Experimental Section

All experiments were performed under a nitrogen atmosphere in a glove box (MBraun) or by using standard Schlenk techniques. [Mo(N-2,6-iPr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$·DME, [Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$]·DME, and [Mo(N-2,6-iPr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OC(CH$_3$)$_3$)$_2$] (**1**) as well as other compounds were prepared following literature procedures.[20] Experimental details can be found in the Supporting Information.

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Ambiphilicity: A Characteristic Reactivity Principle of π-Bound Phosphorus Heterocycles[**]

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Frank W. Heinemann, Matthias Hennemann,
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Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday.

Cyclooligomerization of phosphaalkynes, such as tBuC≡P (**1**), in the coordination sphere of reactive metal complexes predominantly leads to π complexes of the cyclodimer 1,3-diphosphete[1–4] or the cyclotrimer 1,3,5-triphosphabenzene.[5] However, pentaphosphametallocenes, such as the pentaphosphaferrocene derivative **2**, are obtained with reactive iron complexes[6,7] or free metal atoms.[8] Their formation requires that at least one P–C triple bond be broken (Scheme 1).

Oligophosphametallocenes are easily accessible substances with a series of interesting properties.[9] Thus, there is much interest in determining the mechanism of their formation. Because complete cleavage of **1** is very unlikely, even at a transition-metal center, we assume that initially formed cycloaddition products from **1** undergo intra- or intermolec-

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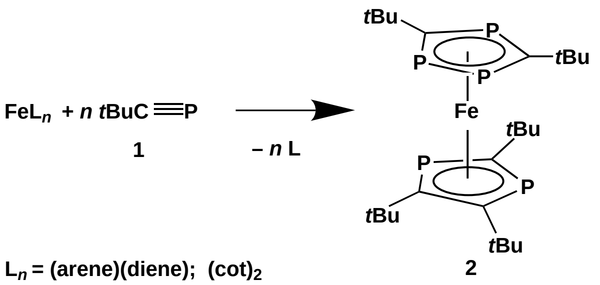
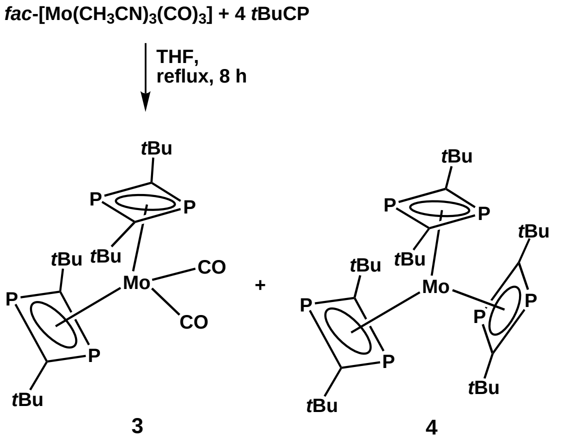
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Formation of pentaphosphaferrocene **2**.

ular interactions with each other that allow the exchange of phosphorus atoms or *t*BuC-fragments under mild conditions. One convincing indication that this is the case, the observation of strong intramolecular interactions between Mo-coordinated 1,3-diphosphete ligands is reported herein. These interactions serve as a novel model for the initial step in the exchange of ring components of π-coordinated P heterocycles.

We treated *fac*-[Mo(CH$_3$CN)$_3$(CO)$_3$] with **1**, with the aim of synthesizing [Mo(CO)$_2$(2,4-di-*t*Bu-1,3-diphosphete)$_2$] (**3**). In contrast to earlier reactions of molybdenum–carbonyl complexes with **1**,[10,11] we were able to isolate **3** as the main product. However, to our surprise we also found the known complex [Mo(2,4-di-*t*Bu-1,3-diphosphete)$_3$] (**4**) as a by-product. The published molecular structure of **4** in the solid state shows an unusual feature, the P–C separation between two of the rings is only 215 pm, a very short distance that is hard to explain (Scheme 2).[12]



Scheme 2. Formation of (1,3-diphosphete)–Mo complexes.

