71 °C; $[\alpha]_D^{23}$ = −20.4 (*c* = 1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1743 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (s, 3 H, 9-H), 1.08 (s, 3 H, 8-H), 1.46−1.33 (m, 1 H, 5-H_{ax}), 1.67−1.55 (m, 1 H, 6-H), 1.91 (d, *J* = 18.2 Hz, 1 H, 3-H_{ax}), 2.06−1.95 (m, 2 H, 5-H_{eq}, 6-H), 2.16 (dd, *J* = 4.9/2.5 Hz, 1 H, 4-H), 2.40 (ddd, *J* = 18.2/4.9/2.0 Hz, 1 H, 3-H_{eq}), 3.12 (d, *J* = 10.3 Hz, 1 H, 10-H_b), 3.31 (d, *J* = 10.3 Hz, 1 H, 10-H_a). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0 (C-10), 19.4 (C-9), 19.6 (C-8), 26.0 (C-5), 29.8 (C-6), 42.2 (C-3), 43.3 (C-4), 47.6 (C-7), 58.3 (C-1), 214.3 (C-2). − MS (EI): *m*/*z* (%) = 278 (9) [M$^+$], 151 (100) [M$^+$ − I], 141 (2), 133 (5), 127 (7), 123 (23) [M$^+$ − I − CO], 109 (56), 107 (10), 93 (17), 81 (70), 79 (19), 77 (13), 69 (11), 67 (38), 55 (16), 53 (15). − HRMS ($C_{10}H_{15}IO$): calcd. 278.0167; found 278.0132. − $C_{10}H_{15}IO$ (278.1): calcd. C 43.18, H 5.44; found C 43.43, H 5.54.

(1*S*,2*R*)-10-Iodo-isoborneol (15): To a cooled suspension of $LiAlH_4$ (647 mg, 17.0 mmol) in Et_2O (20 mL) was added dropwise at 0 °C a solution of 10-iodocamphor **(14)** (6.78 g, 24.4 mmol) in Et_2O (60 mL). The resulting mixture was stirred for 2 h at 0 °C and for another 2 h at room temp. and then hydrolyzed by slow addition of ice-cold H_2O (50 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 70 mL) and CH_2Cl_2 (3

× 50 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4 and evaporated. The crude product was purified by flash chromatography on SiO_2 (hexane/ethyl acetate 7:1) to yield 5.70 g (84%) of a colorless solid; m.p. 30 °C; $[\alpha]_D^{23}$ = −31.9 (*c* = 1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3425 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (s, 3 H, 9-H), 1.06 (m, 4 H, 8-H, 5-H_{ax}), 1.26 (ddd, *J* = 13.2/9.4/4.1 Hz, 1 H, 6-H), 1.54 (ddd, *J* = 13.2/12.9/4.4 Hz, 1 H, 6-H), 1.77−1.66 (m, 2 H, 3-H_{ax}, 5-H_{eq}), 1.83 (ddd, *J* = 13.2/7.6/4.4 Hz, 1 H, 3-H_{eq}), 2.02 (dd, *J* = 4.4/4.4 Hz, 1 H, 4-H), 2.12 (d, *J* = 4.0 Hz, 1 H, OH), 3.18 (d, *J* = 9.4 Hz, 1 H, 10-H_b), 3.45 (d, *J* = 9.4 Hz, 1 H, 10-H_a), 3.78 (ddd, *J* = 7.6/4.0/4.0 Hz, 1 H, 2-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2 (C-10), 20.1 (C-9), 20.8 (C-8), 26.4 (C-5), 33.0 (C-6), 39.2 (C-3), 46.9 (C-4), 47.5 (C-7), 52.5 (C-1), 78.1 (C-2). − MS (EI): *m*/*z* (%) = 280 (1) [M^+], 262 (5), 153 (14), 135 (100), 127 (16), 119 (7), 111 (60), 109 (33), 107 (61), 105 (11), 97 (23), 93 (73), 91 (42), 81 (31), 79 (50), 75 (29), 69 (29), 67 (47), 57 (15), 55 (39). − $C_{10}H_{17}IO$ (280.1): calcd. C 42.87, H 6.12; found C 42.74, H 6.25.

