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New chiral monodentate phospholane ligands by highly stereoselective hydrophosphination

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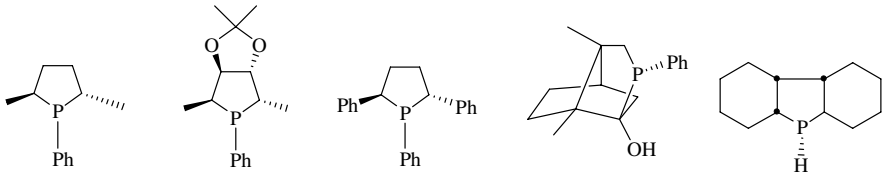
Abstract—New chiral phospholanes **6** were prepared in both enantiomeric forms starting from L- and D-tartaric acid. The key step in the synthetic sequence is the double hydrophosphination of unsaturated chiral bis(lactone) **9** by $NaPhPH(BH_3)$. This method was used for the first time in the formation of chiral phospholanes. The structure of phospholane **6a** was confirmed by X-ray crystallography. σ-Donor properties of the phospholanes were estimated by measurement of $^1J(^{31}P–^{77}Se)$ coupling constants in the corresponding phosphine selenides. The new phospholanes were tested as ligands in the Rh-catalyzed enantioselective hydrogenation of functionalized standard olefins (65–92% ee).

1. Introduction

Catalytic enantioselective hydrogenation is of great importance both for science and industry, as it opens up simple venues to a variety of optically active chemical compounds.[1] In particular, Rh-, Ru-, and Ir-complexes bearing chiral trivalent phosphorus compounds as ancillary ligands play a dominant role. One of the most developed approaches employs heterocyclic phosphines, in particular phospholanes.[2] Prominent examples are commercially available bis(phospholanes) such as DuPHOS,[3] RoPHOS,[4] and ligands of the cat*AS*ium M series.[5] Monophosphines are in general more easily available than the corresponding bidentate phosphines and therefore, also chiral monodentate phospholanes, such as **1**,[6] **2**,[4c,7] **3**,[8] **4**,[9] and **5**,[10] have also been prepared. Some of them form active and enantioselective Rh hydrogenation catalysts.[11,12]



1 **2** **3** **4** **5**

This prompted us to search for a new chiral phospholane motif, involving the development of a simple approach to both enantiomers of the ligands. Therefore, we decided to use inexpensive tartaric acid derivatives available in both enantiomeric forms as starting materials. A literature search revealed that the presence of bulky substituents at 1-, 2-, and 5-position of the phospholane ring seems to be desirable in order to achieve enhanced enantioselectivity in the hydrogenation reaction. Following these criteria, the enantiomeric phospholanes **6a** and **6b** were prepared.

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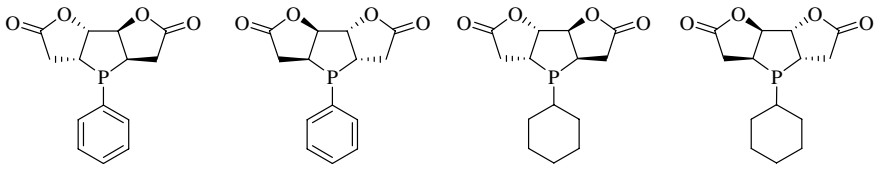


