# Phosphinofenchol or Metastable Phosphorane? Phosphorus Derivatives of Fenchol

**Bernd Goldfuss,* Thomas Löschmann, and Frank Rominger[a][+]**

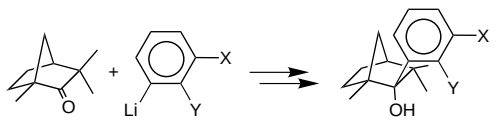
*Dedicated to Prof. Dr. Manfred Regitz on the occasion of his 65th birthday*

**Abstract:** Not the expected phosphinofenchol **1** but phosphorane **2** is obtained after reaction of 2-lithio(diphenylphosphino)benzene with (−)-fenchone. Surprisingly, ONIOM(B3LYP/6-31G*:UFF) computations of **1** and **2** as well as B3LYP analyses of smaller model systems point to a *lower* thermodynamic stability of phosphoranes relative to their isomeric alkoxyphosphines. An analogue inherent instability is computed for the methylphosphorane **10**, which is also synthesized and characterized by X-ray analysis. Decreasing ring size in cyclic phosphoranes, that is, from five- to four-membered ring systems, destabilizes cyclic phosphoranes even more. This computational prediction is verified experimentally by reaction of lithiomethyl(diphenylphosphine) with (−)-fenchone and subsequent isolation of the corresponding phosphinofenchol. Protonation or alkylation of phosphoranide intermediates can account for the formation of metastable phosphoranes.

**Keywords:** chirality · density functional calculations · phosphorus · P ligands · thermochemistry

## Introduction

Enantiopure organophosphorus compounds[1] are precious components for the synthesis of chiral ligands and for the design of enantioselective catalysts.[2] Additions of donor-functionalized organolithiums to fenchone provide efficient one-step routes to chelating fenchylalcohols (Y = e.g. DMG,[3] Scheme 1), which are useful, chiral bicyclo[2.2.1]heptane

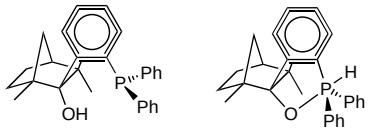



Scheme 1. Synthesis of modular fenchol ligands, Y = e.g. OMe, $CH_2NMe_2$; X = e.g. H, $SiR_3$.

scaffolds.[4] These modular, fenchone-based ligands (e.g. Y = OMe, $CH_2NMe_2$, X = H, $SiMe_3$, Scheme 1) can be used as probes to study origins of enantioselectivities in dialkylzinc additions to benzaldehyde and they are also efficient catalyst precursors in these reactions.[5] Anisylfenchols (Y = OMe, X = H, $SiMe_3$, Scheme 1) are especially versatile ligands, which self-assemble to form modular chiral *n*BuLi traps.[6, 7] Efficient one-step routes to chelating fenchylalcohols prompted analogue syntheses of phosphorus derivatives with chiral bicyclo[2.2.1]heptane skeletons.[8] Like 2-(diphenylphosphino)benzoic acid,[9] enantiopure phosphinofenchols (e.g. Y = $PR_2$, Scheme 1) are promising building blocks for the design of modular chiral ligand systems. Here we present new phosphorus derivatives with fenchane fragments.

## Results and Discussion

The synthesis of the chiral, chelating phosphinofenchol **1** is attempted by addition of 2-lithio(diphenylphosphino)benzene to (−)-fenchone (cf. Scheme 1, Y = $PPh_2$, X = H). However, X-ray crystal analysis reveals phosphorane **2** (Figure 1) as reaction product rather than the expected formation of **1**.




**1** **2**

The X-ray crystal structure of **2** shows that the ligands at the phosphorus center are arranged trigonal-bipyramidal with oxygen and hydrogen atoms in apical positions (Figure 1).[10]

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[+] X-ray analyses



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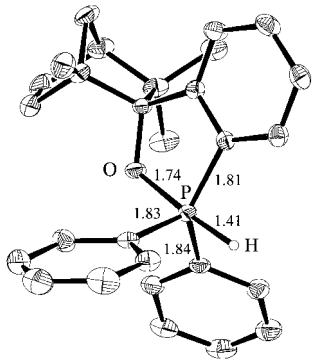
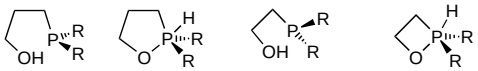



Figure 1. X-ray crystal structure of phosphorane **2**. Hydrogen atoms (except for P–H) are omitted. Bond distances are given in Ångstrom, the probability of the thermal ellipsoides is 30%.