(1*S*,2*R*)-10-Iodo-2-methoxymethyloxybornane (16): To a solution of iodo-isoborneol **(15)** (2.54 g, 9.07 mmol) in CH_2Cl_2 (40 mL) were added formaldehyde dimethylacetal (18 mL, 0.20 mol) and P_2O_5 (8.50 g, 0.06 mol). The mixture was stirred for 1 h at room temp. and then poured into an ice-cooled sat. Na_2CO_3 solution. The solid residue was dissolved in sat. Na_2CO_3 solution. The combined aqueous layers were extracted with Et_2O (3 × 40 mL) and the combined ethereal layers were dried over $MgSO_4$ and evaporated in vacuo. Purification of the crude product by flash chromatography on SiO_2 yielded 2.82 g (96%) of a colorless oil; $[\alpha]_D^{23}$ = −27.8 (*c* = 1, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 1454 cm^{-1}, 1389, 1301, 1152, 1115, 1099, 1073, 1045, 918. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (s, 3 H, 9-H), 1.12−1.00 (m, 4 H, 8-H, 5-H_{ax}), 1.32 (ddd, *J* = 15.4/8.9/3.4 Hz, 1 H, 6-H), 1.78−1.54 (m, 3 H, 3-H_{ax}, 5-H_{eq}, 6-H), 1.91−1.83 (m, 1 H, 3H_{eq}), 2.05 (dd, *J* = 4.3 Hz, 1 H, 4-H), 3.16 (d, ^2J = 9.0 Hz, 1 H, 10-H_b), 3.42 (s, 3 H, CH_2OCH_3), 3.47 (d, *J* = 9.0 Hz, 1 H, 10-H_a), 3.57 (dd, *J* = 3.4/3.4 Hz, 1 H, 2-H), 4.67 (d, *J* = 6.8 Hz, 1 H, CH_2OCH_3), 4.73 (d, *J* = 6.8 Hz, 1 H, CH_2OCH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.9 (C-10), 20.5 (C-9), 20.6 (C-8), 26.5 (C-5), 34.5 (C-6), 38.8 (C-3), 47.4 (C-4), 47.7 (C-7), 52.9 (C-1), 56.1 (C-2′), 83.3 (C-2), 97.2 (C-1′). − MS (EI): *m*/*z* (%) = 324 (0.2) [M^+], 263 (13), 207 (3), 197 (11), 167 (12), 165 (21), 151 (6), 147 (9), 135 (18), 121 (16), 107 (19), 93 (31), 81 (20), 79 (21), 67 (16), 55 (12), 45 (100). − $C_{12}H_{21}IO_2$ (324.2): calcd. C 44.46, H 6.53; found C 44.48, H 6.68.