(*all-R*)-6a (*all-S*)-6a (*all-R*)-6b (*all-S*)-6b

2. Results and discussion

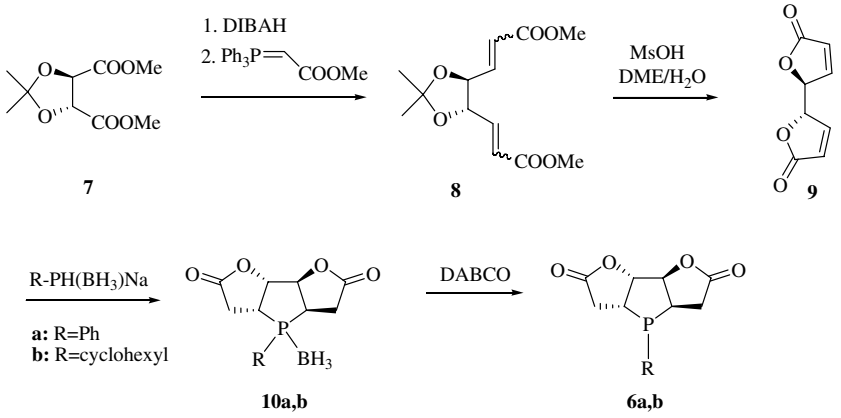
2.1. Synthesis

Our synthesis of **6a** and **6b** commenced from dimethyl 2,3-*O*-isopropylidenetartrate **7**, commercially available in both enantiomeric forms (Scheme 1, only the syntheses of all-*R* enantiomers are shown; the opposite enantiomers were prepared following the same methodology). The key transformation is the double hydrophosphination reaction between phenylphosphine–borane adduct and bis(lactone) **9**. The latter was prepared according to a protocol by Le Corre et al.[13] Diester **8** representing the direct precursor of **9** was obtained following a known procedure.[14] The published procedure for the formation of **9** implies the isolation of the *Z*,*Z*-isomer of **8**, but we found that the use of the diastereomeric mixture of **8** for the lactonization also led to pure bis(lactone) **9** in 26% overall yield from **7**.

The hydrophosphination of α,β-unsaturated carboxylic acid derivatives or chalcones by borane complexes of secondary phosphines is known.[15] It has been used by Le Corre et al. for the synthesis of a related bis(diphenylphosphine) substituted chelating ligand.[13] However, the analogous reaction of monophosphine–borane complexes is less studied.[16] In this case, hydrophosphination is mostly accompanied by hydroboration and decomposition of the rather unstable phosphine–boranes.[16b,c] Therefore, this step required extensive testing in order to identify the optimal conditions. The use of NaH for the generation of the phosphide anion, with THF as solvent, while carrying out the reaction at 0 °C gave highest yields of the phospholane–borane complexes **10a** and **10b**. These compounds were then purified by column chromatography. It is noteworthy that only a single diastereomer was isolated, with no trace of the other diastereomer (possessing a *trans*-fused five-membered ring) being observed. Obviously, the formation of *trans*-fused five-membered rings is energetically less favored. The geometry of the compounds was confirmed by H,H-COSY and NOESY experiments with compound **10a** (Fig. 1), and inspection of the X-ray crystal structure analyses of **6a** and **10b** (Fig. 2). Compounds **10a** and **10b** are stable solids, which can be stored on air for a long time. Free phospholanes **6a** and **6b** were generated by the reaction of phosphine–boranes **10a** and **10b** with 1,4-diazabicyclo[2,2,2]octane (DABCO).

It was of interest to estimate the σ-donor properties of the novel phospholanes.[17] For this purpose, measurement of the $^{31}P–^{77}Se$ NMR coupling constants in corresponding phosphine selenides was suggested.[18] The selenides were prepared in the NMR tube by treating phospholanes **6a** and **6b** with an excess of elemental selenium in $CDCl_3$ at room temperature. In general, the higher the magnitude of the coupling constant, the lower the basicity of the phosphine. The magnitude of $^{1}J(^{31}P–^{77}Se)$ is dependent upon the nature of the organic groups bound to phosphorus. Electron-withdrawing groups increase the coupling constant, whereas electron-donating groups decrease it. The presence of bulky substituents at the phosphorus atom likewise results in a decrease in the *s*-character of the electron lone pair as a result of the widening of the relevant bond angles.[18]

For the selenides obtained from **6a** and **6b**, larger $^{1}J(^{31}P–^{77}Se)$ were observed than for the selenides prepared from phospholanes **1** and **2** (Table 1).[19] It can be concluded that an increase in the number of fused rings at the phospholane core causes a decrease in the σ-donor properties of the phosphine. However, this might also vary due to



Scheme 1. Synthesis of lactone-fused phospholane–borane adducts and free phospholanes **6a** and **6b**.