The apical P–H unit in **2** is also apparent from IR ($\tilde{\nu}_{PH}$ = 1969 cm$^{-1}$) and $^{31}$P NMR ($^{1}J_{PH}$ = 267 Hz) spectroscopy.[11] The formation of **2** with the *electron-rich* fencholate unit is surprising, as the *electron-poor* bis(trifluormethyl)benzylalcoholate moiety ("Martin's ligand")[12] is known to be especially suitable to stabilize "hypervalent"[13] phosphoranes.[14, 15] P–N phosphoranes with P–H[16] and P–Fe[17] moieties are also known.



| | | | | |
|---|---|---|---|---|
| R = H | **3-H** | **4-H** | **5-H** | **6-H** |
| R = Ph | **3-Ph** | **4-Ph** | **5-Ph** | **6-Ph** |

Energetic assessments likewise reflect the unusual nature of phosphorane **2**. ONIOM[18](B3LYP/6-31G*:UFF)[19, 20] computations,[21] which consider both steric and electronic effects, show that phosphinofenchol **1** is >19 kcal mol$^{-1}$ more stable than phosphorane **2** (Figure 2, Table 1).[22] The metastable nature of phosphorane **2** is also apparent for the smaller model systems **3-Ph** versus **4-Ph** (Figure 3) and **3-H** versus **4-H** from higher stabilities of the open phosphines relative to cyclic phosphoranes (10.5 and 19.1 kcal mol$^{-1}$, respectively, Table 2).[23]

**Abstract in German:** *Nicht das erwartete Phosphinofenchol **1**, sondern das Phosphoran **2** bildet sich nach Reaktion von 2-Lithio(diphenylphosphino)benzol mit (–)-Fenchon. Sowohl ONIOM(B3LYP/6–31G*:UFF) Berechnungen von **1** und **2** als auch B3LYP Analysen kleinerer Modellsysteme deuten auf die niedrigere thermodynamische Stabilität der Phosphorane relativ zu isomeren Phosphinoalkoholen hin. Eine analoge inhärente Instabilität wird auch für das Methylphosphoran **10** berechnet, das aus **2** synthetisch zugänglich und röntgenstrukturanalytisch charakterisierbar ist. Eine Verringerung der Ringgröße in zyklischen Phosphoranen von fünf- auf viergliedrige Ringsysteme, führt zur weiteren Destabilisierung der zyklischen Phosphorane und zur Bevorzugung der isomeren Phosphinoalkohole. Diese theoretische Vorhersage wird durch Synthese eines Phosphinofenchols durch Reaktion von Lithiomethyl(diphenylphosphin) mit (–)-Fenchon verifiziert. Die Protonierung oder Alkylierung von Phosphoranid-Intermediaten kann die Bildung der metastabilen Phosphorane erklären.*

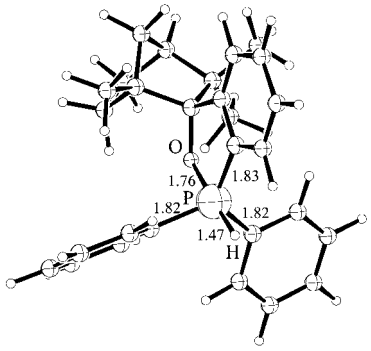



Figure 2. ONIOM (B3LYP/6-31G*:UFF) optimized structure of phosphorane **2**, bond distances are given in Ångstrom.