(1*S*,2*R*)-10-Iodo-2-triethylsilyloxybornane (17): To a cooled solution of 10-iodo-isoborneol **(15)** (2.00 g, 7.14 mmol) and imidazole (580 mg, 8.52 mmol) in DMF (10 mL) was added dropwise triethylchlorosilane (1.18 g, 7.83 mmol) at 0 °C and stirring was continued for 15 min. Then the mixture was stirred for 14 h at room temp. and hydrolyzed by addition of ice-cold H_2O (7 mL). After addition of CH_2Cl_2 (10 mL) the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by flash chromatography on SiO_2 (hexanes/ethyl acetate 10:1) to give 2.71 g (96%) of a colorless oil; $[\alpha]_D^{23}$ = −56.4 (*c* = 1, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 1456 cm^{-1}, 1415, 1369, 1193, 1119, 1088, 1005, 907, 741 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.52 (q, *J* = 8.1 Hz, 2 H, $SiCH_2CH_3$), 0.64 (q, *J* = 8.1 Hz, 4 H, $SiCH_2CH_3$), 0.86 (s, 3 H, 9-H), 0.93 (t, *J* = 8.1 Hz, 3 H, $SiCH_2CH_3$), 0.98 (t, *J* = 8.1 Hz, 6 H, $SiCH_2CH_3$), 1.01−0.95 (m, 1 H, 5-H_{ax}), 1.04 (s, 3 H, 8-H), 1.22 (ddd, *J* = 12.6/8.8/3.5 Hz, 1 H, 6-H_{ax}), 1.51 (m, 3 H, 3-H_{ax}, 5-H_{eq}, 6-H_{eq}), 1.80−1.73 (m, 1 H, 3-H_{eq}), 2.01 (dd, *J* = 4.3/4.3 Hz, 1 H, 4-H), 3.14 (d, *J* = 8.8 Hz, 1 H, 10-H_b), 3.49 (d, *J* = 8.8 Hz, 1 H, 10-H_a), 3.74 (dd, *J* = 7.6/3.3 Hz, 1 H, 2-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.2 ($SiCH_2CH_3$), 6.4 ($SiCH_2CH_3$), 6.8 ($SiCH_2CH_3$), 7.1 ($SiCH_2CH_3$), 10.6 (C-10), 20.3 (C-8), 21.0 (C-9), 26.6 (C-5), 34.1 (C-6), 41.5 (C-3), 47.4 (C-4), 47.5 (C-7), 52.7 (C-1), 77.2 (C-2). − MS (EI): *m*/*z* (%) = 365 (369) [M^+ − Et], 267 (33), 217 (8), 213 (3), 189 (6), 185 (3), 161 (2), 135 (100), 133 (4), 115 (15), 107 (30), 103 (8), 93 (22), 87 (19), 79 (12), 75 (11). − $C_{16}H_{31}IOSi$ (394.4): calcd. C 48.73, H 7.92; found C 48.53, H 8.22.

(1*S*,2*R*)-10-(Boranatodiphenylphosphanyl)-2-(methoxymethyloxy)bornane (18): To a cooled solution of diphenylphosphane (861 mg, 4.62 mmol) in THF (4 mL) was added dropwise *n*BuLi (3.50 mL, 5.60 mmol, 1.6 M solution in *n*-hexane) at 0 °C and the solution was kept for 30 min at 0 °C, 30 min at room temp. and finally refluxed for 1 h. The resulting deep red solution of lithium diphenylphosphide was cooled to 0 °C and then added in one portion to a cooled solution of 10-iodo-2-methoxymethyloxybornane **(16)** (1.00 g, 3.08 mmol) in THF (4 mL). After the