Differences to the published data[12] obtained at low temperatures led us to investigate the structural chemistry of **4** more closely. We therefore performed single-crystal analyses at temperatures of 100, 150, 200, 240, and 293 K. An intramolecular, fully reversible topotactic reaction between the ligands of **4** is observable in the crystal structures. Figure 1 shows the superposition of the two extremes of the molecular structures of **4** at 100 (**4a**) and 293 K (**4b**). Structure **4b** is identical to the published data within the margins of error (Figure 1).[12,13]

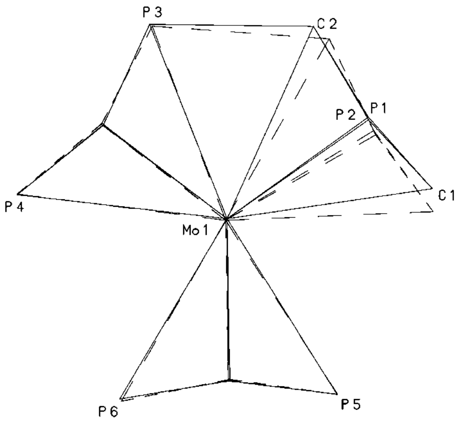
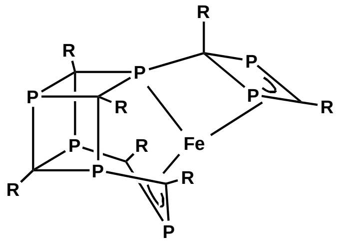


Figure 1. Side view of the superimposed molecular structures of **4** in the single crystal at 100 K (**4a**, full lines) and at 293 K (**4b**, dashed lines). The *t*Bu groups of the rings have been omitted for clarity.[13] Selected distances **4a** {**4b**} [Δ = **4a**–**4b**] in pm: Mo1-C2 256.69(19) {254.2(3)} [+2.48], C2-C21 157.6(3) {156.2(4)} [+1.4], C1-P1 179.3(3) {181.5(3)} [−2.2], C2-P1 189.3(2) {186.4(3)} [+2.9], C3-P3 181.5(2) {180.1} [+1.4], C1-P5 275.9(13) {251.0(21)} [+24.9], C2-P3 198.8(2) {215.1(4)} [−16.3].

Structures **4a** and **4b** are very similar, in accord with the requirements of a topotactic reaction.[14] The main fragment {Mo(C3P3C4P4)(C5P5C6P6)} only changes minimally, whereas in **4a** C1P1C2P2 has moved towards the C3P3C4P4 ring. The unusually short inter-ring separation C2–P3 decreases from 215.1 (**4b**) to 198.8 pm (**4a**), a distance that is consistent with a slightly stretched single bond.[15] The shortening of this separation by 16.3 pm occurs concurrently with a lengthening of the inter-ring distance C1–P5 by 24.9 pm and a localization of the π interaction in the C1P1C2P2 ring in **4a**. The other rings, in contrast, are delocalized, with essentially equivalent bond lengths. The bonds C2−P1 and C2−P2 with an average length of 189.2 pm correspond to P−C single bonds, whereas the C1−P1 and C1−P2 separations (179.2 and 179.3 pm, respectively, see Supporting Information for numbering scheme) suggest significant P−C double bond character.