Table 1. Total [a.u.] and relative [kcal mol$^{-1}$] ONIOM(B3LYP/6-31G*:UFF) energies of phosphines and phosphoranes.[a]

| Extrapol. energies ($E_{ex}$), $E_{Ex}$ + ZPE, and Gibbs free energies | |
|---|---|
| **1** | **2** |
| –688.5478, –687.9979, –688.0485 | –688.5148, –687.9672, –688.0173 |
| 0.0 | 20.7, 19.3, 19.6 |
| **7** | **8** |
| –496.8261, –496.3292, –496.3778 | –496.7583, –496.2641, –496. 3106 |
| 0.0 | 42.5, 40.9, 42.2 |
| **9** | **10** |
| –727.8406, –727.2620, –727.3149 | –727.8121, –727.2347, –727.2850 |
| 0.0 | 17.9, 17.1, 18.8 |

[a] Extrapolated energies ($E_{ex}$), $E_{ex}$ including unscaled zero point energies (ZPE) and Gibbs free energies at 298.15 K and 1 atm with unscaled ZPE. All fully optimized structures were characterized as minima by frequency computations. The ONIOM layer assignment is shown in Scheme 2.

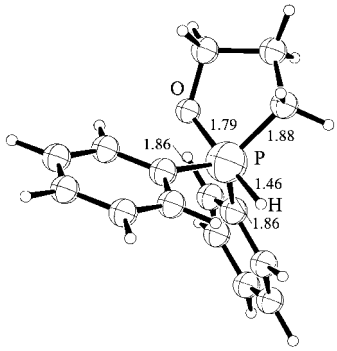



Figure 3. B3LYP/6-31G* optimized structure of phosphorane **4-Ph**, bond distances are given in Ångstrom.

Smaller ring size further increases cyclic phosphorane destabilization: The phosphines **5-Ph** and **5-H** are more stable by 15.1 and 28.5 kcal mol$^{-1}$ relative to phosphoranes **6-Ph** (Figure 4) and **6-H** (Table 2) with four-membered ring structures.[24] Similarly, an increased stabilization of the phosphinofenchol **7** relative to the fencholate-based phosphorane **8** is apparent from ONIOM(B3LYP/6-31G*:UFF) computations (>40 kcal mol$^{-1}$, Table 1).

Experimental verification of these predictions prompts the reaction of lithiomethyl(diphenyl)phosphine with (–)-fenchone. Indeed, phosphinofenchol **7** rather than phosphorane **8**

Table 2. Total [a.u.] and relative [kcal mol$^{-1}$] B3LYP energies of phosphines and phosphoranes.[a]

| B3LYP/6–311+G*[b] | | B3LYP/6–31G*[b] | |
|---|---|---|---|
| **3-H** | **4-H** | **3-Ph** | **4-Ph** |
| –536.2503 | –536.2198 | –998.1137 | –998.0970 |
| 0.0 | 19.1 | 0.0 | 10.5 |
| **5-H** | **6-H** | **5-Ph** | **6-Ph** |
| –496.9575 | –496.9121 | –958.8274 | –958.8033 |
| 0.0 | 28.5 | 0.0 | 15.1 |
| **11-H** | **12-H** | **11-Ph** | **12-Ph** |
| –575.5354 | –575.5250 | –1037.3898 | –1037.3734 |
| 0.0 | 6.5 | 0.0 | 10.3 |

[a] The fully optimized structures were characterized as minima by frequency computations. [b] Unscaled zero point energies (ZPE) are included, ref. [32].

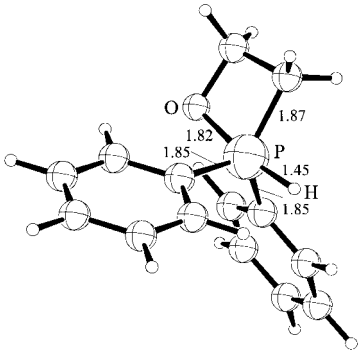
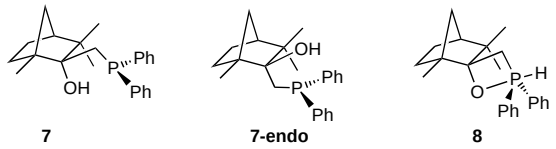



Figure 4. B3LYP/6-31G* optimized structure of phosphorane **6-Ph**, bond distances are given in Ångstrom.

is obtained.[25] Both *exo* (**7**) and *endo* (**7endo**) addition products are formed in a 2:1 ratio.[26, 27] Oxidation of **7** by $H_2O_2$ yields the crystalline phosphinoxides **7-O** (Figure 5) and **7endo-O** (Figure 6), which both form intra-molecular hydrogen bonds.