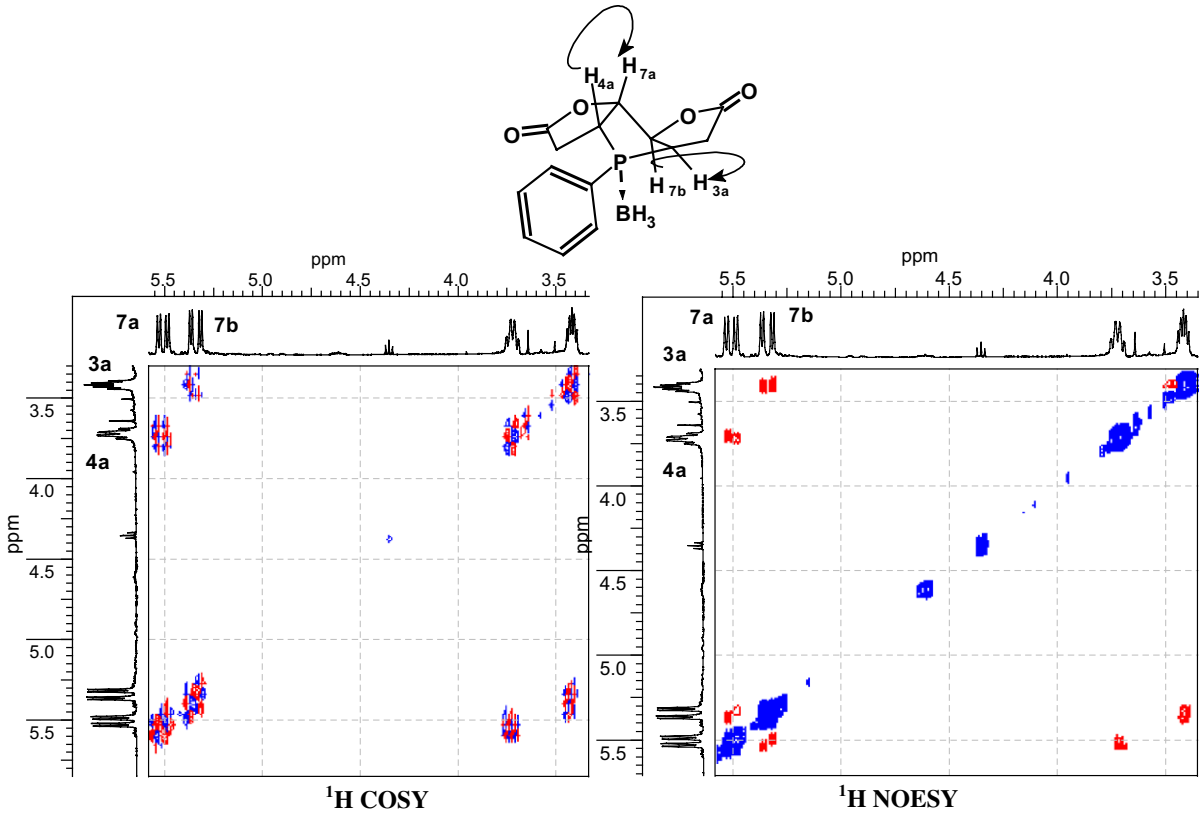


Figure 1. 2D NMR spectra of compound **10a** (measured in $CDCl_3$). Correlations between signals of 4a-H and 7a-H, 3a-H and 7b-H confirm the transoid arrangement of the five-membered rings.