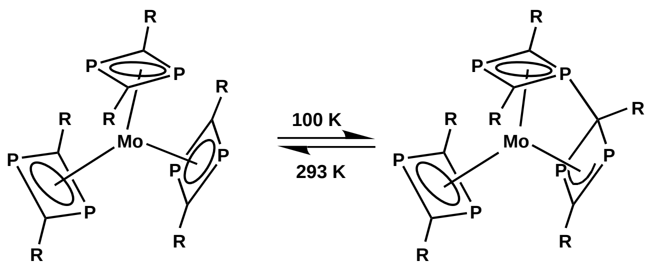
An almost identical structural unit is found in **5**, the iron complex of a polycyclic heptamer of **1**. The four-membered



5 R = *t*Bu

ring in **5** is clearly 1,3-diphosphetenyl, an sp^3-carbon-bridged π-coordinated diphosphaallyl system. The two P–C separations of the diphosphaallyl unit in **5** are 178 pm and the intraannular P−C single bonds are 191 and 192 pm long (Scheme 3).[16]

The same interpretation seems appropriate for **4a**. The P–C contact between the rings, which is short even at room temperature, is so strengthened at low temperatures that the



4b **4a**

Scheme 3. Molecular description of the topotactic bond formation.

C2–P3 interaction can be seen as a covalent bond. Atom C2 is converted into an sp^3-hybridized center on formation of this bond and thus C2 no longer contributes to the delocalized π system of the ring and the Mo1−C2 bond is broken. Both the formation of the P3−C2 bond and the lengthening of the inter-ring distance between C1 and P5 occur continuously within the temperature range investigated and are fully reversible (Figure 2).

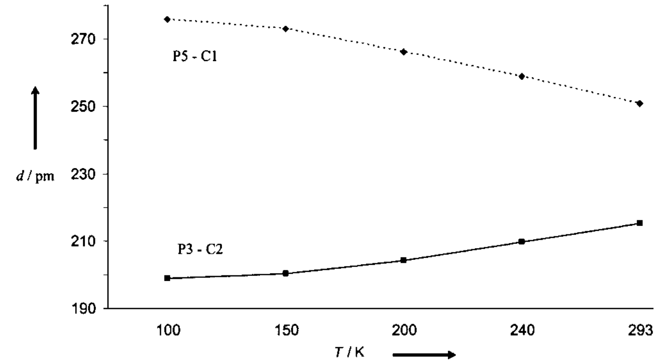


Figure 2. Temperature dependence of the P3–C2 and P5–C1 separations in pm. 100 K: P3-C2 198.8(2), P5-C1 275.9(13); 150 K: 200.3(6), 273.0(14); 200 K: 204.0(1), 266.2(16); 240 K: 209.6(1), 259.0(15); 293 K: 215.1(4), 251.0(21).

To our knowledge such intramolecular bond-formation reactions between π ligands at metal centers have not been described before. The structural type of the new bicyclic ligand is also without precedence. Reversible chemical reactions in which single crystals are conserved are also very rare, at least for metal complexes.[17] To explain this phenomenon qualitatively we assume a nucleophilic attack of the lone pair of P3 on C2. The total number of electrons supplied by the ligands in **4a** remains constant despite the loss of the Mo1−C2 bond because the 1,3-diphosphaallyl fragment can be regarded as a formal anion. In contrast, the aromaticity of the C3P3C4P4-ring is retained, as shown by quantum-mechanical calculations (see below). Thus, P3 formally forms a pyramidal phosphonium center, a further interesting structural detail.[18]

DFT calculations on the model compound [Mo{tris(2,4-dimethyl-1,3-diphosphete)}] (**6**) and the unsubstituted prototype compound **7** were performed to aid the analysis of the bonding situation in **4**. The calculations used Gaussian 98[19] with the B3LYP hybrid functional[20] and the LanL2DZ basis set.[21] The basis set was extended with a set of d-functions with exponents of 0.6 and 0.34 on C and P, respectively, and p-functions with an exponent of 0.072 on the Mo center.[22] Reaction paths in which the P3–C2 separation (comparable to C1–P5) was varied from 180 to 260 pm were calculated for the model compounds. The resulting energy profile for **6** is shown in Figure 3.