addition was finished the mixture was stirred for 1 h at room temp., cooled again to 0 °C and BH_3·THF (5.50 mL, 5.50 mmol, 1 M solution in THF) was added in small portions. After stirring for 30 min at 0 °C, the mixture was quenched with 1 N HCl (5 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and the crude product was purified by flash chromatography on SiO_2 (hexane/CH_2Cl_2 1:1); m.p. 146 °C; $[\alpha]_D^{23}$ = +0.78 (*c* = 16, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2406 cm^{-1}, 2386, 1482, 1435. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.79 (s, 3 H, 9-H), 0.95 (ddd, *J* = 13.6/9.1/4.5 Hz, 1 H, 5-H_{ax}), 1.06 (s, 3 H, 8-H), 1.12 (dd, *J* = 13.1/4.5 Hz, 1 H, 6-H_{ax}), 1.22 (ddd, *J* = 13.1/9.1/4.0 Hz, 1 H, 6-H_{eq}), 1.30−0.65 (br, BH_3), 1.51−1.43 (m, 1 H, 5-H_{eq}), 1.63 (dd, *J* = 7.6/4.0 Hz, 1 H, 4-H), 1.69 (dd, *J* = 13.9/7.6 Hz, 1 H, 3-H_{ax}), 1.87 (ddd, *J* = 13.9/7.6/3.5 Hz, 1 H, 3-H_{eq}), 2.22 (dd, *J* = 15.2/15.2 Hz, 1 H, 10-H_b), 2.79 (dd, *J* = 15.2/10.1 Hz, 1 H, 10-H_a), 3.35 (s, 3 H, CH_2OCH_3), 3.75 (dd, *J* = 7.6/3.5 Hz, 1 H, 2-H), 4.53 (d, *J* = 6.8 Hz, 1 H, CH_2OCH_3), 4.65 (d, *J* = 6.8 Hz, 1 H, CH_2OCH_3), 7.53−7.35 (m, 6 H, *m*-H, *p*-H), 7.67−7.57 (m, 2 H, *o*-H), 7.86−7.79 (m, 2 H, *o*-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (C-9), 20.3 (C-8), 23.0 (d, J_{PC} = 33.4 Hz, C-10), 27.3 (C-5), 29.9 (C-6), 40.1 (C-3), 44.1 (C-4), 49.3 (d, J_{PC} = 10.7 Hz, C-1), 51.2 (C-7), 56.0 (CH_2OCH_3), 84.1 (C-2), 98.4 (CH_2OCH_3), 128.5 (d, J_{PC} = 9.7 Hz, C-*m*), 128.7 (d, J_{PC} = 9.7 Hz, C-*m*), 130.5 (d, J_{PC} = 2.3 Hz, C-*p*), 130.6 (C-*i*), 131.1 (d, J_{PC} = 2.2 Hz, C-*p*), 131.7 (d, J_{PC} = 8.8 Hz, C-*o*), 132.1 (C-*i*), 132.7 (d, J_{PC} = 9.0 Hz, C-*o*). − ^{31}P NMR (162 MHz, $CDCl_3$): δ = 12.76 (d, J_{PB} = 57.5 Hz). − MS (EI): *m*/*z* (%) = 396 (0.2) [M^+], 395 (2), 382 (23), 367 (6), 349 (15), 337 (6), 322 (83), 307 (3), 279 (6), 253 (3), 200 (8), 186 (100), 165 (6), 152 (4), 121 (6), 108 (18), 91 (6), 45 (19). − $C_{24}H_{34}BO_2P$ (396.3): calcd. C 72.74, H 8.65, B 2.73; found C 72.71.53, H 8.79, B 2.42.

