Coordination chemistry of phosphanyl amino acids: solid state and solution structures of neutral and cationic rhodium complexes

Christian Meyer,[a] Markus Scherer,[a] Hartmut Schönberg,[a] Heinz Rüegger,[a] Sandra Loss,[a] Volker Gramlich[b] and Hansjörg Grützmacher*[a]

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Copper phosphide or arsenide complexes, $[Cu(EPh_2)(neo)]$ (E = P, As, neo = 2,9-dimethyl-1,10-phenanthroline; trivial name: neocuprine) react selectively with the N-protected brominated serine derivatives, 2-(*S*)-(alkoxycarbonylamino)-3-bromomethylpropionates **1a–c** (^{ROCO}SerBr, **a**: R = $PhCH_2$, **b**: tBu, **c**: Me) to give the corresponding phosphanylated or arsanylated amino acids, ^{ROCO}SerPhos (**3a–c**: Phos = PPh_2) and ^{Z}SerArs **7** (Ars = $AsPh_2$, Z = $PhCH_2OCO$). The dipeptide ^{Z}AlaSerPhos **3d** was likewise prepared. The phosphanes **3a–d**, and the arsane **7** reacted cleanly with $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ to give the rhodium(I) complexes [RhCl(cod)(^{Z}SerPhos)] **8**, [RhCl(cod)(^{Boc}SerPhos)] **9** (Boc = *t*BuOCO), [RhCl(cod)(^{Z}AlaSerPhos)] **10**, and [RhCl(cod)(^{Z}SerArs)] **11** which were characterized by X-ray diffraction studies. A common structural feature is an intramolecular (N)H $\cdots$ Cl(Rh)-hydrogen bridge which according to NMR investigations remains intact in solution. The abstraction of chloride from the coordination sphere of Rh(I) in **8** or **10** has a profound structural impact. While in **8** and **10**, the ligands bind in a monodentate fashion, *via* the phosphorus atom only, they serve as bidentate ligands *via* the phosphorus centre and the peptidic C=O group in [Rh(cod)(κ^2-^{Z}SerPhos)]PF_6 **12** and [Rh(cod)(κ^2-^{Z}AlaSerPhos)]PF_6 **13**. This causes also the amino acid residue structures to change from α-helix type in **8** and **10** to a β-sheet type in **12** and **13**. Addition of chloride to **12** and **13** fully re-establishes the structures of **8** and **10**. The complexes [RhCl(cod)(^{Z}SerPhos)] **8** and [RhCl(cod)-(^{Boc}SerPhos)] **9** show good activities in homogeneously catalyzed hydrogenations of olefins while the dipeptide complex **10** is less active. Phosphane addition to **8** greatly diminishes the catalytic activity. The cationic complex [Rh(cod)(κ^2-^{Z}AlaSerPhos)]PF_6 shows low activity which, however, is greatly increased by addition of one equivalent of phosphane.

1 Introduction

It is an attractive goal to incorporate the complexity of natural structures into ligands for transition metal complexes used in homogeneous catalysis.[1] Carbohydrates, peptides and proteins offer such structural diversity and hence are potential targets for further functionalization. In order to enhance the stability of the catalytic entities one needs to bind tightly the catalytically active late transition metal centres (*i.e.* Rh, Ir, Pd, Pt, *etc.*) and for that purpose non-natural donor centres may be introduced into the natural ligand framework. Among these, phosphanyl groups, R_2P–, are immediately evident because many phosphane complexes proved to be active catalysts (or precursors to such),[2] phosphanes show sufficiently high binding constants to metals,[3] and phosphanyl groups itself can be sterically and electronically tuned *via* different substituents R. Phosphanes with carbohydrate backbones are meanwhile firmly established as rather easily accessible ligands in enantioselective catalysis.[4] Phosphanyl-substituted peptides have been investigated in the last years mainly by Gilbertson and co-workers as ligands in homogeneously transition metal catalyzed reactions.[1] Especially, serine[5] and proline[6] based phosphanes proved to be suitable for this purpose and for the parallel syntheses of large ligand libraries.[1,7] The (phosphanyl)polypeptides were transformed into rhodium complexes and tested in catalytic hydrogenations. In some cases these experiments were performed with the catalyst precursors still attached to the support used for polypeptide synthesis. A further interesting development in this area is the possibility to incorporate the (phosphanyl)peptides in larger aggregates with some sort of tertiary structures.[7a] This idea has been tested with some success with (phosphanyl)carbohydrates organized on the surface of micelles which led to an increase of the enantioselectivity in catalytic hydrogenations.[4c] The attachment of achiral rhodium complexes to chiral carbohydrate or peptide amphiphiles is particularly interesting, but had little success so far.[8]

Some structural data for bis(phosphanyl)amino peptides and their complexes were obtained from NMR spectroscopic studies in solution and the structure of a dodecamer containing two (diphenylphosphano)serine (SerPhos) units in internal positions *i* and *i* + 4 could be determined by X-ray analyses.[9] However, many fundamental aspects of the coordination chemistry of phosphanyl peptides remain to be investigated. In this paper we report: (i) the details of the synthesis of phosphanyl- and arsanyl-substituted amino acids using a method developed in our laboratory;[10] (ii) the X-ray structure analyses of (phosphanyl)- and (arsanyl)-amino

[a]*Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Hönggerberg, HCI H131, CH-8093, Zürich, Switzerland. E-mail: gruetzmacher@inorg.chem.ethz.ch; Fax: int. +41 1 632 1032*
[b]*Laboratory of Crystallography, Wolfgang-Pauli-Str. 10, ETH Hönggerberg, HCI G 503, CH-8093, Zürich, Switzerland*

acid metal complexes, *i.e.* [RhCl(^{R}SerPhos) and [RhCl(^{R}SerArs)] with R = substituent at the N-terminus of the coordinated amino acid; (iii) a comparison of the solid state structures with the corresponding structures in solution (determined by NMR) and, specifically, how changes in the coordination sphere of the transition metal centre cause significant structural changes of the peptide residues. (vi) Finally, we report results concerning the performance of these complexes as precursors in catalytic hydrogenations.