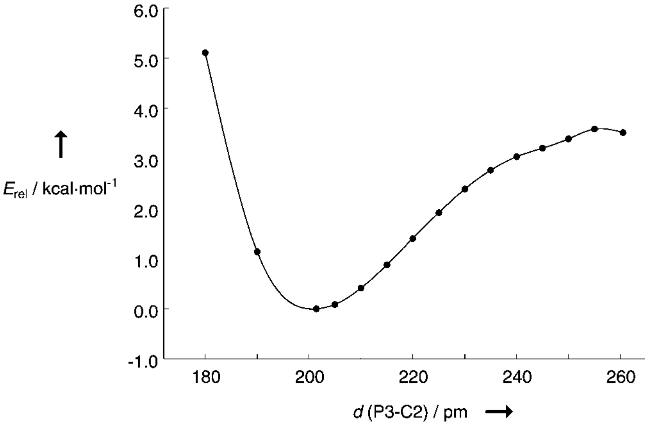


Figure 3. Calculated reaction profile for **6a**→**6b**.

Two isoenergetic minima with C$_s$ symmetry and P3–C2 (or P5–C1) distances of 201.4 pm (**6a**) and a 3.5 kcal mol^{-1} less stable C_{2v} transition structure (**6b**) were obtained for the methyl-substituted compound (Figure 4). In contrast, the prototype compound **7** gives a broad, flat energy profile without a definitive structural preference. The C_s structure **6a** agrees surprisingly well with that found experimentally at 100 K in the crystal (**4a**). Even the critical C2–P3 and Mo1–C2 distances are almost identical. Larger differences are found for the nonbonding inter-ring distances C1–P5 (306.0 com-

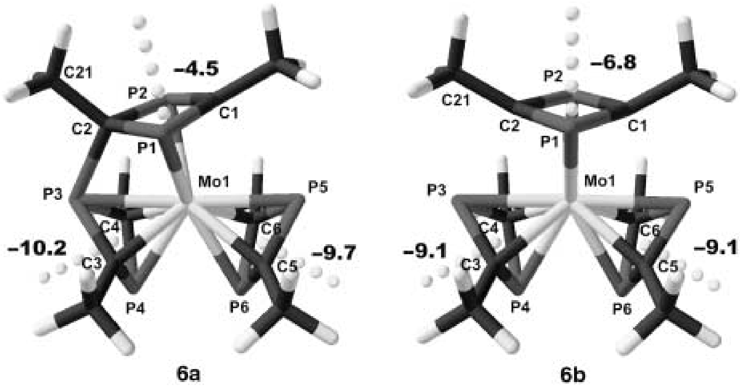
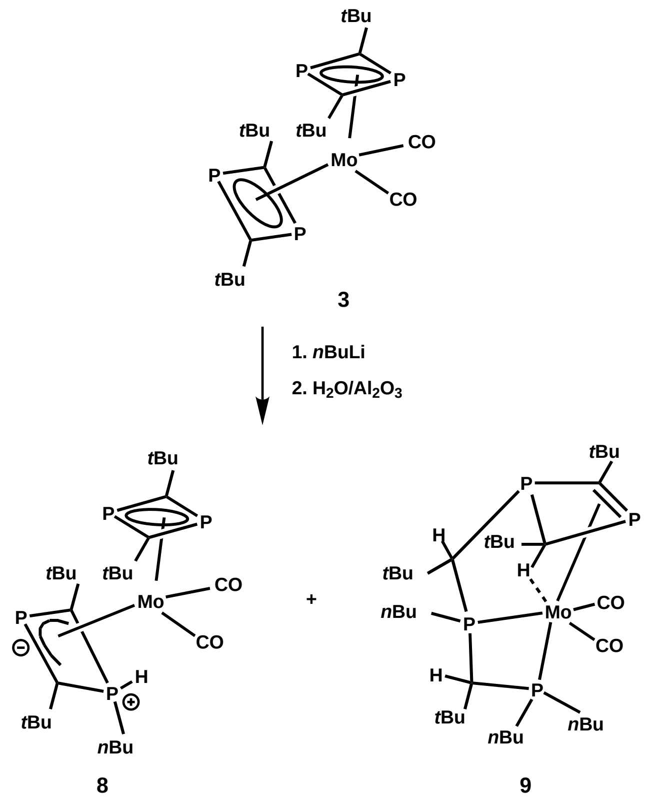