(1*S*,2*R*)-10-(Boranatodiphenylphosphanyl)-2-(trimethylsilyloxy)-bornane (19): To a cooled solution of lithium diphenylphosphide, which was prepared from diphenylphosphane (950 mg, 5.10 mmol) and *n*BuLi (3.60 mL, 5.76 mmol) in THF (6 mL) as described for **18**, 2-triethylsilyl-10-iodobornane **(17)** (1.68 g, 4.26 mmol) was added dropwise at 0 °C. After stirring the mixture for 30 min at 0 °C, 30 min at room temp. and then refluxing for 1 h, the mixture was cooled to 0 °C and BH_3·THF (5.80 mL, 5.80 mmol, 1 M solution in THF) was added dropwise and stirring was continued for 1 h. The reaction was quenched by careful addition of H_2O (6 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification of the crude prod-

uct by flash chromatography on SiO_2 (hexane/ethyl acetate 20:1) yielded 1.58 g (80%) of a colorless solid; m.p. 76 °C; $[\alpha]_D^{23} = -53.7$ (c = 1, $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 2388, 2347 cm^{-1}, 1436. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.70 (q, J = 7.9 Hz, 6 H, $SiCH_2CH_3$), 0.75 (s, 3 H, 9-H), 0.89 (ddd, J = 12.4/9.6/4.3 Hz, 1 H, 5-H_{ax}), 0.97 (t, J = 7.9 Hz, 9 H, $SiCH_2CH_3$), 1.02 (s, 3 H, 8-H), 1.06 (dd, J = 13.4/4.3 Hz, 1 H, 6-H_{ax}), 1.17 (ddd, J = 13.4/9.6/4.3 Hz, 1 H, 6-H_{eq}), 1.80–0.5 (br, BH_3), 1.48–1.37 (m, 1 H, 5-H_{eq}), 1.61 (dd, J = 7.6/4.1 Hz, 1 H, 4-H), 1.66 (dd, J = 12.6/7.6 Hz, 1 H, 3-H_{ax}), 1.76 (ddd, J = 12.6/7.6/3.5 Hz, 1 H, 3-H_{eq}), 2.21 (dd, J = 15.4/15.4 Hz, 1 H, 10-H_b), 2.83 (dd, J = 15.4/8.9 Hz, 1 H, 10-H_a), 4.09 (dd, J = 7.6/3.5 Hz, 1 H, 2-H), 7.53–7.31 (m, 6 H, *m*-H, *p*-H), 7.62–7.54 (m, 2 H, *o*-H), 7.89–7.82 (m, 2 H, *o*-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.5 ($SiCH_2CH_3$), 7.2 ($SiCH_2CH_3$), 20.0 (C-8), 20.7 (C-9), 22.1 (d, J_{PC} = 33.8 Hz, C-10), 27.4 (C-5), 28.6 (d, J_{PC} = 5.0 Hz, C-6), 41.9 (C-3), 44.2 (C-4), 49.1 (d, J_{PC} = 10.0 Hz, C-1), 51.2 (C-7), 76.9 (C-2), 128.4 (d, J_{PC} = 9.6 Hz, C-*m*), 128.6 (d, J_{PC} = 9.7 Hz, C-*m*), 130.3 (d, J_{PC} = 2.3 Hz, C-*p*), 130.7 (d, J_{PC} = 53.6 Hz, C-*i*), 131.0 (d, J_{PC} = 2.4 Hz, C-*p*), 131.4 (d, J_{PC} = 8.7 Hz, C-*o*), 132.8 (d, J_{PC} = 9.1 Hz, C-*o*), 133.1 (d, J_{PC} = 56.0 Hz, C-*i*). – ^{31}P NMR (162 MHz, $CDCl_3$): δ = 12.72 (d, J_{PB} = 53.1 Hz). – MS (EI): *m*/*z* (%) = 466 (1) [M^+], 452 (33), 437 (18), 365 (3), 349 (5), 331 (4), 321 (33), 305 (3), 281 (5), 267 (19), 239 (21), 220 (24), 217 (19), 205 (100), 198 (9), 186 (32), 161 (3), 154 (5), 135 (11), 115 (9), 108 (16), 87 (13), 75 (8), 59 (8). – $C_{28}H_{44}BOPSi$ (466.5): calcd. C 72.09, H 9.51, B 2.31; found C 72.34, H 9.70, B 1.98.