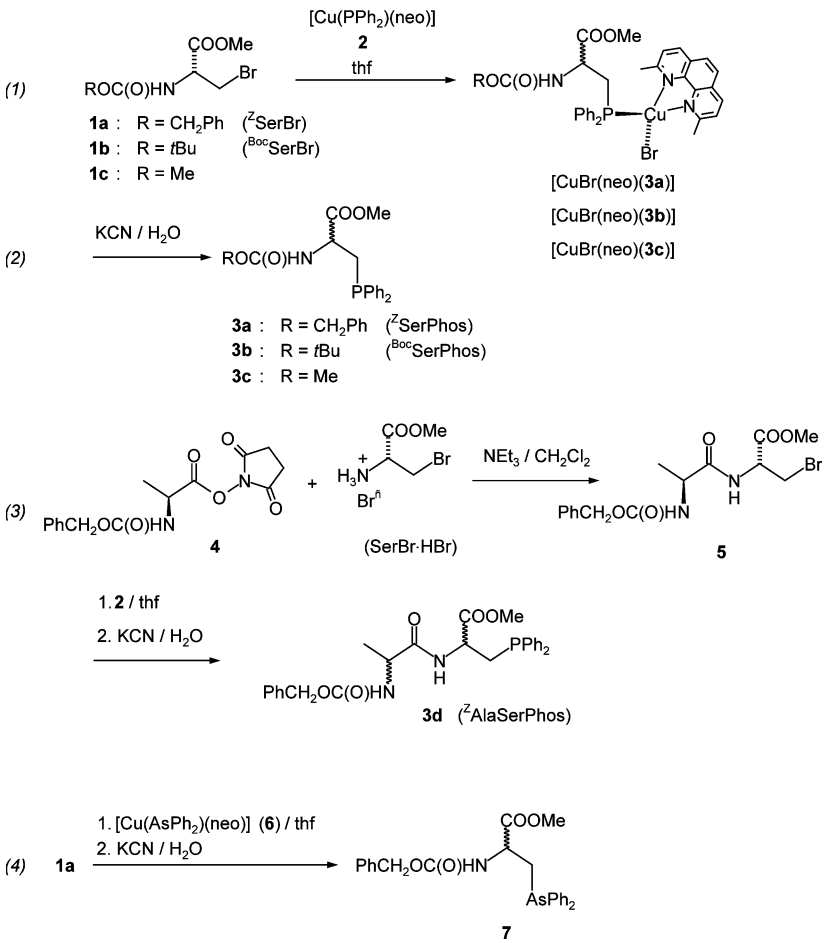
2 Results and discussion

Syntheses

In contrast to Gilbertson's approach consisting in synthesizing a small phosphanyl-substituted amino acid building block which is used in subsequent coupling reactions in order to obtain larger peptides, we thought it might be an equally valuable alternative to find a selective reagent which allows the introduction of the phosphanyl group into the peptide as disclosing step of ligand synthesis. Indeed, copper phosphide complexes with heterocyclic nitrogen ligands like **2** are such reagents and allow the selective replacement of halogenide functionalities for Ph_2P groups.[10] Other functional groups as carbonyl groups do not interfere (Scheme 1). Thus, the 3-bromo-2-*N*-carboxymethylpropionate derivatives **1a–c** derived from serine react smoothly at room temperature with **2** under Br/Ph_2P exchange to give the phosphanyl amino acid copper complexes [CuBr(neo)(**3a–c**)] as orange–yellow substances (neo = 2,9′-dimethylphenanthroline).

As N-protecting groups, we used *N*-benzyloxy carbonyl, $PhCH_2OCO$ = Z, *N*-*tert*-butoxycarbonyl, *t*BuOCO = Boc and *N*-methoxycarbonyl, MeOCO. The copper complexes can be isolated and [CuBr(neo)(**3c**)] was obtained in high yield (87%). Usually, however, the reaction mixtures were treated with KCN/H_2O in order to deliberate the free phosphanyl serine derivatives **3a–c** in about 70% yields.

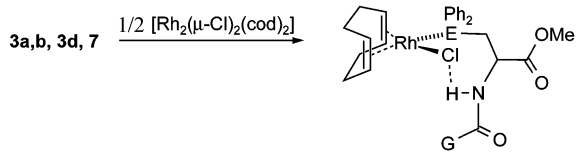
Starting from the *Z*-L-alanine hydroxysuccinimide ester **4** and (*R*)-2-amino-3-bromomethylpropionate hydrobromide (SerBr HBr), the dipeptide **5** was obtained in about 50% yield. Reaction with **2** gave, after work-up with aqueous KCN the desired ligand ^{Z}AlaSerphos **3d** in good isolated yield (~70%). In an analogous way, the arsanyl substituted serine derivative **7** (SerArs) is obtained when the copper arsenide complex [$CuAsPh_2$(neo)] **6** is used in the reaction with **1a**. Unfortunately, the reactions proceed under racemization of the stereogenic centres which is a serious drawback of our method. While our work was in progress, Stelzer and co-workers reported a facile synthesis of SerPhos from *N*-Boc-3-iodo-L-alanine and Ph_2PH in DMF using K_2CO_3 as base.[11] However, this reaction proceeds also under racemization. Only Gilbertson and co-workers reported a short



Scheme 1 Syntheses of ^{ROCO}SerPhos derivatives **3** [**a**: R = CH_2Ph (^{Z}SerPhos), **b**: R = *t*Bu (^{Boc}SerPhos), **c**: R = Me), ^{Z}AlaSerPhos **3d** and ^{Z}SerArs **7**.

and elegant stereospecific synthesis of the P-sulfide of SerPhos using a copper/zinc reagent made from a commercially available iodo amino acid.[12]

Reaction of the phosphanes **3a,b,d** or arsane **7** with $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ in ethanol gave the complexes **8**, **9**, **10** and **11**, respectively, in good yields (Scheme 2). All complexes were obtained in high yield as yellow to orange crystals after re-crystallization from saturated acetonitrile solutions. In the solid state, **8–11** are quite stable and can be handled on air.



E	G	
P	$PhCH_2O$	[RhCl(cod)(^{Z}SerPhos)] **8**
P	*t*BuO	[RhCl(cod)(^{Boc}SerPhos)] **9**
P	$PhCH_2OOC\text{-}NH\text{-}CHMe$	[RhCl(cod)(^{Z}AlaSerPhos)] **10**
As	$PhCH_2O$	[RhCl(cod)(^{Z}SerArs)] **11**

Scheme 2 Syntheses of rhodium(I) complexes **8–11** with ^{Z}SerPhos **3a**, ^{Boc}SerPhos **3b**, ^{Z}AlaSerPhos **3d** and ^{Z}SerArs **7** as ligands.

Structures in the solid state

The single crystals contain the racemates of **8**, **9** and **11** in each case and diastereomers of **10**. One of the stereoisomers of **9**, **10** and **11** is depicted in Fig. 1(A), (B) and (C). The ^{Z}Serphos complex **8** has a structure very similar to the one of the arsenic analogue **11** and is therefore not especially shown in Fig. 1. Selected bond angles and distances of all complexes are compiled in Table 1 and details on the data collection and refinement are given in Table 6 in the Experimental section.

For the ^{Boc}Serphos complex **9** (Fig. 1(A)) and the ^{Z}SerArs complex **11** (Fig. 1(C)), respectively, the enantiomer with the natural *R*-configuration at the α-serine carbon atom is shown. For the dipeptide complex **10** (Fig. 1(B)), the stereoisomer with the non-natural *S*-configuration at the α-carbon of the serine residue is presented. In this compound, the *S*-stereogenic centre in the alanine residue, Ala, appears to be disordered as a consequence of crystal packing.

The most remarkable and common feature in the structures of **8–11** is the N–H···Cl bridge which leads to the formation of a distorted seven-membered ring including the Rh, P, C_β, C_α, N, H and Cl centres. The distance *c* between the N-hydrogen atom and the rhodium-coordinated chlorine atom varies between 2.18 Å (**9**) and 2.62 Å (**8**) and the N–H···Cl angle varies by about 7° from 153° (**8**) to 160° (**9**). The N–H···Cl bridges lead to an arrangement of the N-terminal protecting groups, Z or Boc, above one side of the square planar coordination sphere of the rhodium centres. The deviation from planarity given by the intersection φ of the plane running through Rh and the midpoints of the coordinated $C{=}C_{cod}$ bonds with the plane running through Rh, P and Cl is small for all complexes: **8**: $\varphi = 13°$, **9**, **11** = 6°. All other structural data show values in the expected ranges and do not differ much within series **8–11**. The phenyl groups bonded to phosphorus show the typical edge-to-face arrangements with interplane angles of 50–70°.[4g]

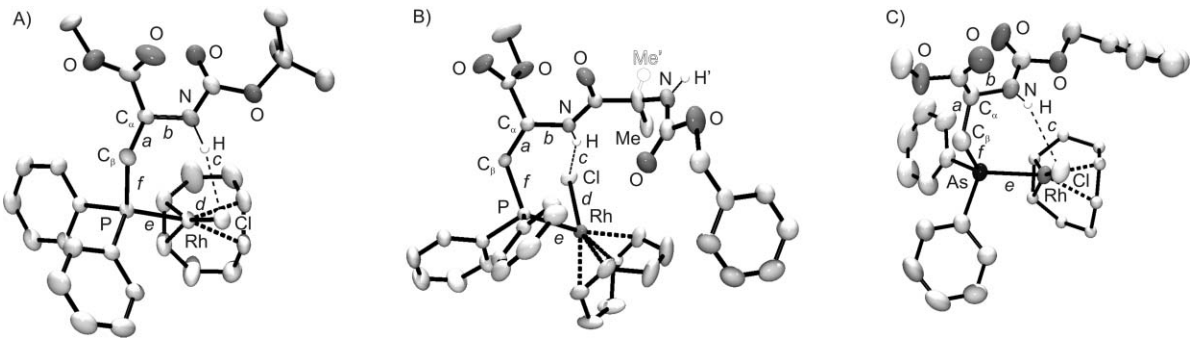


Fig. 1 Structure plots of *R*-[RhCl(cod)(^{Boc}SerPhos)] *R*-**9** (A), *R*,*S*-[RhCl(cod)(^{Z}AlaSerPhos)] *R*,*S*-**10** (B) and *R*-[RhCl(cod)(^{Z}SerArs)] *R*-**11** (C). Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (°) are listed in Table 1.