Figure 4. Calculated structures and NICS-1-values for the minimum-energy structure **6a** and the transition state **6b** from **6**. Selected distances **6a** {**6b**} [Δ = **6a**–**6b**] in pm, the numbering is analogous to **4**: Mo1-C2 256.9 {245.8} [+11.1], C2-C21 154.2 {152.3} [+1.9], C1-P1 180.3 {184.5} [−4.2], C2-P1 192.7 {184.5} [+8.2], C3-P3 186.6 {182.3} [+4.3], C3-P4 185.4 {185.1} [+0.3], C1-P5 306.0 {260.7} [+45.3], C2-P3 201.4 {260.7} [−59.3]. Selected Wiberg bond orders **6a** {**6b**}: Mo1-C2 0.1966 {0.3688}, Mo1-P3 0.2678 {0.3177}, C2-C21 1.0253 {1.0611}, C1-P1 1.0995 {0.9808}, C2-P1 0.8577 {0.9808}, C3-P3 0.9063 {1.0081}, C3-P4 0.9686 {0.9525}, C1-P5 0.1044 {0.2458}, C2-P3 0.6940 {0.2458}.

pared to 275.9 pm) and P4–P6 (263.0 compared to 278.0 pm). These differences are probably caused by simplifying the substituents from *t*Bu to methyl and do not decrease the value of the modeling exercise significantly.

Wiberg bond orders[23] were used to analyze the bonding situation. These support the interpretation derived from the structural data. This is most clearly seen in the P3–C2 interaction, for which a bond order of 0.69 is found in **6a**, compared with only 0.25 in **6b**. The value for the Mo1–C2 interaction decreases significantly (from 0.37 to 0.20) on going from **6b** to **6a**, but the Mo1–P3 interaction is weakened far less (from 0.32 to 0.27). Thus the Mo1-C3P3C4P4 fragment is almost unaffected by the inter-ring P3—C2 bond formation, whereas the Mo1—C2 bond is weakened significantly, which results in the Mo–diphosphaallyl system Mo1-C1P1P2. The C1—P1 and C1—P2 bonds become stronger (bond order: 0.98→1.10) and those between C1—P1 and C2—P2 weaker (bond order: 0.98→0.86). Identical conclusions can be reached from the calculated nucleus independent chemical shifts (NICS)[24] (Figure 4), which describe the cyclic delocalization of the π electrons (i.e. the aromaticity of the ligands), and from the net atomic charges obtained from a natural population analysis (NPA).[25] According to these criteria, the aromaticity of the 1,3-diphosphetenyl ring C1P1C2P2 decreases significantly, whereas it actually increases slightly for the C3P3C4P4-ring. The NPA shows P3 in **6a** to be 0.1 more positive than in **6b**, whereas C2 becomes -0.15 more negative. This suggests a partial charge-transfer from P3 to C2. The NPA charges are thus in accord with the formal view of a nucleophilic attack of P3 on C2. As all the calculated parameters for **6a** agree well with the experimentally determined structure for **4a**, we conclude that **4a** represents the real thermodynamic minimum for the complex **4**. The influence of the *t*Bu substituents and the crystal lattice on the bonding within the ligands is therefore of secondary importance. However, the lattice forces allow for the synchronization of the intramoleular reaction in the crystal, which can thus take place topotactically.

