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Optically active P₅-deltacyclenes: selective oxidation, ligand properties, and a diastereoselective rearrangement reaction†‡

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Cage-chiral tetra-*tert*-butyl-P₅-deltacycene **5** is accessible as a pair of highly enriched enantiomers **5'** and **5''**. The only secondary phosphorus atom P1 of the cage can be selectively oxidized by reaction with *t*-BuOOH. The P1-oxo species **9a'** and **9a''**, allow the direct determination of their ee values. Oxidation occurs with the complete retention of the optical activity of the compounds. The chiroptical properties of **9a'** and **9a''** are strongly dominated by their cage chirality, the oxygen atom does not contribute significantly. Elemental sulfur and selenium oxidize P5 with high preference to yield P5-thio- and P5-seleno-P₅-deltacyclenes **10** and **11** of the intact cages again. Longer reaction time and more than stoichiometric amounts of selenium, leads to tri-seleno-P₅-tetracycloundecane **12**, a partially opened oxidized rearrangement product. The ligand properties of racemic **9a** were determined. Diphosphetane phosphorus atom P2 of **9a** is the active donor center to bind a Cr(CO)₅ fragment, but a tautomerization of **9a** takes place if [(benzene)RuCl₂]₂ is added. A hydrogen atom migrates from P1 to the oxygen atom to form a phosphinous acid ligand. The lone pair of P1 is regenerated and acts as the active ligand function of the cage in this case. As for **5**, the base *n*-BuLi induces an efficient cage rearrangement reaction of **9a**, where P1 and the neighboring carbon atom C4 containing its *t*-Bu substituent change places. C4 moves to its new position without breaking the bond with P5, this way forming the novel P1-oxo-P₅-norsnoutene cage in a highly diastereoselective process.

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Introduction

The preparation of many P–C cage compounds is based on the kinetically stabilized *t*-butylphosphaalkyne **1** of Becker¹ and three research groups established the chemistry of cage structured oligomers of **1** independently.² High-yield preparative routes to P–C cages were established by cyclic addition reactions of **1** with dienes, polyenes or related compounds and gave first access to mechanistic considerations.³ If triorganylstannyl-1,2,4-triphosphols **2** are used as the diene component, stannylated P₅-deltacyclenes **3** are formed.⁴ Alternative approaches utilize cyclic addition reactions of 1,3,5-triphosphabenzene,⁵ 1,3,5-triphospha-Dewar-benzenes,⁶ or 1,3-di- and 1,2,4-triphosphols,⁷ and these heterocycles are prepared preferably from P-alkynes again.⁸ Most of the P–C cages known

to date are chiral and they are generally prepared in excellent diastereoselectivity. **3** and P₆-pentaprismane **4** are formed as one pair of enantiomers, in spite of their many stereogenic centers.⁹ (Scheme 1) In combination with a chiral auxiliary, separated diastereomers of **3**¹⁰ are accessible, which can then be easily transformed by hydrolysis of the P–Sn bond into highly enriched enantiomers **5'** and **5''**.¹¹ (Scheme 2).

The chiroptical properties of the enantiomers of **5** are dominated by their cage-chirality.¹² Chiral P–C compounds are

Scheme 1 Components of P–C cage chemistry.

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‡ Dedicated to Professor Jürgen Heck on the occasion of his 65th birthday.

Scheme 2 Optically active P–C cage compounds and examples for their transition metal complexes.

a novel class of asymmetric ligands. They are represented by only two examples to date, which are available as pairs of optically enriched species, **5'** and **5''** and two diastereomers of bis((*S*)-2-methylbutyl)-tetra-*tert*-butyl- P_6 -pentaprismane **6**.¹³ Due to a configurationally labile P–H moiety, the enantiomers **5'** and **5''** form pairs of epimers **a** and **b** in rapid equilibrium, in contrast (benzene) $RuCl_2$ complex **7b** exists as a single species only for each of its cage enantiomers.¹¹ Chelate ligand **6** forms C_2 symmetric complexes with suitable metals as for *cis*-(di(*S*)-2-methylbutyl)-tetra-*tert*-butyl- P_6 -pentaprismane) $PdCl_2$ **8**.¹³ (Scheme 2) (Arene) $Ru(II)$ complexes are enantioselective hydrogen transfer catalysts with chiral β -diamine or β -aminoalcohol co-ligands.^{14,15} Chiral $Ru(II)$ complexes of tethered arene phosphine ligands are more reactive, but typically produced smaller enantiomeric excesses.¹⁶ We hope to solve this problem in the future with chiral P–C cages. A test hydrogenation reaction of C=C double bonds by dihydrogen utilizing **5** as a co-catalyst with reactive $Rh(I)$ complexes¹⁷ proved the principal utility of P–C cages for catalytic purposes.¹¹

This paper presents an approach to tune the ligand properties of tetra-*tert*-butyl- P_5 -deltacyclene enantiomers **5'** and **5''** by oxidation of the active donor center.¹⁸ Achiral tetraphosphacubane has been successfully reacted with organic peroxides, sulfur, or selenium. One to four phosphorus atoms can be oxidized without opening the heterocubane structure¹⁹ and P_4 -bishomoprismane and seleno- P_4 -deltacyclene were selectively mono oxidized with sulfur or selenium.²⁰ This should be applicable to **5** as well. One of the most impressive properties of **5** is a base induced cage rearrangement reaction that includes the complete inversion of the cage and proceeds without loss of the optical activity for **5'** and **5''**.²¹ Oxidation of the cage should influence that reaction significantly. P–C cage

Scheme 3 Oxidation of P_5 -deltacyclene enantiomers **5'** and **5''** to form optically active $P1$ -oxo- P_5 -deltacyclenes **9a,b'** and **9a,b''**.

rearrangement reactions are in most cases accomplished by photochemical activation, but nothing is known about the stereochemical aspects of these reactions.^{9,22,23} In addition, sp^2 hybridized cage phosphorus atoms have been identified by Binger *et al.* as being particularly reactive centers for rearrangement processes.²⁴

The stereochemical notations of this article follow the rules of Cahn *et al.*,²⁵ but were simplified. The complete stereodescriptor of P_5 -deltacyclene **5a'** was determined as ($P1$ -*R*, $P2$ -*R*, $P3$ -*R*, $P5$ -*R*, $C1$ -*S*, $C2$ -*R*, $C4$ -*S*)- P_5 -deltacyclene.¹¹ (Atom labels see Scheme 3) As the principal cage stereochemistry is unaffected by inversion of $P1$, by oxidation, or co-ordination, this motive is characterized by the indicator ' while ' is related to its mirror image. An **a** indicates positions of $H1$ and $P5$ on the same side of the cage, while **b** characterizes the opposite.

Results and discussion

Oxidation of tetra-*tert*-butyl- P_5 -deltacyclene **5**

Racemic **5** and its two enriched enantiomers **5'** and **5''** have been oxidized by several oxidizing agents. *t*-BuOOH proved to be optimal for mono oxidation. It forms $P1$ -oxo-tetra-*tert*-butyl- P_5 -deltacyclene **9** with high preference. A few percent of a $P5$ oxide was present in the reaction mixture. Like **5**, **9** was shown to form a pair of epimers **9a** and **9b** in 80% yield in the raw product with a molar ratio of 96 : 4. (Scheme 3) Unlike **5a** and **5b** chromatography separated epimer **9a** from the reaction mixture. Due to the pentavalent $P1$, no equilibrium exists between these epimers.

Oxidation of **5** with S_8 results in the $P5$ monosulfurization product **10**, again as a pair of epimers **10a** and **10b**. Due to the necessary base CS_2CO_3 , small percentages of a fully saturated rearrangement product of **5** are formed. Se_x oxidizes $P5$ as well to form **11a,b** as the main product. (Scheme 4).