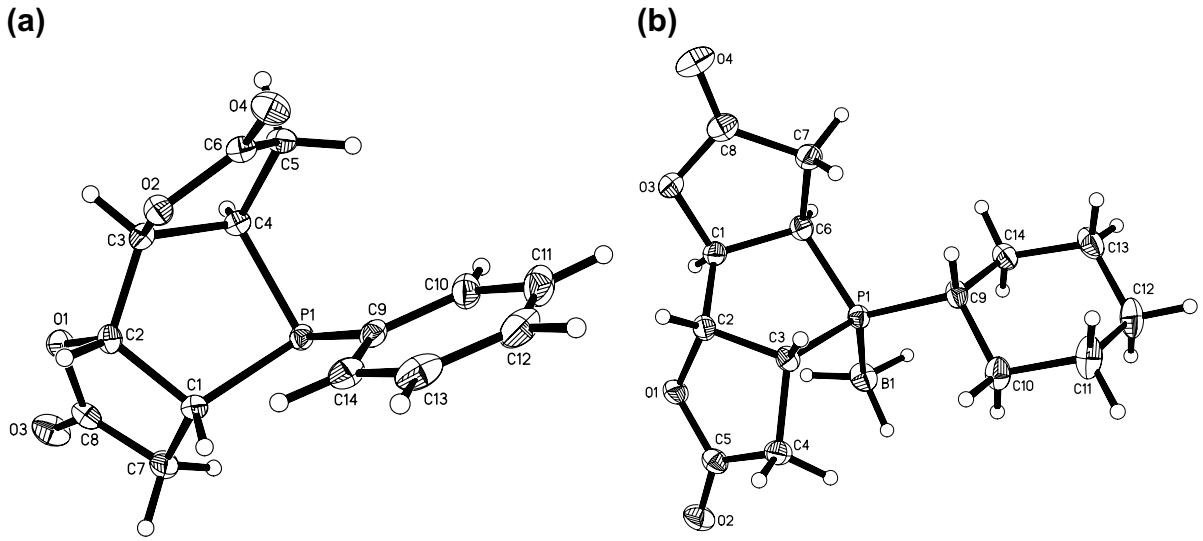


Figure 2. Molecular structures of **6a** (a) and **10b** (b), from X-ray crystallography with only one of the two molecules in the asymmetric unit being depicted. The thermal ellipsoids correspond to 30% probability.

the nature of the substituent at the phosphorus atom (compare Ph and Cy in ligands **6a** and **6b**). The obtained data correlate well with the behavior of **10a** and **10b** during the deprotection with DABCO. Under the same conditions **10a** reacted within 30 min, whereas **10b** required 3 h for complete deboronation. This provides clear evidence that **6b** has a higher basicity than **6a**.

2.2. Asymmetric hydrogenation

Phospholanes **6a** and **6b** were tested as monodentate ligands in the Rh-catalyzed asymmetric hydrogenation of functionalized standard olefins. The required precatalysts were prepared in situ from the corresponding ligands and $[Rh(COD)_2]BF_4$ (2:1 molar ratio). The hydrogenations

Table 1. ^{31}P–^{77}Se coupling constants (Hz) for phospholane selenides

Phospholane	$^{1}J(^{31}P–^{77}Se)$ (Hz)
1	720 (Ref. 19)
2	749 (Ref. 19)
6a	783
6b	760

were carried out at 1 bar of hydrogen pressure at 25 °C. Some typical results are summarized in Table 2.

It can be seen from the data in Table 2 that the phospholane ligands **6a** and **6b** form active and quite selective hydrogenation catalysts. In general, the enantioselectivity of the hydrogenation is comparable with those previously reported with Rh catalysts derived from ligands **1**,[6] **3**,[8] and **5**.[10] It is noteworthy that high enantioselectivity can be found with benzyl *Z*-β-acetylamidobutenoate as the substrate in CF_3CH_2OH as a solvent.

3. Experimental

3.1. General

All reagents unless otherwise mentioned were purchased from commercial sources and used without additional purification. The solvents were dried and freshly distilled under argon before use. All reactions involving phosphines were performed under an argon atmosphere by using standard Schlenk techniques. Thin-layer chromatography was performed on precoated TLC plates (silica gel). Melting points are corrected. The optical rotations were measured on a 'Gyromat-HP' instrument. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at the following frequencies: 250.13 MHz (^{1}H), 75.48 MHz (^{13}C), 121.49 MHz (^{31}P). 2D NMR experiments were recorded at 400.13 MHz. Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in parts per million downfield from TMS as an internal standard. Chemical shifts of ^{31}P NMR spectra are referred to H_3PO_4 as an external standard. Elemental analyses were performed with a LECO CHNS-932. Mass spectra were recorded on an AMD 402 spectrometer. Below, the syntheses of only one enantiomer from each enantiomeric pair are given.