Thus, 1,3-diphospete ligands display electrophilic character additionally to their inherent nucleophilicity; they are thus ambiphilic. There is only one report of the electrophilicity of neutral diphosphete complexes.[26] Therefore, to test our hypothesis, we treated **3** with *n*BuLi as the nucleophile and protonated the resulting reaction products. In this way we were able to add one or three *n*-butyl groups to obtain [Mo(CO)$_2$(1,3-diphosphete)(1,3-diphosphetenyl)] (**8**) and [Mo(CO)$_2$(1,3-diphospheten-3-diphosphaoctyl)] (**9**; Scheme 4, Figure 5).[27]

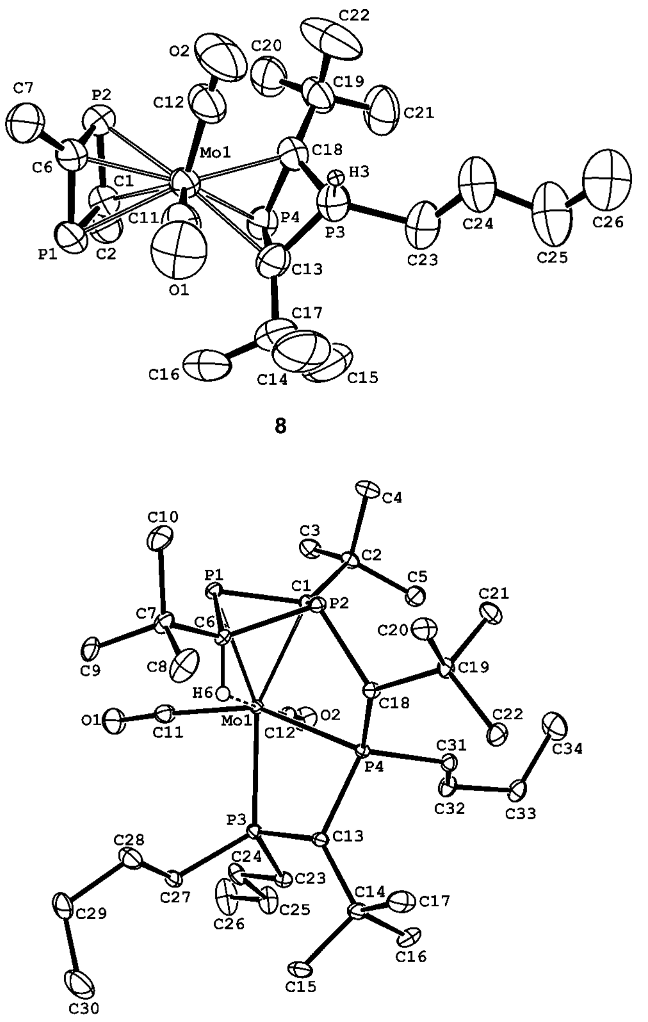


Scheme 4. The addition of nucleophiles.

Both of these complexes have structures that make a detailed theoretical analysis necessary. These investigations are not yet complete. The bonding situation of the P1C1P2C6 four-membered ring in **9** is particularly difficult to understand. Although there seem to be no obstacles to the formation of a phosphaallyl system in the protonation step, as found in **8**, this does not occur, but rather a 1,3-diphosphetene ligand that can only contribute two π electrons to the metal center is formed. The metal attempts nevertheless to attain an 18 valence electron structure by an agostic interaction (C6H1···Mo1).[28] The unequivocably determined connectivity of the molecular components leads us, however, to the central question of this project. The constitution and the molecular structures of **8** and **9** show that Mo^0-coordinated 1,3-diphosphete ligands are electrophilic. However, the initial attack of the nucleophile occurs at the phosphorus atom, analogously to the situation found for the cation of the salt [Mo(CO)$_2$(indenyl)(2,4-di-*t*Bu-1,3-diphosphete)]$^+$BF$_4^-$.[29] The reaction sequence is completed for **8** by a stereoselective protonation of the metal side of the phosphorous atom, which is evidence for the entry of the carbanion from outside.[26] A heteroallyl system is formed, as in the case of **4a**, but in this case it is a 2-phosphaallyl. Because, however, a ring carbon atom plays the role of the electrophile in the intramolecular reaction, but a phosphorous atom plays the role of the electrophile in the intermolecular version, the electrophilicity of these two different types of ring atom in (1,3-diphosphete)Mo^0 units cannot be very different.