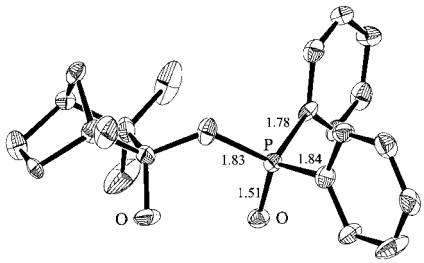




Figure 5. X-ray crystal structure of phosphinoxide **7-O**. Hydrogen atoms are omitted. Bond distances are given in Ångstrom, the probability of the thermal ellipsoides is 30%.

Lithiation of the P–H function in **2** with *n*BuLi and subsequent reaction with methyliodide does not yield the O-methylated phosphine **9** but generates the P-methylated phosphorane **10**.[27, 28] X-ray crystal analysis of **10** reveals a P–Me arrangement in the equatorial and a P–Ph unit in an apical position (Figure 7). The relative energies of **9** versus **10**

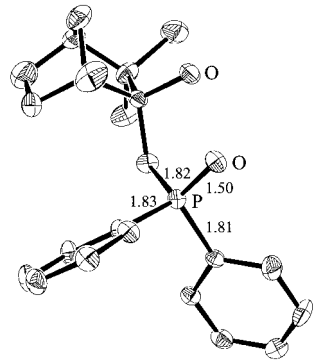



Figure 6. X-ray crystal structure of phosphinoxide **7endo-O**. Hydrogen atoms are omitted. Bond distances are given in Ångstrom, the probability of the thermal ellipsoides is 30%.

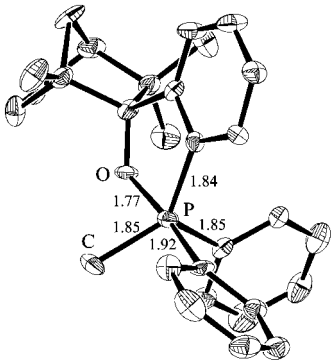
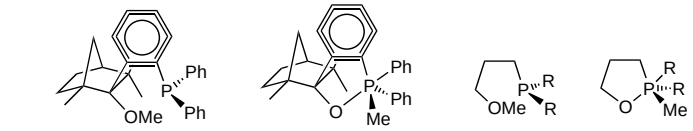



Figure 7. X-ray crystal structure of methylphosphorane **10**. Hydrogen atoms are omitted. Bond distances are given in Ångstrom, the probability of the thermal ellipsoides is 25%.

(>17 kcal mol$^{-1}$, Table 1)[29] and of the smaller model systems **11-Ph** versus **12-Ph** (Figure 8, 10.3 kcal mol$^{-1}$, Table 2) and **11-H** versus **12-H** (6.5 kcal mol$^{-1}$, Table 2) again point to higher thermodynamic stabilities of the open phosphines relative to cyclic phosphoranes.




R = H
R = Ph **9** **10** **11-H** **11-Ph** **12-H** **12-Ph**

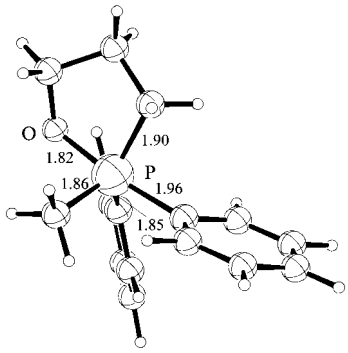



Figure 8. B3LYP/6-31G* optimized structure of methylphosphorane **12-Ph**, bond distances are given in Ångstrom.



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A rationalization for the formation of the metastable phosphoranes is revealed by analyses of the computational model systems in Equations (1) and (2). The formation of phosphorane **15** from methanol **13** and methylphosphine **14** is disfavored by 19.4 kcal mol$^{-1}$ [Eq. (1), Table 3] and again demonstrates the instability of the alkoxyphosphoranes relative to corresponding alkanols and phosphines. In contrast, addition of methanolate (**13a**) to **14** yields phosphoranide **15a**,[30] which is now stable relative to **13a** and **14** ($\Delta E = -9.9$ kcal mol$^{-1}$, Eq. (2), Table 3). This higher stability of **15a** can be rationalized by a better accommodation of negative charge due to polarization.[31]

$$\underset{\mathbf{13}}{H_3COH} + \underset{\mathbf{14}}{H_3CPH_2} \rightleftharpoons \underset{\mathbf{15}}{H_3COPH_3CH_3} \quad +19.4 \text{ kcal mol}^{-1} \qquad (1)$$

$$\underset{\mathbf{13a}}{H_3CO(-)} + \underset{\mathbf{14}}{H_3CPH_2} \rightleftharpoons \underset{\mathbf{15a}}{H_3COPH_2(-)CH_3} \quad -9.9 \text{ kcal mol}^{-1} \qquad (2)$$