Table 1 Selected bond lengths (Å) and angles (°) for **8**, **9**, **10** and **11**. $a = C_\beta\text{–}C_\alpha$, $b = C_\alpha\text{–}N$, $c = NH\cdots Cl$, $d = Rh\text{–}Cl$, $e = Rh\text{–}P(As)$, $f = P(As)\text{–}C_\beta$

	a	*b*	*c*/N···Cl[b]	*d*	*e*	*f*
8[a]	1.52(1)	1.45(1)	2.59/3.42(1)	2.365(3)	2.295(3)	1.838(8)
9	1.536(6)	1.430(6)	2.183/3.276(6)	2.386(1)	2.285(2)	1.848(4)
10	1.529(6)	1.440(5)	2.504/3.299(5)	2.365(1)	2.323(1)	1.845(4)
11	1.530(8)	1.444(8)	2.48/3.269(7)	2.378(1)	2.426(1)	1.965(6)

	$C_\beta\text{–}C_\alpha\text{–}N$	$P\text{–}C_\beta\text{–}C_\alpha$	$Rh\text{–}P(As)\text{–}C_\beta$	Cl–Rh–P(As)
8[a]	112.0(7)	117.4(6)	118.1(3)	88.6(8)
9	110.5(4)	115.7(3)	110.2 (1)	86.70(5)
10	111.7(3)	117.7(3)	118.7(1)	90.13(4)
11	106.8(5)	116.5(4)	120.3(2)	88.60(4)

[a] The average of the two independent molecules is given which have very similar structures. [b] The bridging hydrogen bonds *c* (NH···Cl) were calculated from the experimentally determined N···Cl distances assuming a NH distance of 0.9 Å.

Table 2 Torsion angles Θ_a^1, Θ_a^2 and Θ_b for **8–11** (and Θ_h, Θ_j for **10**) in the solid sate: $\phi^{Serphos} = \Theta_b + 60$ (*R*-isomer) [$\Theta_b - 60$ (*S*-isomer)]; $\phi^{Ala} = \Theta_j + 60$ (*S*-isomer) [$\Theta_j - 60$ (*R*-isomer)]; $\psi^{Ala} = \Theta_h - 60$ (*S*-isomer) [$\Theta_h + 60$ (*R*-isomer)]

	Θ_a^1	Θ_a^2	Θ_b	$\phi^{Serphos}$	Θ_h	ψ^{Ala}	Θ_j	ϕ^{Ala}
R-**8**[a]	−52.2	−168.0	−139.3	−79	—	—	—	
R-**9**	−81.3	163.0	−120	−60	—	—	—	
R,*S*-**10**	−55.7	−171.2	−130.5	−70	31.1	−28.9	−127.7	−67.7
R-**11**	−50.6	−166.6	−159.9	−100	—	—	—	
S,*S*-**10**	55.7	171.2	130.5	70	110.3	50.3	−13.7	46.3

[a] Average of two independent molecules per unit cell.

In Table 2, the torsion angles Θ_a^1, Θ_a^2 and Θ_b (and Θ_h, Θ_j for **10**) are listed which we will use in the following to discuss the coordination spheres created by the phosphanyl substituted amino acids. The corresponding values of the antipodes are simply obtained by multiplying the given data by minus one. As examples, Newman projections along the bonds $C_\beta C_\alpha = a$ and $C_\alpha N = b$, are presented for the *R*-configured SerPhos unit in **9** in Fig. 2(A). For the dipeptide complex **10**, projections for the *R*,*S*- and *S*,*S*-configured ^{Z}AlaSerPhos moieties are presented and the torsion angles along *a* and *b* and *h* and *j* are given. The conformations for the ^{Z}SerPhos and ^{Z}SerArs complexes **8** and **11**, respectively, resemble closely the one presented for *R*,*S*-**10**.

With the exception of complex **9**, similar torsion angles Θ_a^1 and Θ_a^2 are observed which define the position of the Ph_2PCH_2-side chain *vs*. the stereogenic centre C_α of the phosphanyl substituted serine residue. The angle Θ_b defining the orientation of the planar amide NHCO unit *vs*. C_α varies over a broader range from Θ_b(min.) −120.0 in **9** to Θ_b(max) −159.9 in **11** and indicates conformational flexibility. Commonly, the mutual orientation of the peptide planes is defined by the dihedral angles ϕ along the N–C_α bond *b* and ψ along the C_α–C=O bond. With the relations for α-helical conformations, $\phi^{Serphos} = \Theta_b + 60$ and $\phi^{Ala} = \Theta_j + 60$, the angles ϕ were calculated and listed in Table 2 for the *R*-configured isomers. For compound **10**, the angle $\psi^{Ala} = \Theta_h - 60$ is given for the *R*,*S*-diastereomer (entry 3) and *S*,*S*-isomer (entry 5).

In the IR spectra of **8–11**, a shift of the N–H stretching vibration to smaller wavenumbers by more than 100 cm^{-1} indicates the presence of the N–H · · · Cl bridge. Two characteristic amide modes I, II are observed in **8–11** [ν^I(CONH) ≈ 1700 cm^{-1} and ν^{II}(CONH) ≈ 1500 cm^{-1}] and these are not significantly different from the ones seen in the free ligands (see Table 4 below).

Structures in solution

Coupling constants are frequently used to determine the mutual orientation given by ϕ and ψ of the individual peptide units in polypeptides, –CO–NH–$C_\alpha H_\alpha(C_\beta H_2 R)$–C′O–N′H–, where H_α represents the hydrogen linked to the chiral C_α carbon of the amino

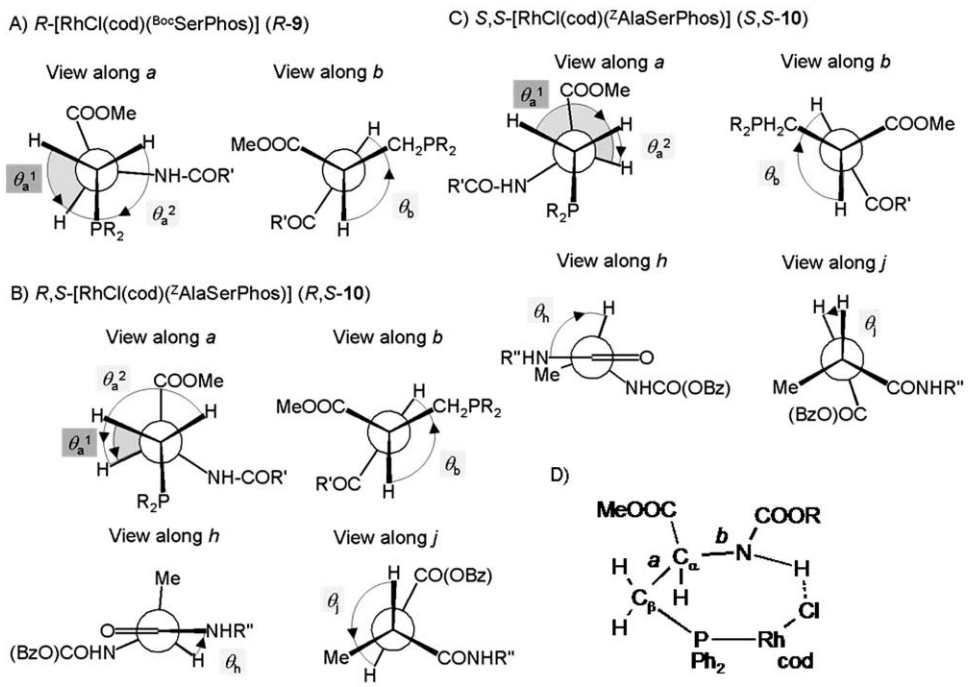


Fig. 2 (A) Newman projections along bonds *a* and *b* in the Serphos unit in *R*-[RhCl(cod)(BocSerPhos)] (*R*-**9**). (B) and (C): Newman projections along bonds *a*, *b*, *c* and *d* in the AlaSerphos unit in the diastereomers *R*,*S*-[RhCl(cod)(^{Z}AlaSerPhos)] (*R*,*S*-**10**) and *S*,*S*-[RhCl(cod)(^{Z}AlaSerPhos)] (*S*,*S*-**10**). The torsion angles Θ_a^1, Θ_a^2, Θ_b, Θ_h and Θ_j. are indicated and the corresponding data are listed in Table 2. (D) Schematic presentation of the seven-membered chelate ring in **8–11**.