The **a** epimers dominate, in the amount of 96% for **10a**, and 97% for **11a**, but they have yet to be separated. Slow equilibria between them and a partial dissociation of the P–Se bond of **11a** and **11b** happen parallel to the purification procedures. The bowl shaped species tri-seleno- P_5 -tetracycloundecane **12**

Scheme 4 Preparation of P5-thio-tetra-*tert*-butyl-P5-deltacyclene epimers **10a** and **10b**, P5-seleno-tetra-*tert*-butyl-P5-deltacyclene epimers **11a** and **11b** and tri-seleno-tetra-*tert*-butyl-P5-tetracycloundecane **12**.

accompanies **11a,b** in traces. **12** become a main product after longer reaction times and with increased amounts of Se_x , albeit with more uncharacterized side products being formed.

Complex chemical properties of **9a**

In situ prepared $[\text{Cr}(\text{CO})_5(\text{THF})]$ was reacted with **9a** at -40°C . Two isomeric mononuclear complexes were formed. Isolated P2-complex **13a** contains ligand **9a**, but side product **14** is composed of a phosphinous acid tautomer of **9a** and P1 is the active donor. (Scheme 5) **9a** and $[(\text{benzene})\text{RuCl}_2]_2$ form the single mononuclear complex **15** in equilibrium with the free ligand in a molar ratio of 61% of **15** and 39% of **9a**. Dissolved crystals of isolated **15** regenerate the equilibrium mixture. (Scheme 6) **15** contains the same phosphinous acid tautomer ligand as **14**.

Scheme 5 Preparation of $[(\text{P1-oxo-tetra-tert-butyl-P}_5\text{-deltacyclene})\text{Cr}(\text{CO})_5]$ **13a** and $[(\text{P1-hydroxo-tetra-tert-butyl-P}_5\text{-deltacyclene})\text{Cr}(\text{CO})_5]$ **14**.

Scheme 6 Preparation of $[(\text{P1-hydroxo-tetra-tert-butyl-P}_5\text{-deltacyclene})\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]$ **15** in equilibrium with free **9a**.

Reactivity of **9a** towards bases

9a was reacted with *n*-BuLi at -80°C . Best preparative results were obtained by dissolving the reaction mixture after removal of the solvent in CDCl_3 . Two P1-oxo-tetra-*tert*-butyl-P5-norsnoutene derivatives **16** and **17** were formed in a ratio of 92:8. (Scheme 7).

Side product **17** is a rearrangement product of **9a**, while the main product **16** is a formal substitution product of **17**, where a chlorine atom replaces the cage hydrogen atom H1. The lack of any significant amount of deuterium in the spectra of **17** show that most probably traces of water from the surface of the glassware supply a proton to a rearranged anionic intermediate $[\mathbf{9a} - \text{H}]^-$ of the reaction, rather than the solvent. Attempts at direct protonation of the anionic intermediate led to smaller yields of P1-oxo-P5-norsnoutene derivatives and more side products. The chlorine atom of **16** obviously stems from CDCl_3 , which reacted with the same anion. We relate the name of the cage to the organic cage structure snoutane. Hypothetical removal of one CH_2 unit and the double bond transforms it into norsnoutene.²⁶

Spectroscopic characterization

$^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR are the most important spectroscopic methods for the compounds,⁷⁷ ^{77}Se adds to that for **11** and **12**. $^{13}\text{C}\{^1\text{H}\}$ NMR is less informative as the cage carbon atoms are only observable for the main components of the reactions. Extensive ^{13}C - ^{31}P coupling and lack of NOE enhancement hamper the observation of side products. An example for the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra is given for racemic **9a** with and without addition of the chiral NMR shift reagent $\text{Eu}(\text{hfc})_3$,²⁷ (Fig. 1).

Paramagnetic $\text{Eu}(\text{hfc})_3$ and the two enantiomers **9a'** and **9a''** form diastereomeric adducts **A** and **B**. The maximal signal split effect for P1 identifies the oxidized P atom. An ee of 93% was determined for **9a'** and 68% ee for **9a''**. The data are identical with the de of the respective diastereomeric stannyl derivatives of **3**, which have been used as the starting materials for the preparation of **5'** and **5''**.¹¹

Table 1 summarizes the ^{31}P NMR shift data of the compounds. The ^1H NMR shifts of the cage hydrogen H1 are included. All *t*-Bu protons are observed in their characteristic range. In comparison to **5a,b**, the spectra of the oxidation products **9**–**11** agree with unchanged P5-deltacyclene cage structures and the unit P1–H1 forming epimers.²¹ Some general trends are observable. The strongest influence of the oxidation on the spectra concern P1 of the oxo species **9a** and **9b**, due to

Scheme 7 Preparation of P1-oxo-tetra-*tert*-butyl-P5-norsnoutene derivatives **16** and **17**.

Fig. 1 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (202.50 MHz, CDCl_3 , 23 °C) of **9a** (top) and **9a' + 9a'' + Eu(hfc)₃** (bottom). The expanded signals of adducts A and B are modified by individual factors.

Table 1 NMR shift data [δ] of ^{31}P nuclei and ^1H cage nucleus H1 of oxidized P–C cage compounds and **5a,b**¹¹

	δ (P4)	δ (P5)	δ (P1)	δ (P2)	δ (P3)	δ (H1)
5a	339.6	105.0	−51.7	−112.5	−120.2	4.91
5b	366.1	88.3	−18.7	−107.1	−107.9	4.14
9a	370.6	77.7	56.0 ^a	−148.7	−118.0	8.78
9b	342.1	86.7	62.9	−160.7	−140.7	7.98
10a	312.4	101.6	−71.5	−114.5	−124.1	4.96
10b	339.2	89.2	−34.1	−109.5	−112.9	3.91
11a	314.6	87.7	−71.6	−113.3	−122.1	5.06
11b	341.6	71.2	−34.8	−107.9	−110.7	3.75
12	74.2	55.4	134.2	80.0	148.2	4.61
13a	370.9	79.8	46.5	−68.9 ^b	−148.5	8.61
14	379.9	73.3	182.9 ^b	−92.6	−116.4	^c
15	367.2	67.0	151.9	−112.2	−123.1	5.2 ^d
16	365.1	−21.8	96.7	−174.5	−171.9	—
17	338.8	−68.5	42.4	−197.9	−178.5	6.20

^a Oxidized P atoms red. ^b Co-ordinated P atoms bold. ^c Not identified.

^d Broad signal.

the formation of a phosphine oxide. The chemical shift of H1 confirms a H1–P1–O1 moiety for **9a** and **9b** and the $^1J_{\text{P1H1}}$ coupling constant supplies evidence for this.²⁸ It grows from 179 Hz for **5a** to 452 Hz for **9a**. δ (H1) proved to be indicative for identifying the epimers of **5**, **9**, **10**, and **11**. The cage hydrogen atom of the **a** epimers is found always 0.8 ppm low field of that of the related **b** epimer.

Neither oxidation, complexation, or cage rearrangement altered the P=C double bond of the cages. sp^2 hybridized P4 appears always in its characteristic region of between 310 and 380 ppm.²⁹ That does not account for Se_3 species **12**. Two sp^2 carbon atoms at 158.2 and 159.6 ppm point to the formation of a C=C double bond for **12** instead and a $^2J_{\text{H1P5}} = 14.7$ Hz proves the migration of H1 to a carbon atom.

^{77}Se contributes to the properties of **11a** and **12**. (Table 2) A small percentage of the isotope and a small concentration of

Table 2 NMR shift data [δ] of ^{77}Se nuclei and Se–P coupling constants [Hz] of **11a** and **12**

	δ (Se)	$^1J_{\text{SeP1}}$	$^1J_{\text{SeP2}}$	$^1J_{\text{SeP4}}$	$^1J_{\text{SeP5}}$	$^2J_{\text{SeP1}}$
Se1 11a	−95.0	—	—	—	765	—
Se1 12	146.6	178	—	169	—	—
Se2 12	300.8	—	222	—	409	—
Se3 12	74.3	—	—	—	715	9.0

11b do not allow the observation of its ^{77}Se NMR signals. $^1J_{\text{P5Se}}$ of more than 700 Hz for **11a** and **12** are characteristic for P=Se double bonds.³⁰ The respective ^{77}Se shifts agree with this assumption. P1, P2, P4, and P5 of **12** exhibit further, but smaller $^1J_{\text{SeP}}$ coupling. It is related to P1–Se1–P4 and P2–Se2–P5 bridges. Only P3 is not directly bound to a selenium atom.