Table 3. Total [a.u.] and relative ($\Delta E$, kcal mol$^{-1}$) B3LYP/6-31+G* energies for Equations (1) and (2).[a]

| **13** | **14** | **15** | $\Delta E$ |
|---|---|---|---|
| −115.6739 | −382.4062 | −498.0492 | +19.4 |
| **13a** | **14** | **15a** | $\Delta E$ |
| −115.0764 | −382.4062 | −497.4984 | −9.9 |

[a] The fully optimized structures ($C_1$ symmetry) were characterized as minima by frequency computations, unscaled zero point energies are included, see ref. [32].

Protonation and alkylation at the phosphorous center converts stable phosphoranides to metastable phosphoranes, which are found experimentally as **2** and **10**. The propensity for electrophilic attack at phosphorus is apparent from the large HOMO coefficient at phosphorus in **15a** (Figure 9).

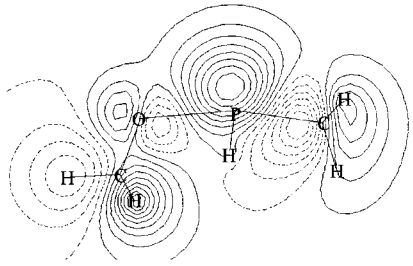



Figure 9. Contour plot of the highest occupied molecular orbital (HOMO) of phosphoranide **15a**.

## Conclusion

Although the open phosphinofenchols **1** and **9** are, according to computational analyses, more stable than the isomeric cyclic phosphoranes **2** and **10**, the latter species are obtained experimentally by reaction of 2-lithio(diphenylphosphino)-benzene with (−)-fenchone. Computational analyses and successful synthesis of phosphinofenchols via addition of lithiomethyl(diphenylphosphine) to (−)-fenchone demonstrate that destabilization by increasing ring strain can suppress the formation of fenchol-based phosphoranes. The formation of metastable alkoxyphosphoranes can be rationalized by protonation or alkylation of phosphoranide intermediates.

## Experimental Section

**General**: The reactions were carried out under argon atmosphere (Schlenk and needle/septum techniques) with dried and degassed solvents. X-ray crystal analyses were performed on a Bruker Smart CCD diffractometer with $Mo_{K\alpha}$ radiation, NMR spectra were recorded on a Bruker AMX300, IR spectra on a Bruker Equinox 55 FT-IR spectrometer and optical rotations on a Perkin–Elmer P241 spectrometer. GC analyses were carried out on a Chrompack (CP9001).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148242–148245. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Synthesis of 2**: (−)-Fenchone (1.8 g, 12 mmol) was slowly added to 2-lithio-(diphenylphosphino)benzene (3.2 g, 12 mmol)[33] in diethyl ether (70 mL), at room temperature. The reaction mixture was stirred overnight and was subsequently hydrolyzed with aqueous $NH_4Cl$ solution. After separation and extraction with diethyl ether, the organic phases were dried ($MgSO_4$) and evaporated in vacuo. Column chromatorgraphic separation (petrol ether/diethylether 10:1) of the yellow oil and recrystallization from methanol yielded **2** as a colorless solid (2.1 g, 42%).