Table 3 Coupling constants $^3J(H_\alpha H_{\beta1})$ and $^3J(H_\alpha H_N)$ and torsion angles $\Theta_a{}^1$, $\Theta_a{}^2$ and Θ_b for **3c,d**, **8**, **9** and both diastereomers of **10** in solution (**3c,d**: C_6D_6; **8**: CD_3CN, **9**: $CDCl_3$, **10**: CD_2Cl_2); $\phi^{Serphos} = \Theta_b + 60$ (*R*-isomer) [$\Theta_b - 60$ (*S*-isomer)]

	$^3J(H_\alpha,H_{\beta1})$/Hz	$\Theta_a{}^1$/°	$^3J(H_\alpha,H_{\beta2})$/Hz	$\Theta_a{}^2$/°	$^3J(H_\alpha,H_N)$/Hz	Θ_b/°	$\phi^{Serphos}$/°
3c					7.7	±150	±90
3d					7.3	±140	±80
8	3.0	±55	12.5	±170	7.5	±155	±95
9	3.5	±70	12.5	±170	7.4	±145	±85
$\mathbf{10}_{diastereomer\_1}$	2.8	±60	13.0	±170	6.8	±140	±80
$\mathbf{10}_{diastereomer\_2}$	3.0	±55	12.0	±160	6.8	±140	±80

acid residue, H_N indicates the amide proton and C_β is the first carbon centre of the side chain (see also Fig. 1).[13] Additionally, NOE experiments can be performed to obtain more structural information. We used the $^3J(H_\alpha,H_N)$, $^3J(H_\alpha,H_{\beta1})$ and $^3J(H_\alpha,H_{\beta2})$ coupling constants in combination with the Karplus correlation in order to determine $\Theta_a{}^1$, $\Theta_a{}^2$ and Θ_b in solution. The resulting data for the racemates of the uncomplexed phosphanyl amino acid **3c**, the dipeptide **3d** and the complexes **8–10** are given in Table 3. The resonances for the *R*,*S*- and *S*,*S*-diastereomers of **3d** could be partly distinguished in the NMR spectra of the complexes **10** (but not for the free ligand) and these are denominated as $\mathbf{10}_{diastereomer\_1}$ and $\mathbf{10}_{diastereomer\_2}$. A more precise assignment of the stereochemistry cannot be made.

Unfortunately, all ^{1}H NMR spectra of solutions containing the mixture of the diastereomers of compound **10** could not be sufficiently resolved and hence we were unable to determine the torsion angles for the alanine residue in **3d** and **10**.

A comparison of the data listed in Tables 2 and 3, respectively, shows that the structures of the central seven-membered rhodium chelates are very similar in the solid state and in solution. The values for the torsion angles $\phi^{Serphos}$ (|60|°–|100|° in the solid state, |80|°–|95|° in solution) compare reasonably well with the ones determined for dodecapeptides containing two SerPhos units in *i* and *i* + 4 positions (−73° in the solid, −60 to −80° in solution).[9] These values fall within the range of −60 to −90° typically found in helical conformations of peptides.[14] Importantly, we assume that the N–H···Cl bridge is conserved in solution as is clearly indicated by the significant high-frequency shifts (>1 ppm) of the H_N resonances of the SerPhos units in complexes **8** [$\delta(H_N)$ 7.18], **9** [$\delta(H_N)$ 6.82], **10** [$\delta(H_N)$ 8.46/8.16] and **11** [$\delta(H_N)$ 6.98] when compared to the corresponding free ligands **3a** [$\delta(H_N)$ 5.48], **3b**, [$\delta(H_N)$ 5.77], **3d** [$\delta(H_N)$ 5.8] and **7** [$\delta(H_N)$ 5.51]. Such large coordination shifts were not observed with the larger peptides where the (*i*, *i* + 4)-bis(serphos)peptide binds *via* the two phosphane residues to a cationic rhodium norbornadiene fragment.[9]

Chloride abstraction reactions from complexes 8 and 10

How will the cleavage of the N–H···Cl bridges affect the structure of the ligand? To answer that question, the metal bonded chloride was exchanged for a weakly coordinating anion and **8** and **10** were reacted with $TlPF_6$ in toluene. The reactions are quantitative and the products **12** and **13** were obtained as yellow powders (Scheme 3). Complex **12** can also be prepared with $AgPF_6$ as reagent but the dipeptide complex **10** decomposes.

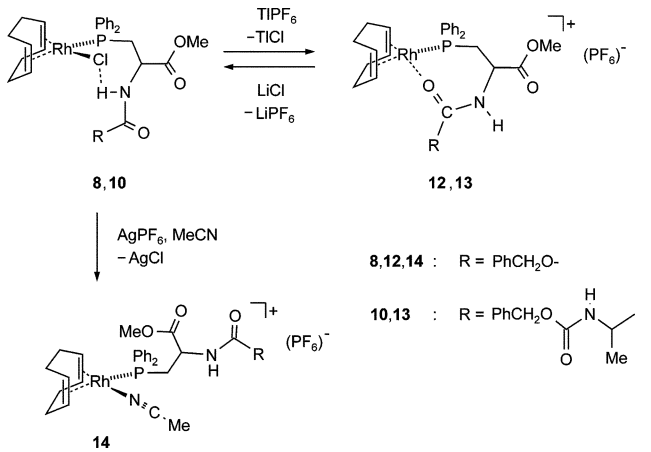
That significant structural changes occur when the chlorine atom is removed from the coordination sphere of the rhodium atom is indicated by the change of some characteristic NMR and IR data of compounds **12–14** (see Table 4).

Unfortunately, none of the products gave suitable crystals for an X-ray analysis, however, reasonable structures for the coordination sphere around the rhodium centre can be proposed. Three different coordination spheres may be assumed for **12** and **13**. (a) The NH group of the amide coordinates to Rh, (b) the C=O unit of the COOMe group binds to Rh, or (c) the C=O group of the carbobenzoxy or alanyl unit, respectively, is bonded. The first two coordination modes give rise to six-membered the third one

Table 4 Selected IR and ^{13}C data of the free phosphanes **3a,d**, the rhodium chloride complexes **8**, **10** and the cationic complexes **12**, **13**

ν(C=O)/cm^{-1}	**3a**	**3d**	**8**	**10**	**12**	**13**
NH	3412	n.d.[a]	3307	3250	3384	3330
COOMe	1742	n.d.[a]	1741	1735	1724	1723
CONH (amide I)	1711	n.d.[a]	1707	1717	1623	1613
CONH (amide II)	1502	1504	1507	1509	—	—
$\delta(^{13}C)$[b]						
COOMe	171.4	≈172[c]	171.9	172.7[d]	171.9	169.2[d]
CONH	155.1	≈172[c]	155.8	171.8[d]	158.5	179.3[d]
$\delta(^1H)$						
H^N (SerPhos)	5.48	5.8	6.98	8.46/8.16	6.26	8.24/8.10

[a] Broadened bands in the range 3450–3380 cm^{-1}, 1750–1710 cm^{-1} due to overlapping absorptions which were not assigned. [b] Solvents: **3a,d**: C_6D_6, **8**: CD_3CN, **9**: $CDCl_3$, **10**: CD_2Cl_2, **12**: $CDCl_3$, **13**: CD_2Cl_2. [c] The resonances for the COOMe and CONH groups overlap. [d] The average of the signals for both diastereomers is given which are very close.