A very close match of the ^{31}P NMR data and a characteristic line broadening for the signal of H1 as part of an OH group within phosphinious acid complexes³¹ **14** and **15** document their structural identity with respect to the cage ligand and the active donor center P1. H1 migrated to the oxygen atom and the lone pair of P1 was regenerated by this tautomerization. Known complexes with non-cyclic PR_2OH ligands have OH protons which appear between 8.6 and 10.0 ppm.³² A significant interaction between H1 and both chloro ligands of **15** indicate a hydrogen bridge in the solid state (*vide infra*). This interaction should strongly influence the average position of the OH proton in solution. In this molecular position, significant NMR signal shifts have been observed due to the ring current of the benzene ligand.³³

The strongest effect of the structural change between **9a** and its rearrangement product **17** concern a shift of 146.2 ppm to high field for P5, however, the spectroscopic data are not sufficient to determine the structure of **17** or its chlorinated derivative **16**.

The IR active stretching modes of the P–H, P=X, (X = O, S, Se) and C=O bond vibrations are especially helpful to characterize the isolated compounds of this study. (Table 3).

A $\nu(\text{P=O})$ of around 1190 cm^{-1} for **9a** and **13a** is consistent with phosphine oxides.³⁴ Due to the bond strengthening effect of the oxygen atom, the $\nu(\text{P–H})$ of the same compounds appear at the highest frequency of the investigated series which include non-oxidized species **5a** (2248 cm^{-1}).³⁵ $\nu(\text{P=X})$ X = S, Se are found in the fingerprint region. The data agree well with the presence of P=S³⁶ and P=Se double bonds.³⁷ Three $\nu(\text{C=O})$ frequencies of **13a** are characteristic for $[\text{LM}(\text{CO})_5]$ complexes.³⁸

Table 3 Selected IR data [cm^{-1}] of oxidized cage compounds

	$\nu(\text{P–H})$	$\nu(\text{P=X})$	X	$\nu(\text{C=O})$
9a	2286	1184	O	—
10a	2255	691	S	—
11a	2242	582	Se	—
12	—	530	Se	—
13a	2297	1192	O	2069, 1953, 1935

Chiroptical properties

The CD spectra of **9a'** and **9a''** form almost mirror symmetric curves. (Fig. 2) The curves are closely related to the CD spectra of **5'** and **5''**. (Table 4) As observed earlier, the Cotton effect is strongly dominated by the cage chirality of the P₅-deltacyclene derivatives. Peripheral units, irrespective of their chemical character, such as hydrogen atoms,¹¹ triorganyl stannyl substituents with or without chiral organyl groups,¹¹ transition metal complex fragments,²¹ or an oxygen atom in this case do not contribute significantly. The specific optical rotation $[\alpha]_{589}$ inverts its direction for the couple **9a'**: +10° ($c = 1.1 \times 10^{-3}$ g mL⁻¹, *n*-hexane, 93% ee) and **9a''**: -7° ($c = 1.1 \times 10^{-3}$ g mL⁻¹, *n*-hexane, 68% ee) and confirms the relative ee values of the samples.

X-ray crystallography

Neither racemic **9a**, nor one of its separated enantiomers **9a'** or **9a''** formed useful crystals, but **10a**, **11a**, **12**, **13a**, **15**, and **16** could be investigated by X-ray crystallography. (Fig. 3–7) A selection of characteristic bond distances is given in Table 5. Crystallographic data, data collection, and refinement details are given in the ESI.† In all cases, the compounds contain both cage enantiomers as symmetry related molecules in the unity cell. The unity cells of **10a**, **11a**, and **12** contain two independent pairs of enantiomers with no significant differences between their structural data.

As **9a** failed to crystallize, structural information about it can be taken from the Cr(CO)₅ complex **13a**. In harmony with the spectra, P1 is oxidized and H1 shares the cage side of P5 to

Fig. 2 CD spectra of **9a'** (black, $c = 2.45 \times 10^{-4}$ mol L⁻¹, *n*-hexane, 20 °C) and **9a''** (red, $c = 2.68 \times 10^{-4}$ mol L⁻¹, *n*-hexane, 20 °C).

Table 4 Wavelength data [nm] and characteristic points of the CD curves of **5'**, **5''**, **9a'**, and **9a''**^a

	e1 [nm]	e2 [nm]	e3 [nm]
9a'	386 (+)	314 (–)	286 (–)
9a''	415 (–)	338 (+)	289 (+)
5'	408 (+)	315 (–)	276 (–)
5''	409 (–)	316 (+)	276 (+)

^a (+): maximum of Cotton effect, (–): minimum of Cotton effect.

Fig. 3 Molecular structures of **10a** (left) and **11a** (right) in the solid state. *tert*-Butyl hydrogen atoms have been omitted for clarity.

Fig. 4 Molecular structure of **12** in the solid state. *tert*-Butyl hydrogen atoms have been omitted for clarity.

Fig. 5 Molecular structure of **13a** in the solid state. *tert*-Butyl hydrogen atoms have been omitted for clarity.

Fig. 6 Molecular structure of **15** in the solid state. *tert*-Butyl and benzene hydrogen atoms have been omitted for clarity.

Fig. 7 Molecular structure of **16** in the solid state. *tert*-Butyl hydrogen atoms have been omitted for clarity.

qualify it as an *a* epimer. The active donor is P2 and the same has been found for its non-oxidized analogue **18** = [5a-Mo(CO)₅].¹¹ With the exception of the P=O bond of **13a** and slightly shortened bonds of P1 with its cage neighbours due to the oxidation, their P–C cage structures are closely related. (Table 5) Analogous and small deviations from the idealized geometry of mono substituted octahedrons for the M(CO)₅ fragments of **13a** and **18** can be explained by an interaction with their bulky cage ligands.¹¹

The situation is different for the ruthenium complex **15** not only because of the co-ordinative bond P1–Ru1. H1 is no longer bound to P1, but has migrated to the oxygen atom, in this way replacing the P=O double bond of **9a** by a P–OH single bond and forming a phosphinous acid ligand. An elongation of the P–O distance of *ca.* 12 pm for the reduction of bond order is appropriate.³⁹ The position of H1 is remarkable. Due to its chemical character it is positively polarized and that initiates a close contact with both chloro ligands of the metal. The distances H1...Cl1 = 259 and H1...Cl2 = 252 pm qualify the interaction as a hydrogen bridge.⁴⁰ The same interaction should contribute significantly to the time average position of the OH group in a non-polar solution. Bond P1–O1 points towards P3 and P1–Ru1 towards P5 of the cage, thus the stereochemistry of P1 resembles that of P1 in **5b** within the (benzene)RuCl₂ complex **7b**. The analogous bond length data of **15** and **7b** outside the P–OH unit differ by less than 1 pm.¹¹ The co-ordination bond P1–Ru1 was determined as 239.82(7) of **15** and 238.91(5) for **7b**. The small elongation of 0.9 pm

forms a contrast to the general observation of length reduction for bonds of phosphorus, when an OH group is introduced. The Ru–P bond of **15** is *ca.* 4–5 pm longer than the 235–236 pm observed for (C₆H₆)Ru(PR₃)Cl₂ complexes normally.⁴¹ We relate the effect to the bulkiness of the cage ligand of **15** which is superior over **5b** although the additional oxygen atom of the OH group is the only extra component. The bond elongation is accompanied by a significant decrease in bond energy for **15**. The direct consequence of which is a destabilization of the complex **15**, to give an equilibrium of [(benzene)RuCl₂]₂ with the free cage **9a**. The formation of a phosphinous acid ligand by tautomerization of **9a** is remarkable as only a few examples of cyclic ligands of this sort are known.³¹ The secondary phosphine oxide isomers are normally more stable, at least with respect to the free molecules.⁴² In the case of complexes **14** and **15**, this process leads to a new cage ligand, whose π -acceptor ability should be significantly enhanced if compared to **5**, for example.¹⁸

The molecular structures of P5-thio and P5-seleno cages **10a** and **11a** look very much alike, but they crystallize in different space groups. P5 is oxidized in both cases, the bond distances P5–S1 for **10a**, P5–Se1 for **11a**, and P5–Se3 for **12** (Table 5) are consistent with P=X double bonds.^{43,44} The two chalcogenide atoms cause only small changes in the P₅-delta-cyclene cage structure. The differences between **10a** and **11a** are below 2° for the bond angles and 3 pm for the bond distances outside the P=X bond.