**Analytic and spectroscopic data of 2**: m.p. 101 °C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 8.10$ (m, 1H), 7.97 (dd, 1H), 7.79 (dd, 1H), 7.56–7.48 (m, 1H), 7.48–7.32 (m, 2H), 7.32–7.15 (m, 8H), 2.48 (m, 1H), 2.13 (m, 1H), 1.84 (m, 1H), 1.75–1.60 (m, 3H), 1.55–1.40 (m, 2H), 0.53 (s, 3H), 0.39 (s, 3H), 0.20 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 134.7$, 132.6, 132.4, 132.3, 131.5, 131.3, 128.9, 128.4, 128.2, 128.1, 127.9, 127.7, 127.6, 127.4, 92.0, 55.0, 49.4, 47.4, 42.7, 32.1, 30.2, 26.4, 26.2, 18.2; $^{31}$P NMR ($CDCl_3$, 121.5 MHz): $\delta = -62.4$ (dd, $^1J_{PH} = 266.9$ Hz, $^3J_{PH} = 15.3$ Hz); elemental analysis calcd (%) for $C_{28}H_{31}OP$ (414.50): C 81.12, H 7.54, P 7.48; found: C 80.98, H 7.46, P 7.31; EI-MS: 413.2 $[M-H]^+$, 399.2 $[M^+ - CH_3]^+$; IR (KBr, cm$^{-1}$): $\tilde{\nu} = 3072-3055$ (aryl, w), 2998–2865 (alkyl, m), 1969 (P–H, s); X-ray crystal data of **2**: $C_{28}H_{31}OP$; $M = 414.50$; space group $P2_1$; monoclinic; $a = 9.8222(1)$ Å, $b = 16.6113(1)$ Å, $c = 14.2297(1)$ Å, $\beta = 95.8551$ (1); $V = 2309.60(3)$ Å$^3$; $Z = 4$; $T = 200(2)$ K; $\mu = 0.14$ mm$^{-1}$; reflections total: 23835, unique: 10591, observed: 8877 ($I > 2\sigma(I)$); R1 = 0.046, $wR2 = 0.115$; GOF = 1.02.

**Synthesis and characterization of 7 and 7*endo***: (−)-Fenchone (7.3 g, 48 mmol) was slowly added to lithiomethyl(diphenyl)phosphine[34] (6.4 g, 32 mmol) in diethyl ether (100 mL) at 0 °C. The reaction mixture was stirred for 48 h at room temperature and was subsequently hydrolyzed with aqueous $NH_4Cl$ solution. After separation and extraction with diethyl ether, the organic phases were dried ($MgSO_4$) and evaporated in vacuo. Column chromatorgraphy yielded a mixture of **7**:**7*endo*** (2:1, GC), which could not be further purified (5.4 g, 49%). $^{31}$P NMR ($CDCl_3$, 121.5 MHz): $\delta = -22.6$ (s, **7**), −24.1 (s, **7*endo***); FAB-MS: 353.3 $[M-H]^+$, 335.3 $[M-OH]^+$; IR (neat, cm$^{-1}$): $\tilde{\nu} = 3485$ (OH), 3053 (aryl, w), 2958 (alkyl, s).

**Synthesis of 7-O and 7*endo*-O**: The mixture of **7** and **7*endo*** (1.0 g, 2.7 mmol) was dissolved in toluene (10 mL) and aqueous $H_2O_2$ (5 mL, 30%) was added at room temperature. The reaction mixture was stirred for 1 h and evaporated in vacuo. Column chromatographic separation (petroleum ether/diethylether 15:1) yielded **7-O** (0.5 g, 70%) and **7*endo*-O** (0.2 g, 70%).

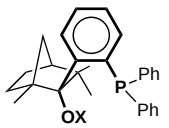
**Characterization** of **7-O**: m.p. 139 °C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta =$ 7.80–7.55 (m, 4H), 7.44–7.37 (m, 6H), 4.10 (s, 1H), 2.95–2.55 (m, 2H), 2.20–2.11 (m, 1H), 2.07–2.04 (m, 1H), 1.75–1.65 (m, 1H), 1.55–1.19 (m, 2H), 1.15–1.07 (m, 7H), 1.01–0.97 (m, 1H), 0.90 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta = 131.4$, 131.3, 131.0, 130.5, 130.2, 128.4, 128.3, 128.2, 83.4, 54.0, 53.3, 49.6, 40.4, 34.5, 29.5, 29.1, 25.5, 21.0, 18.8; $^{31}$P NMR ($CDCl_3$, 121.5 MHz): $\delta = 33.9$ (**7*endo*-O**: 33.5); elemental analysis calcd (%) for $C_{23}H_{29}O_2P$ (368.43): C 74.96, H 7.94, P 8.41; found: C 75.06, H 8.03, P 8.27; CI-MS: 369.3 $[M-H]^+$, 351.3 $[M-OH]^+$; IR (KBr, cm$^{-1}$): $\tilde{\nu} = 3317$ (OH, s), 3054 (aryl, w), 2935 (alkyl, s).