Scheme 3 Chloride abstractions from **8** or **10** with $TlPF_6$ to give **12** or **13**, respectively. Reaction of **8** with $AgPF_6$ in MeCN gives **14**.

to a seven-membered chelate ring. Possibility (a) is rather unlikely because NH units of amides are generally weakly coordinating, no $^{103}Rh^{15}N$ coupling is observed and ν(NH) is not shifted to smaller and ν(C=O) not to higher wavenumbers as would have been expected. Also possibility (b) is unlikely because all spectroscopic data [ν(C=O) and $\delta(^{13}C)$] of the ester group remain unaffected by the chloride abstraction. We propose that **12** and **13** have the seven-membered ring structures as shown in Scheme 3 on the basis of the following observations: (i) both, ν(NH) and ν(C=O) are shifted to lower wavenumbers in **12** and **13** when compared to the rhodium chloride complexes **8** and **10**; (ii) no amide II absorption band is observed in **12** and **13** which is characteristic for cyclic amides, (iii) the $\delta(^{13}C)$ resonance of the CONH group which is supposed to be involved in the coordination is slightly shifted to higher frequencies by 3–7 ppm and (iv) importantly, the $^2J(^{103}Rh^{13}C)$ coupling (1.4 Hz) could be resolved for the carbon nucleus of the amide group in **12**. Similar observations were made for comparable rhodium(I) complexes with seven-membered $P,(C=O)$-chelate rings.[15]

Further information about the structures of **12** could be extracted from the sufficiently resolved $^3J(H_\alpha,H_N)$ $^3J(H_\alpha,H_{\beta1})$ and $^3J(H_\alpha,H_{\beta2})$ coupling constants (8.3, 3.5 and 12.5 Hz, respectively). This results in $\Theta_b \approx \pm 150°$, $\Theta_a{}^1 \approx \pm 70°$ and $\Theta_a{}^2 \approx \pm 170$ which define the torsion along the $C_\alpha N$ bond, *b*, and the $C_\beta C_\alpha$ bond, *a*, respectively. In contrast to the rhodium chloride complex **8**, the methylene protons of the CH_2PPh_2 group show only one cross-peak with the phenyl protons in the NOESY spectrum. This indicates that the CH_2 group has a symmetric and hence eclipsed orientation to the phenyls. With these data, a structure model for the coordination sphere of the rhodium centre in **12** can be constructed and this is shown in Fig. 3(B). Fig. 3(A) shows the NMR structure of **8** in solution for comparison. While the conformation of the SerPhos unit in **8** has a structure resembling the one of serine residues in α-helical peptides, its conformation in **12** is closer to that one in a β-sheet. As in these, an amide proton, H^N, and a C=O group point to the outside of the molecule. This yet unexploited feature would make *inter*molecular donor–acceptor interactions possible. For **13**, the NMR spectra are quite complex because in addition to the doubling of all signals due to the presence of two diastereomers, the fluxional behaviour of the cyclooctadiene ligand leads to line broadening and overlap of some

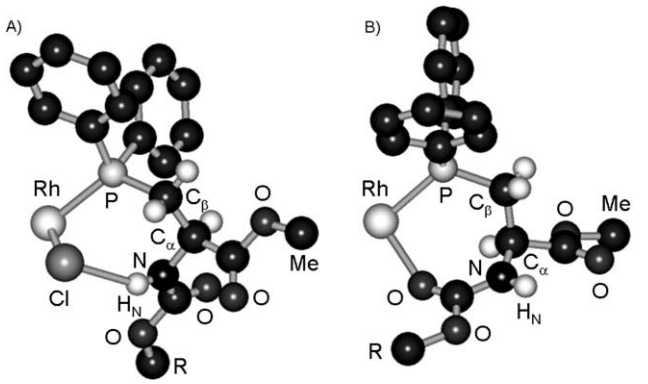


Fig. 3 Proposed structures for the [RhCl(^{Z}SerPhos)] fragment in **8** (A) and the [Rh(^{Z}SerPhos)]$^+$-fragment in **12** (B) in solution based on NMR data.

signals. While the ^{31}P NMR spectra at room temperature show two doublets [$^1J(^{31}P^{103}Rh) \approx 152$ Hz], one for each diastereomer, lowering the temperature to 200 K leads to a (reversible) splitting into four doublets. Also the ^1H NOESY spectra indicate that the alanine residue adopts at least two conformations. This is in contrast to the neutral rhodium chloride complex **10**, where such phenomena were not observed. This finding indicates that the ^{Z}AlaSerPhos ligand **3d** shows a higher flexibility in the cationic complex **13**.[16] Because of the almost identical characteristic bands in the IR spectra for both cationic complexes, **12** and **13**, and the similar $^3J(H_\alpha,H_N)$ coupling constants (7.1 Hz in **13**), we assume rather similar conformations of the ligands within the rhodium coordination sphere as well.

Importantly, when solution of **12** and **13** are treated with lithium chloride, the structural changes caused by the chloride abstraction are reversed and the spectra of the neutral chloro complexes **8** and **10** are fully recovered (Scheme 3).

When the chloro substituent in **10** is abstracted with $[Ag(MeCN)_2]PF_6$ in acetonitrile, the cationic acetonitrile complex **14** is obtained as yellow powder after evaporation of the solvent. Equally, **14** results when **12** is dissolved in MeCN. That the coordinating C=O group in **12** is replaced by a MeCN in **14** is evident from the spectroscopic data: The NH stretching vibration is observed at 3400 cm^{-1}, two amide bands for the CONH group are observed at 1708 and 1503 cm^{-1}, and the $\delta(^{13}C)$ resonance (156.5 ppm) equals almost the one in **3a** and **8**.

Catalytic hydrogenations with rhodium SerPhos complexes

The reactivity of the neutral chloro rhodium complexes **8**, **9**, **10** and **11** and the cationic complex **12** as catalyst precursors in homogeneously catalyzed hydrogenations was tested. For comparison, reactions with $[RhCl(PPh_3)_3]$ and $[RhCl(cod)(PPh_3)]$ were included in the investigation. All reactions were performed in EtOH as solvent with 0.1 mol% catalyst at room temperature under about 4.5 bar H_2 pressure. After two hours, the reaction mixtures were analyzed by gas chromatography (GC). As substrates, the olefins cyclohexene (***ch***), 1-hexene (***1-h***), acrylic acid methylester (***am***) and 2,3,-dimethyl-2-butene (***dmb***) were employed. The results are compiled in Table 5. It is generally assumed that monophosphane rhodium(I) complexes are not very reactive in catalytic hydrogenations[2] and by comparison

Table 5 Catalytic hydrogenation of cyclohexene (***ch***), 1-hexene (***1-h***), acrylomethylate (***am***) and 2,3,-dimethylbutene (***dmb***) with various rhodium(I) complexes

			Conversion (%)			
Entry	Catalyst precursor	t/h	***ch***	***1-h***	***am***	***dmb***
1	[RhCl(cod)(PPh_3)]	2	4	20	0	0
2	[RhCl(PPh_3)$_3$][a]	2	25	86	100	0
3	[RhCl(cod)(^{Z}SerPhos)] (**8**)[a]	2	50	100	100	0
4	[RhCl(C_2H_4)$_2$(^{Z}SerPhos)][b]	2	55	100	100	0
5	[RhCl(cod)(^{Boc}SerPhos)] (**9**)	2	92	100	100	5
6	[RhCl(cod)(^{Z}AlaSerPhos)] (**10**)	2	1	10	12.6	0
7	[RhCl(cod)(^{Z}SerArs)] (**11**)	2	0	1	0	0
8	[Rh(cod)(^{Z}SerPhos)](PF_6) (**12**)	2	13.8	4.6	4.3	0
9	**8** + 1 eq. PPh_3	2	0.6	5.3	9.1	0
10	**12** + 1 eq. PPh_3	2	50	100	100	0

[a] After 18 h the following yields were obtained: [RhCl(PPh_3)$_3$]: 40 (***ch***), 90 (***1-h***), 100 (***am***), 0 (***dmb***); **8**: 100 (***ch***), 100 (***1-h***), 100 (***am***), 0 (***dmb***). [b] Prepared *in situ* from equimolar amounts of ligand **3a** and [$Rh_2(\mu\text{-}Cl)_2(C_2H_4)$].

of entries 1 [catalyst source: RhCl(cod)(PPh_3)] and 2 [catalyst source: [RhCl(PPh_3)$_3$] this is confirmed under our conditions. Interestingly, however, the monophosphane complex **8** (entry 3) shows a significant higher activity than the classical Wilkinson-catalyst [RhCl(PPh_3)$_3$]. As entry 4 shows, the activity is not dependent on the co-ligand in the pre-catalyst; that is the complex [RhCl(C_2H_4)$_2$(^{Z}SerPhos)] (prepared *in situ*) shows the same activity as **8** indicating the absence of any significant induction phase. The highest reactivity is found with complex **9** containing the Boc-protected SerPhos ligand **3b** which is the only one who gives detectable amounts of 2,3-dimethylbutane as hydrogenation product of the tetrasubstituted olefin ***dmb***. On the other hand, the dipeptide complex [RhCl(cod)(^{Z}AlaSerPhos)] (**10**) (entry 6) shows the lowest activity of the neutral phosphane complexes. The arsane complex **11** is inactive (entry 7).