(1*S*,2*R*)-10-(Boranatodiphenylphosphanyl)isoborneol (20): To a solution of bornane derivative **19** (2.00 g, 4.29 mmol) in THF (4 mL) was added TBAF (11.0 mL, 11.0 mmol, 1 M solution in THF) and the mixture was stirred for 1.5 h at room temp. Then, H_2O (6 mL) and CH_2Cl_2 (10 mL) were added, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and the crude product was purified by flash chromatography on SiO_2 (hexane/CH_2Cl_2 1:1) to give 1.42 g (94%) of a colorless solid; m.p. 149 °C; $[\alpha]_D^{23} = -91.6$ (c = 1, $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 3549 cm^{-1}, 2398, 2388, 1434. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.59 (ddd, J = 14.9/11.1/5.8 Hz, 1 H, 5-H_{ax}), 0.78 (s, 3 H, 9-H), 0.94–0.80 (m, 2 H, 6-H_{ax}, 6-H_{eq}), 1.08 (s, 3 H, 8-H), 1.50–1.37 (m, 1 H, 5-H_{eq}), 1.60–0.75 (br, 3 H, BH_3), 1.63 (dd, J = 7.8/4.0 Hz, 1 H, 4-H), 1.68 (dd, J = 13.1/8.3 Hz, 1 H, 3-H_{ax}), 1.78 (ddd, J = 13.1/7.8/4.0 Hz, 1 H, 3-H_{eq}), 2.33 (dd, J = 17.4/14.4 Hz, 1 H, 10-H_b), 2.58 (dd, J = 14.4/7.3 Hz, 1 H, 10-H_a), 3.10 (br, 1 H, OH), 4.14 (dd,J = 8.3/4.0 Hz, 1 H, 2-H), 7.56–7.37 (m, 6 H, *m*-H, *p*-H), 7.64–7.57 (m, 2 H, *o*-H), 7.89–7.81 (m, 2 H, *o*-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.8 (C-9), 20.4 (C-8), 24.1 (d, J_{PC} = 33.1 Hz, C-10), 27.3 (C-5), 30.2 (d, J_{PC} = 2.0 Hz, C-6), 39.3 (C-3), 43.7 (C-4), 48.9 (d, J_{PC} = 11.7 Hz, C-1), 51.1 (d, J_{PC} = 1.5 Hz, C-7), 76.0 (C-2), 128.7 (C-*m*), 128.7 (d, J_{PC} = 54.2 Hz, C-*i*), 128.8 (C-*m*), 130.7 (d, J_{PC} = 2.4 Hz, C-*p*), 131.1 (d, J_{PC} = 8.7 Hz, C-*o*), 131.6 (d, J_{PC} = 2.4 Hz, C-*p*), 132.0 (d, J_{PC} = 58.2 Hz, C-*i*), 133.2 (d, J_{PC} = 9.4 Hz, C-*o*). – ^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.4 (d, J_{PB} = 70.6 Hz). – MS (EI): *m*/*z* (%) = 352 (1) [M^+], 349 (34), 338 (63), 321 (12), 310 (2), 279 (3), 269 (3), 251 (2), 198 (10), 186 (100), 165 (9), 152 (5), 135 (3), 133 (3), 121 (5), 108 (33), 91 (8), 79 (7), 77 (7), 67 (5). – $C_{22}H_{30}BOP$ (352.3): calcd. C 75.01, H 8.58, B 3.07; found C 74.98, H 8.66, B 2.60.

(1*S*,2*R*)-10-(Boranatodiphenylphosphanyl)-2-(boranatodiphenylphosphanyloxy)bornane (21). – Method B: To a cooled solution of 10-(boranatodiphenylphosphanyl)isoborneol (**20**) (100 mg, 0.28 mmol) in THF (4 mL) was added dropwise *n*BuLi (0.19 mL, 0.30 mmol, 1.6 M solution in hexane) at −78 °C and the mixture was stirred for 1 h at this temperature. Then chlorodiphenylphosphane (75 mg, 0.34 mmol) was added and stirring was continued for 2 h at −78 °C, 7 h at room temp. and finally the mixture was refluxed for 2 h. After cooling the mixture to 0 °C, BH_3·THF (0.60 mL, 0.60 mmol, 1 M solution in THF) was added dropwise and stirring was continued for 1 h at 0 °C. The mixture was hydrolyzed by careful addition of H_2O (10 mL) and CH_2Cl_2 (4 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to a final volume of 1 mL. The oily residue was further purified by chromatography on SiO_2 (hexanes/Et_2O 5:1) to give 81 mg (53%) of a colorless solid.