The ambiphilicity of 1,3-diphosphete ligands caused by the phosphorus atoms is a characteristic that has not been observed previously in this type of complex. We can only begin to judge the effect of this ambiphilicity on the reactivity of the complexes because 1,3-diphosphete complexes have proven to be very robust.[30] The polydentate ligand in **9** shows that the ambiphilic intramolecular reactivity of 1,3-diphosphete ligands can also operate despite strong competition from other nucleophiles. The P2–C18 bond between the remaining ring and its new side chain is the result of an intramolecular step although three carbanions are added to one ring. The ring that is attacked thus not only loses its π system, but is also ring-opened.

1,3-Diphosphetes, and probably other unsaturated P heterocycles, can, by reason of their ambiphilicity, take part in



8

9

Figure 5. Molecular structures of **8** (298 K) and **9** (100 K). All hydrogen atoms except H3 and the methyl groups on the quaternary carbons C2 and C7 in **8** have been omitted for clarity. All hydrogens are ommitted in **9** except H6.[27]

nucleophilic or electrophilic intramolecular interactions. This situation is a new starting point for determining the complex reaction sequences of π ligands with lone pairs in the coordination spheres of metal centers, which, for instance, we must assume to take place in the formation of pentaphosphametallocenes from phosphaalkynes. If we assume the process that forms 1,3-diphosphete and 1,3,5-triphosphinine ligands[1–5] to be the first step, as discussed in the introduction, a P–C bond can be formed between the ligands as in **4**. We have used preliminary DFT calculations for [Fe(1,3-diphosphete)(1,3,5-triphosphinine)] to investigate the viability of this approach. Given this linkage between the ligands, there are no more fundamental theoretical problems in the exchange of ring components.

Other ligand-construction reactions that are at present not understood may also be traced back to the ambiphilicity of P atoms in coordinated heterocycles. This is, for instance, the case for [W(2,4-di-*t*Bu-1,3-diphosphete)$_3$] with a P–C inter-ring distance of 207.1 pm at 200 K,[31] for the P–C bond between the pentamer cage and the four-membered ring of the heptamer ligand in **5**,[16] or the formal addition product of coordinated 1,3-diphosphetes or 1-phosphetes with phosphaalkynes. In these cases, π-coordinated phosphaallyl structures are found once again.[32]