Although most often the activity of cationic rhodium(I) complexes with weakly coordinating anions (CF_3SO_3, BF_4, PF_6, *etc.*) is higher than with the neutral chloro complexes, this is not true for **12** (entry 8). The catalyst derived from this complex is much less active than the one obtained with **8**, especially against the alkene ***1-h*** and ester ***am***. Remarkably, the activity of the neutral complex **8** drops dramatically when one equivalent PPh_3 is added (entry 9). On the other hand, addition of one equivalent PPh_3 to the cationic complex **12** increases the activity which becomes comparable to the one of the neutral complexes **8** and [RhCl(C_2H_4)$_2$(^{Z}SerPhos)] (entry 10).

We interpret these results as follows: (1) We assume that the seven-membered Rh–P–C–C–N–H $\cdots$ Cl ring remains intact and the solvated [RhCl(^{R}SerPhos)] fragment is the catalytically active species in reactions with **8**, **9** and **10**. Note, that the group R is orientated above the metal center in the structures of **8**, **9** and **10** whereby the steric shielding increases in the order Boc < Z < ^{Z}Ala (see Fig. 1). In the same order the activity decreases. (2) Adding PPh_3 to these complexes blocks a coordination site, further increases the steric shielding and makes olefin binding difficult. Low catalytic activity is the result. (3) When the chloro ligand in **8** is exchanged for PF_6^- and an ion pair like **12** is generated, the slower oxidative H_2 may be the reason for the lower catalytic activity. (4) In reactions with [Rh(cod)(^{Z}SerPhos)](PF_6), addition of PPh_3 likely leads to a "classical" solvated diphosphane complex fragment [Rh(PPh_3)(^{R}SerPhos)]$^+$ in which only the phosphorus atom of the SerPhos ligand binds to Rh. This complex then shows the usual high catalytic activity for cationic rhodium bis(phosphane) complexes.[2]

Conclusions

In rhodium chloro complexes with phosphanyl- or arsanyl-substituted serine derivatives, SerPhos or SerArs, an intramolecular (N)H $\cdots$ Cl(Rh)-hydrogen bridge is observed in the solid state and in solution. As a result, the amino acid residue adopts a α-helix type structure. Removal of the chloro ligand from the coordination sphere and consequently cleavage of the NH–Cl bridge, leads to a structural change of the amino acid residue to a β-sheet type. This structural transformation which is triggered by a change in the coordination sphere of the transition metal is fully reversible.

In contrast to established rhodium hydrogenation catalysts, the neutral chloro [RhCl(cod)(SerPhos)] complexes give rise to significantly more active catalysts than the corresponding cationic complexes [Rh(cod)(κ^2-^{Z}SerPhos)]$^+$. Electronic and, especially, steric reasons may be responsible for this observation. These results encourage to use also larger *mono*-phosphanyl substituted peptides as ligands for catalysts instead of the formerly investigated disubstituted ones.

In view of the enormous potential of proteins as ligands for catalytically active-transition metal complexes, we also hope that the presented structural and spectroscopic data obtained with the small models discussed in this paper may serve for the design and better understanding of the interaction of metal complex fragments with peptides.

Experimental

General techniques

All syntheses were performed in flame-dried glassware under an atmosphere of argon using standard Schlenk techniques. Solvents were freshly distilled from sodium/benzophenone (thf), from sodium/tetraglyme/benzophenone (hexane, toluene) or calcium hydride (dichloromethane) prior to use. Air sensitive compounds were stored and weighed in an argon filled glovebox (Braun MB

150 B–G system) and reactions on small scale were performed directly in the glovebox.

NMR spectra were either taken on an AMX-500, Avance DRX-400, Avance DPX-300, or Avance DPX-250 system. The chemical shifts are given as dimensionless δ values. Spectra were referenced with external standards: for ^{1}H and ^{13}C NMR with TMS, for ^{15}N NMR with NH_3, for ^{19}F NMR with $CFCl_3$, for ^{31}P NMR with H_3PO_4 and for ^{103}Rh NMR with the frequency reference $\Xi = 3.16$ MHz. Coupling constants J are given in Hertz [Hz] as positive values regardless of their absolute signs. The multiplicity of the signals is indicated as s, d, t, q or m for singlets, doublets, triplets, quartets or multiplets, respectively. Quaternary carbons are indicated as C_{quat}, aromatic as C_{ar}, when not noted otherwise. IR-spectra were measured on a Perkin-Elmer 2000 FT-IR spectrometer using a KBr beamsplitter. The absorption bands are described as follows: very strong (ss), strong (s), middle (m), weak (w), or broad (br). The UV/Vis-spectra were measured with the UV-Vis Lambda 19 spectrometer in 0.5 cm-quartz cuvettes. Melting points were determined with an Büchi melting point apparatus and are not corrected.

Syntheses of 1a–c. The synthesis of 2-(*S*)-(benzyloxycarbonylamino)-3-bromomethylpropionate **1a** follows closely the published methods for the preparation of (*S*)-3-bromo-2-(*N*-*tert*-butoxycarbonyl)methylpropionate **1b** (^{tBoc}SerBr)[17] and (*S*)-3-bromo-2-(*N*-carbomethoxy)methylpropionate **1c**.[18]

2-(*S*)-(Benzyloxycarbonylamino)-3-bromomethylpropionate 1a (^{Z}SerBr). Under cooling in an ice bath, a solution of 1.39 g dry LiBr (16 mmol) in 30 mL dry acetone was added slowly to a solution of 3.26 g (8.0 mmol) of the serine tosylate (*S*)-2-(benzyloxycarbonylamino)-3-(*p*-toluolsulfonyl)methylpropionate (^{Z}SerOTs)[19] in 40 ml dry acetone. After the addition was complete, the reaction mixture was warmed up to room temperature and stirred for 2 h whereby lithium tosylate precipitated. To complete the substitution reaction, the mixture was heated under reflux for 1 h. Insoluble material was filtered off and the solution was concentrated under vacuum. First an almost colourless oil was obtained which solidified rapidly. The raw product was dissolved in $CHCl_3$, again filtered in order to remove residual salt, concentrated to dryness under vacuum and recrystallized from ethanol at 4 °C. Yield: 1.95 g (77%); mp 63 °C. $^{25}[a]_{589} = -18.9$ in DMF (20 mg/2 mL). ^{1}H NMR ($CDCl_3$): δ 7.37 (s, 5H, H_{aromat}), 5.70 (br, 1H, NH), 5.14 (s, 2H, OCH_2Ph), 4.83 (br, 1H, CH), 3.87–3.71 (br, 2H, CH_2Br), 3.8 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 169.3 (s, *C*OOCH$_3$), 155.3 (s, ONH), 135.8 (s, C_{ipso}), 128.5 (s, C_{ortho}), 128.3 (s, C_{para}), 128.1 (s, C_{meta}), 67.3 (s, OCH$_2$Ph), 54.2 (s, COO*C*H$_3$), 53.1 (s, H), 33.7 (s, H_2Br). IR (KBr pellet) [ν/cm^{-1}]: 696, 751, 1067, 1059 (s), 1214.0 (s), 1279.0, 1320, 1532 [ss, (N–H) amide II] 1688 [ss, (C=O) amide I], 1732.0 (ss, C=O), 2941 (m, CH str.), 3324 (ss, NH str.).