Method A: To a suspension of NaH (52 mg, 1.30 mmol, 60 wt% suspension in mineral oil, previously washed with 2 × 2 mL pentane) was added a solution of **20** (352 mg, 1.00 mmol) in THF (8 mL) and the suspension was refluxed for 2 h. After cooling to room temp. chlorodiphenylphosphane (290 mg, 1.31 mmol) was added in small portions. The mixture was stirred for 1 h at room temp., refluxed for 7 h and cooled again to 0 °C. Then BH_3·THF (2.00 mL, 2.00 mmol, 1 M solution in THF) was added dropwise and stirring was continued for 1 h at 0 °C. The mixture was quenched with H_2O (6 mL) and warmed to room temp. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, concentrated in vacuo to a final volume of 1 mL and purified by chromatography as described in method A to give 100 mg (18%) of a colorless solid; m.p. 183 °C (dec.); $[\alpha]_D^{23} = -52.3$ (c = 1, $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 2493 cm^{-1}, 2382, 1483, 1437. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.83 (m, 5 H, 9-H, 5-H_{ax}, 6-H), 1.06 (s, 3 H, 8-H), 1.53–1.44 (m, 1 H, 5-H_{eq}), 1.70–0.75 (br, 6 H, BH_3), 1.70–1.57 (m, 3 H, 3-H_{ax}, 4-H, 6-H), 1.88 (ddd, J = 13.9/7.6/3.3 Hz, 1 H, 3-H_{eq}), 2.26 (dd, J = 15.4/12.6 Hz, 1 H, 10-H_b), 2.79 (dd, J = 15.4/12.6 Hz, 1 H, 10-H_a), 4.49 (ddd, J = 7.6/7.6/3.3 Hz, 1 H, 2-H), 7.82–7.29 (m, 20 H, aryl-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9 (C-8), 20.1 (C-9), 22.8 (d, J_{PC} = 34.6 Hz, C-10), 27.0 (C-5), 28.9 (d, J_{PC} = 6.2 Hz, C-6), 40.3 (C-3), 44.2 (C-4), 49.3 (d, J_{PC} = 6.6 Hz, C-1), 51.4 (d, J_{PC} = 7.2 Hz, C-7), 85.2 (C-2), 128.4 (d, J_{PC} = 5.7 Hz, C-*o*), 128.5 (d, J_{PC} = 5.7 Hz, C-*o*), 128.6 (d, J_{PC} = 9.7 Hz, C-*m*), 128.7 (d, J_{PC} = 9.8 Hz, C-*m*), 130.7 (d, J_{PC} = 54.4 Hz, C-*i*), 130.8 (d, J_{PC} = 2.4 Hz, C-*p*), 130.9 (d, J_{PC} = 2.3 Hz, C-*p*), 131.4 (d, J_{PC} = 11.3 Hz, C-*m*), 131.7–131.1 (m, 4C, C-*m*, C-*p*, C-*i*), 132.1 (d, $^2J_{PC}$ = 4.3 Hz, C-*o*), 132.2 (d, $^2J_{PC}$ = 4.5 Hz, C-*o*), 132.4 (d, $^1J_{PC}$ = 66.2 Hz, C-*i*), 133.6 (d, J_{PC} = 63.9 Hz, C-*i*). – ^{31}P NMR (162 MHz, $CDCl_3$): δ = 12.6 (s, 2-P), 102.6 (d, J_{PB} = 69.6 Hz, 1-P). – MS (EI): *m*/*z* (%) = 550 (0.2) [M^+], 545 (3), 535 (100), 458 (2), 446 (5), 400 (1), 387 (2), 349 (6), 337 (7), 332 (8), 320 (15), 311 (4), 291 (4), 279 (5), 245 (2), 215 (6), 201 (13), 185 (41), 183 (44), 165 (4), 152 (5), 121 (4), 108 (13), 91 (6), 77 (5). – $C_{34}H_{42}B_2OP_2$ (550.3): calcd. C 74.21, H 7.69, B 3.93; found C 73.61, H 7.70, B 3.15.