The bowl shaped Se₃-species **12** with its four fused five membered rings, however, has no identified structural relation to the starting cage **5**, but its elemental composition points to the ongoing existence of polycyclic P₅(CR)₄H species even under harsh chemical conditions. Selenium adds to **5** and rearrangement processes are initiated, leading to one P=Se unit, two P–Se–P bridges and a P–H bond being replaced by a C–H bond. The new C=C double bond has already been identified by ¹³C NMR.

The rearrangement and chloro substitution product **16** is a specific case, in that the molecule is related to iso-P5-delta-cyclene **19** by being formed by a base induced rearrangement reaction. (Scheme 8) P1 and C4 change places in both cases, but preparation of **19** from **5** includes a unique cage inversion process which transforms **5'** into **19'**.²¹ For **16**, and the same

Table 5 Selected bond lengths [pm] of **7b**,¹¹ **10a**, **11a**, **12**, **13a**, **15**, **16**, and **18** = [5a-Mo(CO)₅]¹¹

	P–X ^{a,b}	P1–C4	P1–P2	P4=C3	P2–P3	P2–C1
7b	—	189.1 (2)	217.09 (7)	168.1 (2)	221.00 (7)	188.8 (2)
10a ^c	195.5 (1)	188.9 (3)	217.7 (2)	169.5 (3)	221.0 (2)	187.8 (3)
11a ^c	210.55 (7)	187.9 (3)	217.7 (1)	168.7 (3)	220.7 (1)	187.3 (3)
12 ^c	210.72 (6)	—	—	—	—	187.2 (2)
13a	148.5 (2)	184.7 (2)	214.88 (7)	168.5 (2)	219.78 (7)	187.7 (2)
15	160.7 (2)	189.2 (3)	217.4 (1)	167.5 (3)	220.7 (2)	188.6 (3)
16	147.4 (2)	181.4 (2)	—	167.7 (2)	220.44 (5)	189.4 (2)
18	—	187.7 (2)	214.88 (6)	168.8 (2)	219.51 (6)	186.1 (2)

^a X = O, S, Se, or OH. ^b P1 for **13a**, **15**, **16**; P5 for **10a**, **11a**, **12**. ^c One of two independent pairs of enantiomers in the unity cell. In the case of **10a** and **11a** one of the *t*-Bu groups of the second pair of enantiomers is disordered.

Scheme 8 Base induced rearrangement reactions of **5'** and **9a**. Mobile parts of the molecules are shown in red.

accounts for rearrangement product **17**, C4 moves to the former place of P1 while maintaining the bond C4–P5, this way forming the new P₅-norsnoutene cage. In contrast to **19**, P1 of **16** is connected by only two bonds with the cage and C4 has bonds with three other cage elements.

Molecular building blocks of **16** with a constant connectivity, such as the diphosphetane ring C1–P2–P3, P4=C3 or P1=O1 double bonds for example, remain almost unchanged if compared to **9a** as the ligand of complex **13a**. With respect to the stereochemistry of P1, O1 shares the cage side with P5, which indicates an inversion of P1 with respect to **9a**. As we have not yet investigated the rearrangement experiment with enantiomerically enriched **9a'** or **9a''**, no information is available that sheds light on whether a cage inversion is part of the rearrangement of **9a** as well. One pair of enantiomers is transformed into one pair of enantiomers for each of the two products only, with the diastereoselectivity of the process being excellent.

Conclusions

Cage-chiral P₅-deltacyclenes represent a very specific group of optically active phosphorus(III) ligands whose potential has not yet been fully developed. Their most important property is their bulky, pronounced asymmetric and highly rigid cage structure, which is designed to control the reactivity of a transition metal. All determined structure parameters of the P₅-deltacyclene family such as intra cage bond lengths and bond angles are very close to each other, even for oxidized, substituted or co-ordinated cages. Three extraordinary chemical properties can be stated.

- All reactions utilizing enriched enantiomers or diastereomers proceeded with complete retention of their optical activity. These reactions include: destannylation,¹¹ protonation,¹ deprotonation,¹ complexation,^{11,21} oxidation, (this paper) and cage rearrangement including cage inversion.²¹ This finding corresponds to the excellent diastereoselectivity of chiral P–C cage forming reactions, which are based on Beckers *tert*-butylphosphaalkyne **1**.^{1–5,8,9} Both can be related to

the big size difference of the *t*-Bu substituent of the carbon atom and the P-lone pair, which have to find their positions at the surface of the cages and reduce the number of energetically possible stereoisomers of P_x(*t*-BuC)_yR species significantly.

- The ability of P–C cages to undergo rearrangement reactions without disintegration and without loss of optical activity has been extended by this study to account for an oxidation product as well. This opens a way to new optically active P–C cages with modified ligand properties on the basis of one single pair of separated enantiomers **5'** and **5''**.

- A matter of concern for the practicability of P–C cages for co-catalytic purposes was the multitude of P lone-pairs, which are oriented radial to the outside, but (benzene)RuCl₂ fragments proved unequivocal interactions with the P₅-deltacyclene ligands **5b** and **9a**. Both adopt spontaneous reactions of the periphery to optimize their bonding with the Ru(II) ion, with the cages themselves remaining almost unchanged at the same time. In the case of **9a**, the resulting phosphinous acid function influences the electronic situation of the donor atom P1 by inducing the targeted π -acceptor property. This points to an optimistic perspective for the use of **9a** and related compounds as potential co-catalysts for organic transformations by transition metals. Phosphinous acid complexes have been used successfully in that sense already⁴⁵ and (arene)Ru(II)L complexes proved to be highly interesting catalysts anyway.^{14,15}

Experimental

General

All reactions were carried out in heat gun dried glassware under an oxygen-free atmosphere of dry nitrogen using Schlenk techniques. Solvents including NMR solvents were dried by standard methods, degassed or distilled under N₂ and stored over 4 Å molecular sieves. NMR spectra were recorded on Bruker AVANCE DPX300 NB, Bruker AVANCE DRX400 WB, JEOL JNM-LA400 and JEOL Alpha500. NMR chemical shifts references: ¹H and ¹³C: residual solvent peaks; ³¹P: external H₃PO₄ (85%), ⁷⁷Se: external 60% Me₂Se in CDCl₃. NMR data were analyzed with the program MestReNova version 5.2.2.⁴⁶ Mass spectra: Jeol The MStation, JMS 700, UHR-TOF Bruker Daltonik maXis; chiroptical properties: polarimeter MC 240; circular dichroism measurements: JASCO J-710 spectropolarimeter. Elemental analysis was performed locally by the microanalytical laboratory at the Department Chemie und Pharmazie der Universität Erlangen-Nürnberg. The starting materials racemic tetra-*tert*-butyl-P₅-deltacyclene **5** and its enantiomerically enriched versions **5'** and **5''** were prepared as published.¹¹ [(Benzene)RuCl₂]₂, Cr(CO)₆, NMR solvents, solvents for chemical reactions and chromatography, and static phases were purchased from standard commercial resources. The spectroscopic data of the minority epimer components are given in the ESI.†