Syntheses of (2,9′-dimethylphenanthroline)(diphenylphosphanide)-copper(I) 2, [Cu(PPh$_2$)(neo)] and (2,9′-dimethylphenanthroline)-(diphenylarsanide)copper(I) 6 [Cu(AsPh$_2$)(neo)]: General synthesis for [Cu(EPh$_2$)(N∩N)] complexes (E = P, As; N∩N = 2,2′-bipyridyl or 1,10-phenanthroline derivative). First, the coordination polymers, $[Cu(PPh_2)]_8$ and $[Cu(AsPh_2)]_8$ were prepared according to a method published by Caulton and co-workers.[20] *[Cu(PPh$_2$)]$_8$*: 1.48 g (0.011 mol) copper(I) *tert*-butanolate was dissolved in 40 mL THF. Under vigorous stirring, a solution of 2.01 g (0.011 mol) diphenylphosphane, Ph_2PH, in 10 mL THF was added. It is important to adjust the addition at the beginning of the reaction such that the immediately formed precipitate re-dissolves in the reaction medium. After the addition was complete, a bright red precipitate formed which was filtered off, washed several times with Et_2O, and dried under high vacuum. Yield: 2.05 g (75.3%); mp (decomp.): 150 °C. IR (KBr pellet) [ν/cm^{-1}]: 3050.0 (m), 1576.0 (m), 1471.0 (s), 1428.0 (s), 1125.0 (br), 1022.0 (br), 803.0, 731.0 (s), 691.0 (s), 467.0.

[Cu(AsPh$_2$)]$_8$: 0.296 g (2.2 mmol) copper(I) *tert*-butanolate was dissolved in 60 mL THF and cooled to −40 °C. Under vigorous stirring, a solution of 0.5 g (2.2 mmol) diphenylarsane, Ph_2AsH, in 10 mL THF was added. After the addition was complete, the deeply coloured solution was stirred for 45 min. at $T = -40$ °C and subsequently warmed to room temp. Thereby a brown precipitate was formed which was filtered off and washed twice with 10 mL of pentane. Yield: 0.62 g (98%); mp (decomp.): 148 °C. IR (KBr pellet) [ν/cm^{-1}]: 471, 690, 728 (s), 800, 1019 (br), 1260 (m), 1428 (s), 1472 (s).

In the second part of the synthesis, 0.2 mmol copper pnictogenide $[Cu(EPh_2)]_8$ (E = P, As) were suspended in 40 mL thf and were vigorously stirred at room temp. Slowly an equimolar amount of the N∩N ligand in 10 mL thf was added and the mixture was stirred for another hour at room temp. The intensely green coloured solutions were concentrated to a few milliliters whereby the products precipitate as fine crystalline powders. These were filtered off, eventually re-crystallized from toluene, and dried under high vacuum. **2**: Yield: 53%; mp (decomp.): 135 °C. ^{1}H NMR (C_6D_6): δ 8.1–6.8 (m, H_{ligand}, H_{phenyl}), 2.7–2.46 (br, 6H, CH_3). ^{31}P NMR (C_6D_6): −24.0 (br). All ^{13}C-resonances in the aromatic region were strongly broadened. IR (KBr pellet) [ν/cm^{-1}]: 475, 546, 694 (s), 727 (s), 845, 1040.0 (s), 1429.0 (s), 1469.0 (m), 1496 (m), 1574.0 (s), 3040–2860 (m). UV/VIS (toluene) λ_{max}/nm (ε/l mol^{-1} cm^{-1}): 556 (3192). **6**: Yield: 71%; mp (decomp.): 127 °C. ^{1}H NMR (C_6D_6): δ 7.78 (br, 1H, H_{ligand}), 7.57 (br, 1H, H_{ligand}), 7.32 (br, 1H, H_{ligand}), 7.25 (s, 3H, H_{phenyl}), 6.94 (br, 3H, H_{phenyl}), 2.83 (br, 3H, CH_3). All ^{13}C-resonances in the aromatic region were strongly broadened. IR (KBr pellet) [ν/cm^{-1}]: 3039 (s, CH str.), 1614, 1569, 1494, 1471, 1427 (s), 1060, 1020, 846 (ss), 728, 695. UV/VIS (thf) λ_{max}/nm (ε/l mol^{-1} cm^{-1}): 714.6 (217.4).

General method for the reaction of an organohalide with a [Cu(EPh$_2$)(N∩N)] complex. Syntheses of the phosphanyl amino acids 3a–d and the arsanyl amino acid 7. Oxygen has to be strictly excluded in the following manipulations. Air oxidation of phosphanes is greatly enhanced in the presence of copper. 0.81 mmol [Cu(EPh$_2$)(neo)] **2** (E = P) or **6** (E = As) were dissolved in a few mL of thf. Alternatively, these copper complexes can be prepared *in situ* from $[Cu(EPh_2)]_8$ and one aliquot of 2,9′-dimethylphenanthroline in thf. Subsequently, an equimolar amount of the organohalide **1a–c** or **5** was added in 30 mL at room temperature. After stirring for about 12 h at room temp., an orange precipitate was formed and the supernatant solution had a bright red colour. All volatiles were removed in vacuum and 50 mL Et_2O was added. To this suspension, a saturated aqueous solution of KCN was added at room temp. until two almost colourless phases had formed. The organic layer was separated, extracted twice with H_2O, twice with 2 M aqueous HCl, and dried over Na_2SO_4. After evaporation of

all volatiles, a colourless oil was obtained which was once again washed with *n*-pentane to give either a colourless oil or solid.

*R(S)-3-Diphenylphosphanylmethyl-N-carbobenzyloxyserinate (ZSerphos) (**3a**).* Yield: 63.3%; mp 68 °C. ^{1}H NMR (C_6D_6): δ 7.48–7.26 (m, 10H, H_{aromat}), 7.2 (br, 5H, H_{aromat}), 5.48 (br, 1H, N–H), 5.1 (s, 2H, OH_2), 4.83 (br, 1H, CH), 3.19 (s, 3H, OCH_3), 2.65 (dd, 1H, $^2J_{HCH} = 14.1$ Hz, $^3J_{HCCH} = 5.4$ Hz, PH_2, 2.41 (dd, 1H, $^2J_{HCH} =$ 14.1 Hz, $^3J_{HCCH} = 5.4$ Hz, PCH_2). ^{13}C NMR (C_6D_6): δ 171.4 (d, $^3J_{CP} = 5.8$ Hz, *C*$OOCH_3$), 155.1 (s, $C_{urethan}$), 136.6 (s, C_{ipso}), 133.8 (d, $^1J_{PC} = 17.0$ Hz, C_{ipso}), 132.7 (d, $^2J_{PC} = 19.8$ Hz, C_{ortho}), 128.5 (C_{ortho}), 128.3 (C_{para}), 128.3 (d, $^3J_{PC} = 14$ Hz, C_{meta}), 128.1 (C_{meta}, C_{para}), 66.4 (OCH_2), 51.7 (d, $^2J_{CP} = 17.4$ Hz, CH) 51.2 (s, CO_2CH_3), 31.8 d, $^1J_{PC} = 16.6$ Hz, CH_2P). ^{31}P NMR (C_6D_6): δ −23.4. IR (KBr pellet) [ν/cm^{-1}]: 696 (s, monosub. arene), 741 (s, monosub. arene), 1036, 1176 (s, CO), 1205 (m, P–CH_2), 1222 (m, P–CH_2), 1431 (m, P–C str.), 1502.0 (ss, amide II), 1711 (ss, amide I), 1742.0 (ss, C=O), 2960 (w, CH str.), 3412 (ss, NH str.). Optical rotation $[a]^{20}_D$ 0.3 (*c* 0.01, DMF). Anal. Calc. for $C_{24}H_{24}NO_4P$ (421.42 g mol^{-1}) C: 68.4%, H: 5.74, N: 3.32. Found: C: 68.3%, H: 5.74%, N: 3.28%