X-ray structure analysis of **22**: $C_{34}H_{42}B_2OP_2$, M_r = 550.24, crystal size 0.45 × 0.44 × 0.05 mm, monoclinic, space group $P2_1$, a = 12.6281(18) Å, b = 9.4094(13) Å, c = 14.035(2) Å, β = 111.008(3)°, V = 1556.8(4) $Å^3$, $\rho_{calcd.}$ = 1.174 Mg m^{-3}, T = 143(2) K, Z = 2, λ = 0.71073 Å. Bruker SMART 1000 CCD diffractometer, 21945 reflections collected, 1.55 ≤ θ ≤ 28.28°, 7643 independent reflections, 378 refined parameters, $R1$ = 0.0604, $wR2$ = 0.1597. Program used: SHELXL-97. See ref.[30]

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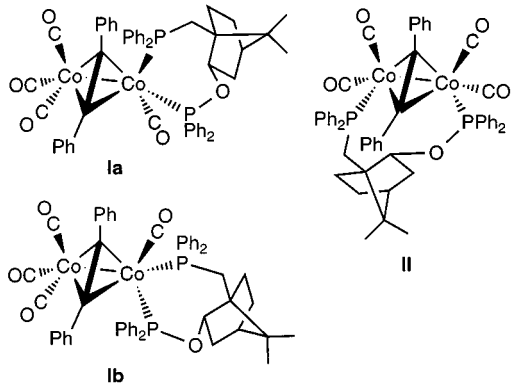
[23] Treatment of ligand **21** with 2 equiv. of DABCO in toluene at 60 °C for 6 h, followed by addition of 1 equiv. of (tolane)-$Co_2(CO)_6$ and heating the mixture at 60 °C for 6 h yielded, after flash chromatography (hexane/ethyl acetate 25:1), 20% of complex **I** and 21% of complex **II** (see formula scheme below). Unfortunately, the ^1H and ^{13}C NMR spectra of **II** were only poorly resolved because of extreme line broadening, and thus were not useful for spectroscopic identification. The ^{31}P NMR spectra of compounds **I**, **II** differed remarkably. Whereas complex **I** gave two broad singlets at δ = 39.2 and 32.4, the spectrum of **II** displayed two broad singlets at δ = 156.3 and 20.2. It is known from McGlinchey[24] that ^{31}P NMR chemical shifts are not reliable for identification of different environments in chiral phosphane-substituted acetylene-dicobalt complexes and therefore the distinct IR spectra of **I**, **II** were used for a tentative structural assignment. The IR spectrum of **I** displayed two very strong carbonyl absorptions at 2055 and 2006 cm^{-1}, a shoulder at 1994 cm^{-1} and a strong signal at 1956 cm^{-1}. The IR spectrum of **II** contained a signal of medium intensity at 2038 cm^{-1}, a strong absorption at 2018 cm^{-1} and two very strong signals at 1990 and 1965 cm^{-1}. An additional weak absorption at 2055 cm^{-1} was probably due to impurities caused by **I** and the shoulder at 1944 cm^{-1} can be assigned as a ^{13}C satellite. Based on symmetry arguments both the *apical-basal chelated* geometry (**Ia**) and the *basal-chelated* geometry (**Ib**) should produce three CO absorptions (A_1, E) resulting from the local C_{3v} symmetry of the $Co(CO)_3$ moiety plus one CO signal from the remaining cobalt center. This latter signal should occur at lower energy due to the increased Co−CO backbonding as compared to $Co(CO)_3$. In contrast, a *basal-bridged* geometry (**II**) possesses a distorted local C_{2v} symmetry resulting in four CO signals (A_1, A_2, E). These assignments are in good agreements with the results obtained by McGlinchey (ref.[24]), Cullen (ref.[25]), Moyano (ref.[26]), and Haley (ref.[27]) for other cobalt alkyne phosphane complexes.



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[30] Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145075. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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