P1-oxo-tetra-*tert*-butyl-P₅-deltacyclene 9a'. 71 mg (0.164 mmol) **5'** was dissolved in 10 mL of toluene and 35 μ L of *t*-BuOOH (0.197 mmol; 5.5 M in decane) added. After 24 h stirring at

room temperature the solvent was removed in vacuum. Column chromatography at water deactivated (6%) silica with *n*-hexane/ethyl acetate 10:1 yielded 36 mg (0.080 mmol, 49%) **9a'** (93% ee) as a yellow oil. (Found C, 53.70%, H, 8.25%; C₂₀H₃₇OP₅ requires C, 53.57%, H, 8.33%). Analogous preparation of **9a''**: **5** (0.232 g, 0.54 mmol), (CH₃)₃COOH (150 μL, 0.83 mmol; 5.5 M in decane) yielded **9a''** (0.021 g, 0.047 mmol, 48%, 68% ee). Analogous preparation of **9a**: **5** (0.042 g, 0.097 mmol), (CH₃)₃COOH (22 μL, 0.116 mmol; 5.5 M in decane) yielded **9a** (0.120 g, 0.27 mmol, 50%) as a yellow solid; chromatography solvent *n*-hexane. Analytical, NMR and MS data of **9a**, **9a'**, and **9a''** are identical within the experimental limits.

NMR: δ_H (300 MHz, CDCl₃) 1.09 (d, ⁴J_{H,P} = 0.6 Hz, 9H, ^tBu), 1.49 (s, 9H, ^tBu), 1.51 (s, 9H, ^tBu), 1.67 (d, ⁴J_{H,P} = 1.8 Hz, 9H, ^tBu), 8.78 (dddd, ¹J_{H1,P1} = 452 Hz, ²J_{H1,P2} = 32.3 Hz, ³J_{H1,P} = 5.4 Hz, ³J_{H1,P} = 1.8 Hz, 1H, H1); δ_P (³¹P{¹H}, 121.5 MHz, CDCl₃) -148.7 (dd, ¹J_{P2,P1} = 260 Hz, ¹J_{P2,P3} = 162 Hz, 1P, P2), -118.0 (d, ¹J_{P3,P2} = 162 Hz, 1P, P3), 56.0 (dd, ¹J_{P1,P2} = 260 Hz, ²J_{P1,P5} = 128 Hz, 1P, P1), 77.7 (dt, ²J_{P5,P1} = 128 Hz, ²J_{P5,P4} = 9.8 Hz, 1P, P5), 370.6 (d, ²J_{P4,P5} = 11.2 Hz, 1P, P4); δ_P (121.5 MHz, CDCl₃, signals with resolved P-H coupling) -150.5 (ddd, ¹J_{P2,P1} = 261 Hz, ¹J_{P2,P3} = 162 Hz, ²J_{P2,H1} = 31.9 Hz, P2), 55.2 (ddd, ¹J_{P1,H1} = 454 Hz, ¹J_{P1,P2} = 261 Hz, ²J_{P1,P5} = 129 Hz, P1); δ_C (75.5 MHz, CDCl₃) 33.1 (ddd, ³J_{C,P} = 9.3 Hz, ³J_{C,P} = 4.6 Hz, ²J_{C,P} = 4.5 Hz, C(CH₃)₃), 34.2 (dd, ³J_{C,P} = 13.4 Hz, ³J_{C,P} = 9.1 Hz, C(CH₃)₃), 35.3 (dddd, ²J_{C,P} = 11.4 Hz, ²J_{C,P} = 8.8 Hz, ²J_{C,P} = 8.4 Hz, ³J_{C,P} = 3.0 Hz, C(CH₃)₃), 35.9 (ddd, ³J_{C,P} = 10.3 Hz, ³J_{C,P} = 7.4 Hz, ²J_{C,P} = 2.9 Hz, C(CH₃)₃), 36.0 (m, C(CH₃)₃), 39.0 (d, ²J_{C,P} = 8.7 Hz, C(CH₃)₃), 39.2 (dd, ²J_{C,P} = 15.7 Hz, ²J_{C,P} = 11.3 Hz, C(CH₃)₃), 41.7 (ddd, ²J_{C,P} = 18.9 Hz, ²J_{C,P} = 14.1 Hz, ³J_{C,P} = 3.4 Hz, C(CH₃)₃), 64.0 (ddd, ¹J_{C,P} = 52.7 Hz, ¹J_{C,P} = 46.6 Hz, ¹J_{C,P} = 44.6 Hz, ²J_{C,P} = 11.0 Hz, C1), 89.0 (dddd, ¹J_{C,P} = 31.1 Hz, ¹J_{C,P} = 26.3 Hz, ²J_{C,P} = 7.1 Hz, ²J_{C,P} = 3.5 Hz, ²J_{C,P} = 3.5 Hz, C4), 91.5 (ddt, ¹J_{C,P} = 59.3 Hz, ¹J_{C,P} = 56.2 Hz, ²J_{C,P} = 7.6 Hz, C2), 220.6 (dddd, ¹J_{C,P} = 64.9 Hz, ¹J_{C,P} = 53.7 Hz, ³J_{C,P} = 17.0 Hz, ³J_{C,P} = 12.7 Hz, C3); IR (KBr) ν_{max}/cm⁻¹ 2957m, 2864sh (C-H), 2286w (P-H), 1460m (C-H), 1395m, 1364m (^tBu), 1184m (P=O); FD mass spectrum (*n*-hexane): *m/z* 448 (M⁺, 100%). Spectroscopic data of **9b** in the ESI.[†]

P5-thio-tetra-tert-butyl-P₅-deltacyclene 10. 458 mg (1.06 mmol) **5** was dissolved in 25 mL of toluene and 47 mg (1.48 mmol) of sulfur powder added. After 24 h stirring at 50 °C 88 mg (0.27 mmol) Cs₂CO₃ was added to the yellow mixture and stirred at 50 °C for 3 d. The color changed slowly to orange. Filtration, removal of the solvent in vacuum and column chromatography at water deactivated (6%) silica with *n*-hexane/ethyl acetate 10:1 yielded 329 mg (0.71 mmol, 67%) **10a** + **10b** in a ratio of 96:4 as a pale yellow solid. (Found C, 51.99%, H 8.26%, S 7.19%; C₂₀H₃₇P₅S requires C, 51.71%, H 8.05%, S 6.90%). Data of **10a** (96 mol%) NMR: δ_H (300 MHz, CDCl₃) 1.19 (s, 9H, ^tBu), 1.44 (s, 9H, ^tBu), 1.58 (s, 9H, ^tBu), 1.68 (d, ⁴J_{H,P} = 1.8 Hz, 9H, ^tBu), 4.96 (dd, ¹J_{H1,P1} = 192 Hz, ³J_{H1,P5} = 10.5 Hz, 1H, H1); δ_P (³¹P{¹H}, 121.5 MHz, CDCl₃) -124.1 (ddd, ¹J_{P3,P2} = 175 Hz, ²J_{P3,P5} = 15.4 Hz, ²J_{P,P} = 9.2 Hz, P3), -114.5 (ddd, ¹J_{P2,P1} = 242 Hz, ¹J_{P2,P3} = 173 Hz, ²J_{P,P} = 8.6 Hz, P2), -71.5