For the synthesis of **8** we followed the method described by Krief et al.,[14] except that the product was used in the next step without further purification.

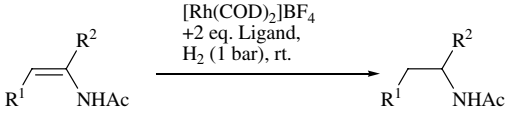
3.2. (5*S*)-5-[(2*S*)-5-Oxo-2,5-dihydro-2-furanyl]-2,5-dihydro-2-furanone 9

The crude mixture of **8** (26 g), obtained by the reported method of Krief et al.,[14] was refluxed in DME (160 ml) with H_2O (16 ml) and methanesulfonic acid (0.15 ml). The mixture was evaporated to half and kept in a refrigerator. Then it was filtered and the precipitate was washed with hexane and ethanol to give 4.7 g of **9** (26% yield based on dimethyl 3,4-*O*-isopropylidenetartrate). Mp = 184 °C, Ref. 14. 183–184 °C. $[\alpha]_D^{25} = -1.8$ (*c* 1, ethyl acetate), Ref. 14. $[\alpha]_D^{25} = -1.8$ (*c* 1, ethyl acetate).

3.3. BH_3 complex of (3a*R*,4a*R*,7a*R*,7b*R*)-4-phenylperhydrofuro[2′,3′:4,5]phospholo[3,2-*b*]furan-2,6-dione 10a

To a solution of phenylphosphine–BH_3 complex (1.5 g, 12 mmol) in THF (80 ml) was added NaH (580 mg, 60% in oil, 14.5 mmol) at 0 °C. The mixture was stirred for 20 min at 0 °C and 3 h at room temperature. Then the solution was added to a solution of **9** (2 g, 12 mmol) in THF (800 ml) at 0 °C. After 15 min the cooling bath was removed and the mixture stirred for 1.5 h at room temperature, then HOAc (1.3 ml) was added. The solution was evaporated under vacuum and the product purified by chromatography to give 0.5 g (15% yield) of compound **10a**. Anal. Calcd for $C_{14}H_{16}BO_4P$: C, 57.97; H, 5.56. Found: C, 56.24; H, 5.42. $[\alpha]_D^{25} = +74.2$ (*c* 3.0, $CHCl_3$). MS: $m/z = 290$ (M^+, $C_{14}H_{16}BO_4P$), 276 (M^+ of free phosphine), 235, 192, 164, 149, 133, 108, 91, 57. ^{1}H NMR ($CDCl_3$) δ: 0.80 (br, 3H, BH_3), 2.04 (dd, 1H), 2.88 (ddd, 1H), 3.05 (ddd, 1H), 3.24 (ddd, 1H), 3.42 (m, 1H), 3.72 (m, 1H), 5.34 (dd, 1H, $^{3}J_{H,P} = 19.1$ Hz, $^{3}J_{H,H} = 5.7$ Hz),

Table 2. Rh-catalyzed enantioselective hydrogenation of selected olefins using phospholanes **6a**,**b** as ligands



Ligand	R^1	R^2	Molar ratio Rh/substrate	Solvent	Time[a] (min)	ee (%)
(all-*S*)-**6a**	Ph	COOMe	1:50	MeOH	230	76[b] (*S*)
(all-*S*)-**6b**	Ph	COOMe	1:50	THF	55	65[b] (*S*)
(all-*S*)-**6a**	H	COOMe	1:100	MeOH	35	68[c] (*S*)
(all-*S*)-**6a**	H	COOMe	1:50	CF_3CH_2OH	17	81[c] (*S*)
(all-*S*)-**6b**	H	COOMe	1:50	THF	6	78[c] (*S*)
(all-*S*)-**6b**	COOMe	Me	1:50	CF_3CH_2OH	200	82[d] (*S*)
(all-*S*)-**6b**	COOBn	Me	1:50	CF_3CH_2OH	180	92[e] (*S*)

[a] Determined after full conversion. Analysis of reaction products.
[b] Determined by GC, 25 m Chirasil-Val, Alltech, 110 °C.
[c] Determined by GC, 4 m, XE 60 L-Valin-(*tert*.-butylamide), 85 °C.
[d] Determined by GC, 50 m, Chiraldex β-PH.
[e] Determined by HPLC, Chiralcel OJ, Daicel, *n*-hexane–ethanol/95:5, 1.4 ml/min.