X-ray crystal data of **7**: $C_{23}H_{29}O_2P$; $M = 368.43$; space group $P2_1$; monoclinic; $a = 12.7152(3)$ Å, $b = 8.7140(2)$ Å, $c = 18.6813(1)$ Å, $\beta = 98.576(2)$; $V = 2046.75(7)$ Å$^3$; $Z = 4$; $T = 200(2)$ K; $\mu = 0.15$ mm$^{-1}$; reflections total: 21293, unique: 9302, observed: 3726 ($I > 2\sigma(I)$); $R1 = 0.089$, $wR2 = 0.198$; GOF = 0.92.

X-ray crystal data of **7*endo*-O**: $C_{23}H_{29}O_2P$; $M = 368.43$; space group $P2_1$; monoclinic; $a = 12.4849(1)$ Å, $b = 8.6628(2)$ Å, $c = 19.1973(3)$ Å, $\beta = 96.15^\circ$; $V = 2064.33(6)$ Å$^3$; $Z = 4$; $T = 200(2)$ K; $\mu = 0.15$ mm$^{-1}$; reflections total: 21264, unique: 9309, observed: 5581 ($I > 2\sigma(I)$); $R1 = 0.061$, $wR2 = 0.145$; GOF = 0.97.

**Synthesis of 10**: Compound **2** (0.15 g, 0.36 mmol) was dissolved in diethyl ether (10 mL) and *n*butyllithium (1.6 M, 0.22 mL, 0.36 mmol) was added at room temperature. After the reaction mixture was stirred for 15 min a colorless solid precipitated, and after an additional 30 min of stirring, iodomethane (0.05 g, 0.36 mmol) was added to the suspension, which was stirred thereafter for 24 h. Filtration of the white lithium iodide precipitate and cooling of the solution to $-25\,^\circ$C yielded colorless crystals of **10**.

**Analytic and spectroscopic data of 10**: m.p. 161 °C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.7-6.8$ (m, 14H), 2.29 (dd, 3H), 2.18 (dd, 1H), 2.05 (m, 1H), 1.76 (m, 1H), 1.69 (dd, 1H), 1.40 (m, 1H), 1.22 (dd, 1H), 0.90 (m, 1H), 0.76 (s, 3H), 0.49 (s, 3H), 0.40 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz): $\delta =$ 135.9, 132.9, 131.1, 130.0, 129.7, 128.9, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 126.8, 125.8, 95.0, 54.2, 48.7, 46.8, 42.0, 31.6, 29.6, 28.4, 25.2, 24.2, 18.1; $^{31}$P{$^1$H} NMR ($CDCl_3$, 121.5 MHz): $\delta = -61.8$; elemental analysis calcd (%) for $C_{29}H_{33}OP$ (428.52): C 81.28, H 7.76; found: C 81.08, H 7.70; X-ray crystal data of **10**: $C_{29}H_{33}OP$; $M = 428.52$; space group $P1$; triclinic, $a =$ 9.0144(2) Å, $b = 11.6446(1)$ Å, $c = 12.6052(3)$ Å, $\alpha = 79.734(1)$, $\beta =$ 71.231(1), $\gamma = 73.715(1)$, $V = 1196.88(4)$ Å$^3$; $Z = 2$; $T = 200(2)$ K; $\mu =$ 0.13 mm$^{-1}$; reflections total: 12397, unique: 10249, observed: 5819 ($I > 2\sigma(I)$); $R1 = 0.065$, $wR2 = 0.154$; GOF = 1.00.




Scheme 2. ONIOM(B3LYP/6–31G*:UFF) layers. Bold atoms (X = H, Me) and bold bonds represent the B3LYP/6-31G* layer, which also applies to analogous phosphorane structures.

**Computational details**: All computed structures were fully optimized using GAUSSIAN 98.[21] For ONIOM computations, hydrogen atoms were used as linkers between two layers (Scheme 2). The structures were analyzed by frequency computations and showed no imaginary frequencies.

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