(ddd, ¹J_{P1,P2} = 240 Hz, ²J_{P1,P5} = 24.1 Hz, ²J_{P,P} = 11.1 Hz, P1), 101.6 (dddd, ²J_{P5,P4} = 34.3 Hz, ²J_{P5,P1} = 24.5 Hz, ²J_{P5,P3} = 15.8 Hz, ²J_{P,P} = 8.9 Hz, P5), 312.4 (ddd, ²J_{P4,P5} = 35.2 Hz, ²J_{P,P} = 10.2 Hz, ³J_{P,P} = 9.5 Hz, P4); δ_P (121.5 MHz, CDCl₃, signals with resolved P-H coupling) -71.5 (dddd, ¹J_{P1,P2} = 242 Hz, ¹J_{P1,H1} = 193 Hz, ²J_{P1,P5} = 24.9 Hz, ²J_{P,P} = 10.8 Hz, P1); δ_C (75.5 MHz, CDCl₃) 32.1 (m, C(CH₃)₃), 32.4 (ddd, ³J_{C,P} = 8.4 Hz, ³J_{C,P} = 5.6 Hz, ²J_{C,P} = 2.8 Hz, C(CH₃)₃), 34.1 (ddd, ³J_{C,P} = 13.2 Hz, ³J_{C,P} = 3.7 Hz, ²J_{C,P} = 2.4 Hz, C(CH₃)₃), 36.2 (m, C(CH₃)₃), 36.3 (mdd, ³J_{C,P} = 3.7 Hz, ²J_{C,P} = 2.4 Hz, C(CH₃)₃), 40.07 (dd, ²J_{C,P} = 16.1 Hz, ²J_{C,P} = 4.4 Hz, C(CH₃)₃), 40.10 (dd, ²J_{C,P} = 22.6 Hz, ²J_{C,P} = 16.6 Hz, C(CH₃)₃), 43.2 (dt, ²J_{C,P} = 13.2 Hz, ²J_{C,P} = 2.7 Hz, C(CH₃)₃), 56.9 (dddt, ¹J_{C,P} = 52.1 Hz, ¹J_{C,P} = 47.6 Hz, ¹J_{C,P} = 43.2 Hz, ²J_{C,P} = 4.6 Hz, C1), 70.0 (tdd, ¹J_{C,P} = 53.9 Hz, ¹J_{C,P} = 21.9 Hz, ²J_{C,P} = 9.1 Hz, C4), 86.1 (ddt, ¹J_{C,P} = 49.5 Hz, ¹J_{C,P} = 38.6 Hz, ²J_{C,P} = 2.8 Hz, C2), 201.7 (ddt, ¹J_{C,P} = 58.1 Hz, ³J_{C,P} = 10.8 Hz, ³J_{C,P} = 3.6 Hz, C3); IR (KBr) ν_{max}/cm⁻¹ 2953sh, 2923m, 2854sh (C-H), 2255w (P-H), 1458m (C-H), 1394m, 1363m (^tBu), 1185m (P=C), 691m (P=S). FD mass spectrum (*n*-hexane): *m/z* 464 (M⁺, 100%). Spectroscopic data of **10b** in the ESI.[†]

P5-seleno-tetra-tert-butyl-P₅-deltacyclene 11. 162 mg (0.37 mmol) **5** was dissolved in 10 mL of toluene and 40 mg (0.51 mmol) of selenium powder added. After 27 h stirring at 70 °C, filtration and removal of the solvent in vacuum, column chromatography at water deactivated (6%) silica with *n*-hexane/ethyl acetate 10:1 yielded 102 mg (0.14 mmol, 38%) yellow **11a** + **11b**. The product is accompanied by ca. 30% of regenerated **5** due to an instability of **11a,b** on the column. Recrystallization from *n*-hexane at +4 °C led to 26 mg (0.051 mmol, 14%) of pure yellow **11a,b** in a ratio of 97:3. (Found C, 46.83%, H, 7.50%; C₂₀H₃₇P₅Se requires C, 46.97%, H, 7.31%). Data of **11a** (97 mol%) NMR: δ_H (300 MHz, CDCl₃) 1.19 (s, 9H, ^tBu), 1.45 (s, 9H, ^tBu), 1.60 (s, 9H, ^tBu), 1.70 (d, ⁴J_{H,P} = 1.5 Hz, 9H, ^tBu), 5.06 (dd, ¹J_{H1,P1} = 193 Hz, ³J_{H1,P5} = 11.4 Hz, 1H, H1). δ_P (³¹P{¹H}, 121.5 MHz, CDCl₃) -122.1 (dddd, ¹J_{P3,P2} = 174 Hz, ²J_{P,P} = 15.4 Hz, ²J_{P,P} = 8.7 Hz, ²J_{P,P} = 4.1 Hz, P3), -113.3 (ddd, ¹J_{P2,P1} = 244 Hz, ¹J_{P2,P3} = 173 Hz, ²J_{P,P} = 8.3 Hz, P2), -71.6 (dddd, ¹J_{P1,P2} = 245 Hz, ²J_{P1,P5} = 26.6 Hz, ²J_{P,P} = 11.2 Hz, ²J_{P,P} = 3.8 Hz, P1), 87.7 (dddd, ¹J_{P5,Se1} = 765 Hz, ²J_{P5,P4} = 35.0 Hz, ²J_{P5,P1} = 25.1 Hz, ²J_{P,P} = 16.8 Hz, ²J_{P,P} = 8.3 Hz, P5), 314.6 (dt, ²J_{P4,P5} = 35.6 Hz, ²J_{P,P} = 9.8 Hz, P4); δ_P (121.5 MHz, CDCl₃, signals with resolved P-H coupling) -71.55 (dddd, ¹J_{P1,P2} = 243 Hz, ¹J_{P1,H1} = 193 Hz, ²J_{P1,P5} = 26.3 Hz, ²J_{P,P} = 9.9 Hz, P1); δ_C (75.5 MHz, CDCl₃) 32.3 (m, C(CH₃)₃), 32.52 (ddd, ³J_{C,P} = 8.5 Hz, ³J_{C,P} = 5.7 Hz, ²J_{C,P} = 2.9 Hz, C(CH₃)₃), 33.9 (ddd, ³J_{C,P} = 13.6 Hz, ³J_{C,P} = 3.1 Hz, ²J_{C,P} = 2.5 Hz, C(CH₃)₃), 36.4 (m, C(CH₃)₃), 36.8 (tdd, ²J_{C,P} = 10.4 Hz, ³J_{C,P} = 4.0 Hz, ²J_{C,P} = 2.5 Hz, C(CH₃)₃), 40.1 (ddd, ²J_{C,P} = 16.2 Hz, ²J_{C,P} = 13.0 Hz, ²J_{C,P} = 9.4 Hz, C(CH₃)₃), 40.4 (dd, ²J_{C,P} = 16.2 Hz, ²J_{C,P} = 5.2 Hz, C(CH₃)₃), 43.6 (dt, ²J_{C,P} = 13.1 Hz, ²J_{C,P} = 2.9 Hz, C(CH₃)₃), 57.0 (ddt, ¹J_{C,P} = 59.7 Hz, ¹J_{C,P} = 41.2 Hz, ²J_{C,P} = 5.2 Hz, C1), 72.7 (tdd, ¹J_{C,P} = 54.3 Hz, ¹J_{C,P} = 18.8 Hz, ²J_{C,P} = 8.9 Hz, C4), 86.7 (tt, ¹J_{C,P} = 39.5 Hz, ²J_{C,P} = 2.8 Hz, C2), 200.3 (ddm, ¹J_{C,P} = 58.8 Hz, ³J_{C,P} = 10.1 Hz, ³J_{C,P} = 3.9 Hz, C3). δ_{Se} (76.3 MHz, CDCl₃) -94.96 (d, ¹J_{Se1,P1} = 766 Hz); IR (KBr)

$\nu_{\max}/\text{cm}^{-1}$ 2954m, 2901sh, 2865sh (C–H), 2242w (P–H), 1456m (C–H), 1394m, 1362m (^tBu), 1181m (P=C), 582m (P=Se); ESI-ToF mass spectrum (DCM/MeOH) m/z 513.08 (MH^+ , 21%) 433.17, ($(\text{M} - \text{Se})\text{H}^+$, 100%). Spectroscopic data of **11b** in the ESI.[†]