5.51 (dd, 1H, $^3J_{H,P} = 17.4$ Hz, $^3J_{H,H} = 6.5$ Hz), 7.57 (m, 2H), 7.67 (m, 3H). ^{13}C NMR ($CDCl_3$) δ: 31.1 (d, $J = 6.5$ Hz, CH_2), 31.6 (d, $J = 2.9$ Hz, CH_2), 37.3 (d, $J = 32.3$ Hz, CH), 39.8 (d, $J = 29.3$ Hz, CH), 85.9 (d, $J = 1.7$ Hz, CH), 86.5 (CH), 123.1 (d, $J = 45.8$ Hz, CP), 130.3 (d, $J = 10.5$ Hz, CH), 133.4 (d, $J = 9.5$ Hz, CH), 133.9 (d, $J = 2.9$ Hz, CH), 173.6 (C=O), 173.7 (C=O). ^{31}P NMR ($CDCl_3$) δ: 55.7.

3.4. (3a*R*,4a*R*,7a*R*,7b*R*)-4-Phenylperhydrofuro-[2′,3′:4,5]phospholo[3,2-*b*]furan-2,6-dione 6a

To a solution of **10a** (0.5 g, 1.74 mmol) in THF (20 ml) was added DABCO (0.2 g, 1.78 mmol) and the mixture stirred at 55 °C for 30 min. The solvent was evaporated and the phosphine purified on silica gel ($CHCl_3$/MeOH, 20/1) to give 0.38 g (78% yield) of phospholane **6a**. Analytical sample and crystals suitable for X-ray analysis were obtained by crystallization from benzene. Mp = 164 °C. ^{1}H NMR (C_6D_6) δ: 1.42–1.54 (m, 1H), 1.66–1.82 (m, 1H), 2.13–2.4 (m, 3H), 2.57–2.67 (m, 1H), 4.46 (t, $J = 6.9$ Hz, 1H), 4.77 (t, $J = 6.6$ Hz, 1H), 7.02–7.08 (m, 5H). ^{13}C NMR (C_6D_6) δ: 31.0 (CH_2), 34.1 (d, $J = 34.6$ Hz), 37.2 (d, $J = 24$ Hz, CH), 38.4 (d, $J = 13.2$ Hz, CH), 88.4 (d, $J = 3.3$ Hz, CH), 90.1 (d, $J = 4.4$ Hz, CH), 128.9 (d, $J = 7.2$ Hz, CH), 130.4, 131.3 (d, $J = 23.2$ Hz, CP), 134.4 (d, $J = 21.4$ Hz, C=H), 173.3 (C=O), 173.5 (d, $J = 4$ Hz, C=O). ^{31}P NMR(C_6D_6) δ: 20.8. For the corresponding selenide ^{31}P NMR ($CDCl_3$) δ: 69.4.