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[13] Crystal data for **4**: $C_{30}H_{54}MoP_6$, $M_r = 696.49$, triclinic, space group $P\bar{1}$. Measurements taken with a Bruker AXS Smart1000 area detector ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 100, 150, 200, 240, 293 K up to $\Theta = 32°$. The structure was solved with direct methods, least-squares refinement against F^2 (SHELXTL NT V5.10).[33] Cell parameters at 100 K (**4a**): $a = 10.7538(14)$ $b = 11.0127(14)$, $c = 14.9561(19)$ Å; $\alpha = 79.585(3)$, $\beta = 74.568(3)$, $\gamma = 89.650(3)°$; $V = 1677.6(4)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.379\ g\,cm^{-3}$; $\mu = 0.696\ mm^{-1}$; $F(000) = 732$. $R_1 = 0.0354$ (for 10962 Reflections with $I > 2\sigma(I)$, $wR_2 = 0.0925$ (for all data).
Cell parameters at 293 K (**4b**): $a = 10.7548(12)$, $b = 11.0149(13)$, $c = 15.3513(18)$ Å, $\alpha = 78.310(2)$, $\beta = 74.916(2)$, $\gamma = 87.842(2)°$, $V = 1719.3(3)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.345\ g\,cm^{-3}$; $\mu = 0.679\ mm^{-1}$; 8524 independent reflections. $R_1 = 0.0373$ (for 8524 reflections with $I > 2\sigma(I)$, $wR_2 = 0.089$ (for all data). CCDC 184248–184252 (**4** at 100, 150, 200, 240, and 293 K) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[27] Crystal data for **8**: ($C_{26}H_{46}MoO_2P_4$), $M_r = 610.45$, triclinic, space group $P\bar{1}$; cell parameters $a = 10.116(5)$, $b = 11.312(5)$, $c = 13.960(6)$ Å; $\alpha = 77.17(4)$; $\beta = 89.52(4)$; $\gamma = 87.07(4)°$; $V = 1556(2)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.303\,g\,cm^{-3}$; $\mu = 0.647\,mm^{-1}$; $F(000) = 640$. Measurements taken on an automatic four circle diffractometer (Nicolet R3m/V, graphite monochromatized $Mo_{K\alpha}$-radiation, $\lambda = 0.71073$ Å) at 298 K in the 2θ-range from 3.70 to 54.00°. 6790 symmetry-independent reflections. The structure was solved as for **4**, $R_1 = 0.0479$ (for 4782 reflections with $F_0 \geq 4.0\sigma(F)$), $wR_2 = 0.1179$ (for all data). The position of the H atom bonded to P3 was obtained from a difference-Fourier analysis. All other hydrogen atoms are positioned according to geometrical considerations. Crystal data for **9**: ($C_{34}H_{66}MoO_2P_4$), $M_r = 726.69$, orthorhombic, space group *Pbca*; cell parameters $a = 14.4264(4)$, $b = 20.6977(3)$, $c = 25.7650(6)$ Å; $V = 7693.3(3)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.255\,g\,cm^{-3}$; $\mu = 0.534\,mm^{-1}$; $F(000) = 3104$. Measurements taken on a Nonius KappaCCD ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 100 K in the 2θ-range from 6.7° to 64.0°. 13322 symmetry-independent reflections. The structure was solved as for **4**, $R_1 = 0.0445$ (for 8044 reflections with $F_0 \geq 4.0\sigma(F)$), $wR_2 = 0.0923$ (for all data). The position of all H atoms could be obtained from a difference-Fourier analysis. CCDC-184253 (**8**) and CCDC-184254 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Enantioselective Stereoinversion in the Kinetic Resolution of *rac-sec*-Alkyl Sulfate Esters by Hydrolysis with an Alkylsulfatase from *Rhodococcus ruber* DSM 44541 Furnishes Homochiral Products**

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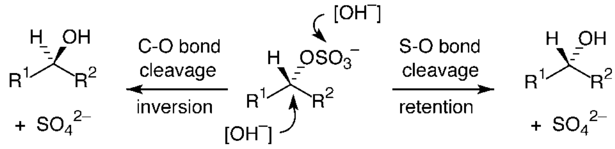
Sulfatases catalyze the hydrolytic cleavage of the sulfate ester bond by liberating inorganic sulfate and the corresponding alcohol.[1] Depending on the nature of the enzyme and its catalytic mechanism, enzymatic hydrolysis of *sec*-alkyl sulfates may proceed through retention—by cleavage of the S–O bond—or inversion—by the cleavage of the C–O bond—of configuration at the chiral carbon atom (Scheme 1).[2,3]



Scheme 1. Stereochemical pathways of enzymatic sulfate ester hydrolysis.

The ability of *sec*-alkylsulfatases to effect stereoinversion during catalysis makes them prime candidates for their application in so-called enantioconvergent processes,[4] which allow the enantioselective transformation of enantiomers by opposite stereochemical pathways to furnish a single stereoisomeric product in 100% theoretical yield. Other enzymes, which potentially show this ability are a) epoxide hydrolases,[5] b) dehalogenases,[6] and c) glycosidases.[7] A limited number of alkylsulfatases have been biochemically characterized[1] but to date, these enzymes have not been applied to preparative biotransformations.[8]

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