Tri-seleno-tetra-tert-butyl-P₅-tetracycloundecane 12. 320 mg (0.74 mmol) **5** was dissolved in 20 mL of toluene and 117 mg (1.48 mmol, 2.0 äq) of selenium powder added. After 76 h stirring at 70 °C, the mixture was filtrated and the solvent removed in vacuum. Column chromatography at silica with *n*-hexane/DCM 1:1 and repeated recrystallization from *n*-hexane at –20 °C yielded 90 mg (0.13 mmol, 18%) pale yellow **12**. (Found C, 36.19%, H, 5.42%, $\text{C}_{20}\text{H}_{37}\text{P}_5\text{Se}_3$, requires C, 35.89%, H, 5.58%). NMR: δ_{H} (300 MHz, CDCl_3) 1.40 (d, $^4J_{\text{H,P}} = 2.7$ Hz, 9H, ^tBu), 1.42 (s, 9H, ^tBu), 1.52 (br s, 18H, ^tBu), 4.61 (d, $^2J_{\text{H1,P5}} = 14.7$ Hz, 1H, H1); δ_{P} ($^{31}\text{P}\{^1\text{H}\}$, 121.5 MHz, CDCl_3) 55.36 (dq, $^1J_{\text{P5,Se3}} = 715$ Hz, $^1J_{\text{P5,Se2}} = 409$ Hz, $^1J_{\text{P5,P1}} = 315$ Hz, $^2J_{\text{P5,P2}} = 30.7$ Hz, P5), 74.22 (dtd, $^1J_{\text{P4,P3}} = 413$ Hz, $^1J_{\text{P4,Se1}} = 169$ Hz, $^2J_{\text{P4,P1}} = 30.6$ Hz, $^2J_{\text{P,P}} = 3.8$ Hz, P4), 79.98 (dt, $^1J_{\text{P2,Se2}} = 222$ Hz, $^2J_{\text{P2,P5}} = 29.9$ Hz, $^2J_{\text{P,P}} = 4.7$ Hz, P2), 134.22 (ddm, $^1J_{\text{P1,P5}} = 316$ Hz, $^1J_{\text{P1,Se1}} = 178$ Hz, $^2J_{\text{P1,P4}} = 31.2$ Hz, P1), 148.23 (ddd, $^1J_{\text{P3,P4}} = 413$ Hz, $^2J_{\text{P,P}} = 31.8$ Hz, $^2J_{\text{P,P}} = 6.9$ Hz, P3). δ_{P} (121.5 MHz, CDCl_3 , signals with resolved P–H coupling) 55.37 (dddd, $^1J_{\text{P5,Se3}} = 714$ Hz, $^1J_{\text{P5,Se2}} = 408$ Hz, $^1J_{\text{P5,P1}} = 315$ Hz, $^2J_{\text{P5,P2}} = 30.6$ Hz, $^2J_{\text{P5,H1}} = 14.5$ Hz, P5); δ_{C} (75.5 MHz, CDCl_3) 33.06 (t, $^3J_{\text{C,P}} = 5.4$ Hz, $\text{C}(\text{CH}_3)_3$), 34.22 (s, $\text{C}(\text{CH}_3)_3$), 34.28 (d, $^3J_{\text{C,P}} = 3.4$ Hz, $\text{C}(\text{CH}_3)_3$), 34.42 (s, $\text{C}(\text{CH}_3)_3$), 37.95 (d, $^2J_{\text{C,P}} = 10.3$ Hz, $\text{C}(\text{CH}_3)_3$), 39.49 (d, $^2J_{\text{C,P}} = 29.7$ Hz, $\text{C}(\text{CH}_3)_3$), 40.07 (d, $^2J_{\text{C,P}} = 28.4$ Hz, $\text{C}(\text{CH}_3)_3$), 41.90 (dddd, $^2J_{\text{C,P}} = 30.2$ Hz, $^2J_{\text{C,P}} = 24.7$ Hz, $^2J_{\text{C,P}} = 19.6$ Hz, $^3J_{\text{C,P}} = 5.0$ Hz, $\text{C}(\text{CH}_3)_3$), 54.67 (dddt, $^1J_{\text{C,P}} = 76.6$ Hz, $^1J_{\text{C,P}} = 55.2$ Hz, $^1J_{\text{C,P}} = 50.3$ Hz, $^2J_{\text{C,P}} = 4.8$ Hz, C1), 84.92 (dddd, $^1J_{\text{C,P}} = 74.0$ Hz, $^1J_{\text{C,P}} = 21.2$ Hz, $^2J_{\text{C,P}} = 7.3$ Hz, $^2J_{\text{C,P}} = 4.7$ Hz, C2), 158.13 (ddd, $^1J_{\text{C,P}} = 58.2$ Hz, $^2J_{\text{C,P}} = 6.7$ Hz, $J_{\text{C,P}} = 2.1$ Hz, C3 or C4), 159.59 (ddt, $^1J_{\text{C,P}} = 42.8$ Hz, $^2J_{\text{C,P}} = 8.1$ Hz, $J_{\text{C,P}} = 3.2$ Hz, C4 or C3); δ_{Se} (76.3 MHz, CDCl_3) 74.34 (dt, $^1J_{\text{Se3,P5}} = 715$ Hz, $^2J_{\text{Se3,P1}} = 9.0$ Hz, Se3), 146.63 (ddm, $^1J_{\text{Se1,P1}} = 178$ Hz, $^1J_{\text{Se1,P4}} = 169$ Hz, Se1), 300.84 (dd, $^1J_{\text{Se2,P5}} = 409$ Hz, $^1J_{\text{Se2,P2}} = 222$ Hz, Se2); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 2954s, 2860sh, 2820sh (C–H), 1629w, 1609w (C=C), 1461m (C–H), 1390m, 1361m (^tBu), 1208 (C–H), 530s (P=Se); ESI-ToF mass spectrum (DCM/MeOH) m/z 670.92 (MH^+ , 60%) 1366.79 ($\text{M}_2\text{H}_2\text{Na}^+$, 100%).

[(P1-oxo-tetra-tert-butyl-P₅-deltacyclene)Cr(CO)₅] 13a. 40 mg (0.18 mmol) $\text{Cr}(\text{CO})_6$ was photolyzed in 5 mL of THF with a mercury vapor lamp for 30 min. The resulting orange solution of $[\text{Cr}(\text{CO})_5(\text{THF})]$ was added to a mixture of 55 mg (0.12 mmol) **9a** in 10 mL of THF at –40 °C, stirred for 40 min, allowed to reach room temperature slowly and stirred for 3d. After removal of the solvent in vacuum, 95% raw product contained the two complexes **13a** and **14** in a ratio of 89:11. Recrystallization from *n*-hexane at 4 °C led to 31 mg (0.048 mmol, 40%) yellow **13a**. Found C, 47.14%, H, 5.72%, $\text{C}_{25}\text{CrH}_{37}\text{O}_6\text{P}_5$ required C, 46.88%, H, 5.83%. Data of **13a** NMR: δ_{H} (300 MHz, CDCl_3) 1.23 (s, 9H, ^tBu), 1.51 (s, 9H, ^tBu), 1.56 (s, 9H, ^tBu), 1.69(d, $^4J_{\text{H,P}} = 1.2$ Hz, 9H, ^tBu), 8.61 (dddd, $^1J_{\text{H1,P1}} = 466$ Hz, $^2J_{\text{H1,P2}} = 37.4$ Hz, $^3J_{\text{H,P}} = 4.1$ Hz, $^3J_{\text{H,P}} = 1.4$ Hz,