3.5. BH_3 complex of (3a*S*,4a*S*,7a*S*,7b*S*)-4-cyclohexylperhydrofuro[2′,3′:4,5]phospholo[3,2-*b*]furan-2,6-dione 10b

Compound **10b** was obtained analogously to **10a** in 11% yield, but after chromatographic purification the product was stirred in $CHCl_3$–cyclohexane (1:1) mixture until crystallization started. Mp = 101–102 °C. $[\alpha]_D^{21} = -33.5$ (*c* 5, acetone) ^{1}H NMR (acetone-d_6) δ: −0.32 to 1.14 (br q, $J = 95$ Hz, 3H, BH_3), 1.25–1.62 (m, 5H), 1.7–1.9 (m, 5H), 2.14–2.36 (m, 1H), 2.67–3.17 (m, 4H), 3.4–3.55 (m, 1H), 3.65–3.81 (m, 1H), 5.14–5.35 (m, 2H). ^{13}C NMR (acetone-d_6) δ: 26.8 (d, $J = 15$ Hz, CH_2), 27.1 (d, $J = 5$ Hz, CH_2), 28.1 (s, CH_2), 29.8 (d, $J = 5.6$ Hz, CH_2), 31.3 (d, $J = 3.4$ Hz, CH_2), 33.3 (d, $J = 28.2$ Hz, CH), 34.3 (d, $J = 32.2$ Hz, CH), 37.8 (d, $J = 33.9$ Hz, CH), 88.1 (d, $J = 6.8$ Hz, CH), 88.6 (d, $J = 2.8$ Hz), 173.6 (d, $J = 2.3$ Hz, C=O), 173.7 (d, $J = 5.8$ Hz, C=O). ^{31}P NMR (acetone-d_6) δ: 56.7 (br).

3.6. (3a*S*,4a*S*,7a*S*,7b*S*)-4-Cyclohexylperhydrofuro-[2′,3′:4,5]phospholo[3,2-*b*]furan-2,6-dione 6b

To a solution of **10b** (0.2 g, 0.69 mmol) in THF (10 ml) was added DABCO (81 mg, 0.72 mmol) and the mixture stirred at 55 °C for 3 h. The solvent was evaporated and the phosphine purified on silica gel ($CHCl_3$/MeOH, 20/1) to give 0.14 mg (75% yield) of phospholane **6b**. Mp = 157 °C. MS: $m/z = 282$ (M^+, $C_{14}H_{19}O_4P$), 227, 201, 159, 135, 128, 116, 108, 107, 83, 82, 81, 79, 67, 57, 55, 41. ^{1}H NMR (C_6D_6) δ: 0.88–1.12 (m, 6H), 1.4–1.59 (m, 4H), 1.75–2.38 (m, 7H), 4.3–4.39 (m, 1H), 4.49–4.57 (m, 1H). ^{13}C NMR (C_6D_6) δ: 26.5 (d, $J = 12.4$ Hz, CH_2), 26.8 (d, $J = 9.6$ Hz, CH_2), 29.5 (d, $J = 12.9$ Hz, CH_2), 31.9 (d, $J = 19.8$ Hz, CH_2), 34.3 (d, $J = 18.1$ Hz, CH), 35.0 (d, $J = 31$ Hz, CH_2), 35.7 (d, $J = 24.3$ Hz, CH), 37.4 (d, $J = 14.7$ Hz, CH), 88.3 (s, CH), 88.9 (s, CH), 174.0 (d, $J = 1.7$ Hz, C=O), 174.7 (s, C=O). ^{31}P NMR (C_6D_6) δ: 13.2 (s). For the corresponding selenide ^{31}P NMR ($CDCl_3$) δ: 73.1.

3.7. X-ray crystallographic study of compounds 6a and 10b

Data were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved by direct methods (SHELXS-97) [G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97). [G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997] XP (BRUKER AXS) was used for graphical representation.

Compound **6a**: space group $P2_12_12_1$, orthorhombic, $a = 11.014(2)$, $b = 11.543(2)$, $c = 19.755(4)$ Å, $V = 2511.7(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.461$ g cm^{-3}, 38,627 reflections measured, 5775 were independent of symmetry and 5360 were observed ($I > 2\sigma(I)$), $R1 = 0.024$, wR^2 (all data) = 0.057, 375 parameters.

Compound **10b**: space group $P2_12_12_1$, orthorhombic, $a = 6.943(1)$, $b = 15.812(3)$, $c = 31.454(6)$ Å, $V = 3453.3(12)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.323$ g cm^{-3}, 43,526 reflections measured, 6072 were independent of symmetry and 5096 were observed ($I > 2\sigma(I)$), $R1 = 0.036$, wR^2 (all data) = 0.086, 431 parameters.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 607514 (**6a**) and 607515 (**10b**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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