1H, H1); δ_{P} ($^{31}\text{P}\{^1\text{H}\}$, (121.5 MHz, CDCl_3) –148.49 (dm, $^1J_{\text{P3,P2}} = 200$ Hz, P3), –68.87 (ddd, $^1J_{\text{P2,P3}} = 200$ Hz, $^1J_{\text{P2,P1}} = 133$ Hz, $^2J_{\text{P,P}} = 7.4$ Hz, P2), 46.46 (dd, $^1J_{\text{P1,P2}} = 133$ Hz, $^2J_{\text{P1,P5}} = 122$ Hz, P1), 79.84 (dt, $^2J_{\text{P5,P1}} = 122$ Hz, $^2J_{\text{P,P}} = 9.0$ Hz, P5), 370.93 (s, P4); δ_{P} (121.5 MHz, CDCl_3 , signals with resolved P–H coupling) –70.21 (dddd, $^1J_{\text{P2,P3}} = 200$ Hz, $^1J_{\text{P2,P1}} = 133$ Hz, $^2J_{\text{P2,H1}} = 37.5$ Hz, $^2J_{\text{P,P}} = 7.1$ Hz, P2); δ_{C} (75.5 MHz, CDCl_3) 32.18 (q, $^3J_{\text{C,P}} = 5.0$ Hz, $\text{C}(\text{CH}_3)_3$), 33.45 (dd, $^3J_{\text{C,P}} = 13.2$ Hz, $^3J_{\text{C,P}} = 9.0$ Hz, $\text{C}(\text{CH}_3)_3$), 34.09 (dd, $^2J_{\text{C,P}} = 10.9$ Hz, $^2J_{\text{C,P}} = 7.8$ Hz, $\text{C}(\text{CH}_3)_3$), 35.32 (ddd, $^3J_{\text{C,P}} = 9.8$ Hz, $^3J_{\text{C,P}} = 7.1$ Hz, $J_{\text{C,P}} = 2.7$ Hz, $\text{C}(\text{CH}_3)_3$), 35.32 (m, $\text{C}(\text{CH}_3)_3$), 38.22 (dm, $^2J_{\text{C,P}} = 7.0$ Hz, $\text{C}(\text{CH}_3)_3$), 38.44 (dd, $^2J_{\text{C,P}} = 15.2$ Hz, $^2J_{\text{C,P}} = 10.5$ Hz, $\text{C}(\text{CH}_3)_3$), 41.10 (ddd, $^2J_{\text{C,P}} = 18.7$ Hz, $^2J_{\text{C,P}} = 14.3$ Hz, $^3J_{\text{C,P}} = 3.9$ Hz, $\text{C}(\text{CH}_3)_3$), 59.70 (m, C1), 84.43 (dddd, $^1J_{\text{C,P}} = 34.6$ Hz, $^1J_{\text{C,P}} = 28.8$ Hz, $J_{\text{C,P}} = 4.4$ Hz, $J_{\text{C,P}} = 2.7$ Hz, C4), 92.86 (ddm, $^1J_{\text{C,P}} = 61.2$ Hz, $^1J_{\text{C,P}} = 52.9$ Hz, C2), 213.36 (dd, $^2J_{\text{C,P2}} = 11.5$ Hz, $^3J_{\text{C,P}} = 2.3$ Hz, *cis*-CO), 216.47 (m, C3), 219.00 (d, $^2J_{\text{C,P2}} = 2.1$ Hz, *trans*-CO); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 2959m, 2866sh (C–H), 2297w (P–H), 2069s, 1953s, 1935s (C=O), 1458m (C–H), 1396m, 1365m (^tBu), 1192m (P=O); FD mass spectrum (*n*-hexane): m/z 640 (M^+ , 100%), 448 [$\text{M} - \text{Cr}(\text{CO})_5$] $^+$, 39%). Spectroscopic data of **14** in the ESI.[†]

[(P1-hydroxo-tetra-tert-butyl-P₅-deltacyclene)Ru(C₆H₆)Cl₂] 15. 73 mg (0.16 mmol) **9a** and 64 mg (0.13 mmol) $[(\text{benzene})\text{RuCl}_2]_2$ were suspended in 5 mL of CH_2Cl_2 and stirred at room temperature for 5 h. The mixture was filtrated and the solvent removed in vacuum to yield 100 mg of a mixture of 61 mol% **15** and 39 mol% of $[(\text{benzene})\text{RuCl}_2]_2$. Crystallization from THF at –20 °C led to a few red crystals of **15**. Solutions of the crystals generate mixtures of **15** and **9a**/ $[(\text{benzene})\text{RuCl}_2]_2$ in a ratio of *ca.* 6:4. Data of **15** from the mixture NMR: δ_{H} (300 MHz, CDCl_3) 1.18 (s, 9H, ^tBu), 1.57 (s, 9H, ^tBu), 1.64 (s, 9H, ^tBu), 5.20 (br s, 1H, OH), 5.89 (s, 6H, C_6H_6); δ_{P} ($^{31}\text{P}\{^1\text{H}\}$, 121.5 MHz, CDCl_3) –123.12 (dt, $^1J_{\text{P3,P2}} = 157$ Hz, $^2J_{\text{P,P}} = 7.3$ Hz, P3), –112.23 (ddd, $^1J_{\text{P2,P1}} = 301$ Hz, $^1J_{\text{P2,P3}} = 157$ Hz, $^2J_{\text{P,P}} = 6.2$ Hz, P2), 66.99 (dddd, $^2J_{\text{P5,P1}} = 129$ Hz, $^2J_{\text{P5,P4}} = 9.4$ Hz, $^2J_{\text{P,P}} = 8.9$ Hz, $^2J_{\text{P,P}} = 8.7$ Hz, P5), 151.88 (ddt, $^1J_{\text{P1,P2}} = 301$ Hz, $^2J_{\text{P1,P5}} = 129$ Hz, $^2J_{\text{P,P}} = 5.1$ Hz, P1), 367.21 (dd, $^2J_{\text{P4,P5}} = 12.2$ Hz, $^2J_{\text{P,P}} = 3.2$ Hz, P4); no clear separation of ^{13}C NMR signals; ESI-ToF mass spectrum (cryospray, –40 °C) m/z 912.96 [$\{(\text{C}_{20}\text{H}_{37}\text{OP}_5)\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}\}^+$, 100%), 876.99 [$\{(\text{C}_{20}\text{H}_{37}\text{OP}_5)\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}\text{Ru}(\text{C}_6\text{H}_6)\}^+$, 7%).

P1-oxo-P1-chloro-tetra-tert-butyl-P₅-norsnoutene 16. 62 mg (0.14 mmol) **9a** in 20 mL of THF were cooled down to –80 °C. 100 μL (0.16 mmol) of *n*-BuLi in *n*-hexane (1.6 mol L $^{-1}$) was added and the color turned to dark blue. After 30 min stirring, the cooling bath was removed and the mixture stirred for 24 h at room temperature. While warming up, the color changed slowly to red brown. Removal of the solvent in vacuum led to a dark red residue. A CDCl_3 solution of the residue contained P1-oxo-tetra-tert-butyl-P₅-norsnoutene **17** and its derivative **16** in a ratio of 8:92. Recrystallization from *n*-hexane at –20 °C led to 13 mg (0.027 mmol, 19%) yellow $\text{C}_{20}\text{H}_{36}\text{ClOP}_5$ **16**. Data of **16** NMR: δ_{H} (300 MHz, CDCl_3) 0.97 (s, 9H, ^tBu), 1.40 (s, 9H, ^tBu), 1.44 (d, $^4J_{\text{H,P}} = 2.4$ Hz, 9H, ^tBu), 1.75 (s, 9H, ^tBu); δ_{P} ($^{31}\text{P}\{^1\text{H}\}$, 121.5 MHz, CDCl_3) –174.50 (dddd, $^1J_{\text{P2,P3}} = 165$ Hz,

$^2J_{P2,P5} = 26.7$ Hz, $^2J_{P2,P1} = 16.1$ Hz, $^2J_{P,P} = 10.7$ Hz, P2), -171.89 (dt, $^1J_{P3,P2} = 165$ Hz, $^2J_{P,P} = 9.0$ Hz, P3), -21.80 (dd, $^2J_{P5,P2} = 26.5$ Hz, $^2J_{P5,P1} = 13.2$ Hz, P5), 96.68 (dddd, $^2J_{P1,P2} = 17.1$ Hz, $^2J_{P1,P5} = 13.4$ Hz, $^2J_{P,P} = 8.5$ Hz, P1), 365.05 (q, $^2J_{P,P} = 11.3$ Hz, P4); ESI-ToF mass spectrum (DCM/CH₃CN 1 : 2) m/z 505.10 (MNa⁺, 94%), 987.22 (M₂Na⁺, 100%). Spectroscopic data of 17 in the ESI.†

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