*R(S)-3-Diphenylphosphanylmethyl-N-(tert-butoxycarbonyl)-serinate (BocSerphos) (**3b**).* Yield: 53%; Oil. ^{1}H NMR (C_6D_6): δ 7.47–7.42 (m, 4H, H_{aryl}), 7.13–7.07 (m, 6H, H_{aryl}), 5.77 (br, 1H, NH), 4.81 (m, 1H, CH), 3.24 (s, 3H, CH_3), 2.7 (m, 2H, PCH_2), 1.42 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (C_6D_6): δ 171.9 (d, $^3J_{CP} = 7.3$ Hz, C=O), 154.7 (s, $C_{urethan}$), 133.6 (d, $^1J_{PC} = 14.6$ Hz, C_{ipso}), 132.7 (d, $^2J_{PC} = 17.9$ Hz, C_{ortho}), 128.5 (C_{para}), 128.3 (d, $^3J_{PC} = 14$ Hz, C_{meta}), 78.7 (s, *C*$(CH_3)_3$), 51.5 (d, $^2J_{PC} = 14.9$ Hz, CH), 51.1 (s, O*C*H_3), 31.5 (d, $^1J_{PC} = 10.05$ Hz, PCH_2), 27.8 (s, C(*C*$H_3)_3$). ^{31}P NMR (C_6D_6): δ −22.8 (s). Anal. Calc. for $C_{21}H_{26}NO_4P$ (387.41 g mol^{-1}): C: 65.10%, H: 6.76%, N: 3.61%. Found: C: 65.08%, H: 6.63%, N: 3.63%.

*R(S)-3-Diphenylphosphanylmethyl-N-(carbomethoxy)serinate (MetSerphos) (**3c**).* Yield: 67%; oil. ^{1}H NMR (C_6D_6): δ 7.47–7.42 (m, 4H, H_{aryl}), 7.13–7.07 (m, 6H, H_{aryl}), 5.34 (d, 1H, $^3J = 7.7$, NH), 4.75 (m, 1H, CH), 3.44 (s, 3H, CH_3), 3.19 (s, 3H, CH_3), 2.64 (dd, 1H, $^2J = 14.0$ Hz, $^3J = 5.6$ Hz, PCH_2), 2.38 (dd, 1H, $^2J = 13.6$ Hz, $^3J = 8.0$ Hz, PCH_2). ^{13}C NMR (C_6D_6): δ 169.3 (d, $^3J_{PC} = 6.5$ Hz, *C*$OOCH_3$), 154.4 (s, $C_{urethan}$), 133.6 (d, $^1J_{PC} =$ 13.6 Hz, C_{ipso}), 132.7 (d, $^2J_{PC} = 17.9$ Hz, C_{ortho}), 128.5 (d, $^3J_{PC} =$ 7 Hz, C_{meta}), 128.1 (C_{para}), 53.1 (CO_2CH_3), 52.9 ppm (COO*C*H_3), 51.1 (s, CH), 32.4 (d, $^1J_{PC} = 14.3$ Hz, CH_2P). ^{31}P NMR (C_6D_6): δ −24.4 (s). ZAlaSerphos (**3d**): Yield: 65%; oil. ^{1}H NMR (C_6D_6): δ 7.64–7.11 (m, 15H, H_{aryl}), 6.1 (br, 1H, NH_{ala}), 5.8 (br, 1H, NH_{ser}), 5.17 (s, 2H, C*H*$_2$Ph), 4.99 (m, 1H, CH_{Ser}), 4.2 (m, 1H, CH_{Ala}), 3.22 (s, 3H, CH_{3Ser}), 2.77 (dd, 1H, $^2J = 12.7$ Hz, $^3J = 5.7$ Hz, CH_2P), 2.56 (dd, 1H, $^2J = 13.8$ Hz, $^3J = 6.8$ Hz, CH_2P), 1.21 (d, 3H, $^3J = 6.9$ Hz, CH_{3ala}). ^{13}C NMR (C_6D_6): δ 171.5 (d, $^3J =$ 7.5 Hz, *C*$OOCH_3$), 156.5 (s, CONH), 156.1 (s, CONH), 136.7 (s, C_{ipso}), 134.6 (d, $^1J = 12$ Hz, C_{ipso}), 132.3 (d, $^3J = 17.4$ Hz, C_{ortho}), 128.6–128.4 (s, C_{ortho}, C_{meta}, C_{para}, C_{meta}, C_{para}), 66.4 (s, CH_2O) 51.2 (s, CH_3O), 50.5 (s, CH_{ala}), 50.25 (d, $^2J = 11.0$ Hz, CH_{ser}), 31.7 (d, $^1J_{PC} = 17.4$ Hz, CH_2P), 18.0 (s, CH_{3ala}). ^{31}P NMR (C_6D_6): δ − 22.5. Anal. Calc. for $C_{27}H_{29}N_2O_5P$ (492.51 g mol^{-1}): C: 66.85%, H: 5.93%, N: 5.69%. Found: C: 66.81%, H: 6.01%, N: 5.58%.

*R(S)-3-Diphenylarsanylmethyl-N-carbobenzyloxyserinate (ZSerars) (**7**).* Yield: 62%; oil. ^{1}H NMR (C_6D_6): δ 7.47–7.29 (m, 4H, H_{aromat}), 7.19–7.09 (m, 11H, H_{aromat}), 5.51 (d, 1H, $^3J = 8.1$ Hz, NH), 5.11 (s, 2H, OCH_2), 4.81 (br, 1H, CH), 3.17 (s, 3H, OCH_3), 2.60 (dd, 1H, $^2J_{HCH} = 12.9$ Hz, $^3J_{HCCH} = 5.7$ Hz, PCH_2), 2.33 (dd, 1H, $^2J_{HCH} = 14.1$ Hz, $^3J_{HCCH} = 5.4$ Hz, PCH_2). ^{13}C NMR (C_6D_6): δ 171.8 (s, *C*$OOCH_3$), 155.2 (s, $C_{urethan}$), 139.7 (s, C_{ipso}), 136.6 (s, C_{ipso}), 132.8 (s, C_{ortho}), 132.8 (s, C_{ortho}), 128.7 (C_{meta}), 128.5 (C_{meta}), 128.3 (s, C_{para}), 128.2 (s, C_{para}), 66.5 (OCH_2), 51.7 (s, CH), 51.2 (s, CO_2CH_3), 31.2 (s, CH_2As).

Synthesis of 2-(*N*-Benzyloxycarbonyl)succinimidylpropionate (4). Our synthesis follows closely a method described in ref. 21. A solution of 2.3 g Zalanine in 180 mL of CH_2Cl_2 was cooled in an ice-bath and 1.52 g *N*-hydroxysuccinimide (13 mmol) were added under stirring. After 15 min under these conditions, 2.75 g dicyclohexylcarbodiimide (DCCI, 13 mmol) were added. After 48 h of stirring at 4 °C, the precipitate was filtered off and all volatiles were evaporated from the solution. The resulting oil was washed with *n*-pentane–CH_2Cl_2 (1 : 1), dried under vacuum and finally dissolved in a minimum amount of EtOH. Upon storing at about −20 °C, a colourless oil separated which was washed once with Et_2O and then vacuum dried. The colourless oil slowly starts to solidify. Yield: 66%; mp 115 °C. ^{1}H NMR ($CDCl_3$): δ 7.31 (s, 5H, H_{aryl}), 5.43 (d, 1H, $^3J = 7.6$ Hz, NH), 5.13 (m, 2H, C*H*$_2$OPh), 4.77 (m, 1H, CH), 2.80 (s, 4H, $CH_{2succin}$), 1.58 (d, 3H $^3J = 7.2$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 168.47 (s, C=O_{ester}), 168.37 (s, C=O_{succin}), 155.03 (s, $C_{urethan}$), 135.7 (s, C_{ipso}), 128.25, 127.96, 127.9 (C_{ortho}, C_{meta}, C_{para}), 66.98 (s, CH_2O), 47.8 (s, CH), 25.25 (s, $CH_{2succin}$), 18.30 (s, CH_3).

Synthesis of Z-AlaSerBr (5). 0.67 g (2.6 mmol) (*S*)-2-amino-3-bromomethylpropionate hydrobromide and 0.36 g triethylamine (3.4 mmol, 1.3 equivalents) were stirred for 15 min. at room temp. Subsequently, 0.83 g 2-(*N*-Benzyloxycarbonyl)succinimidyl propionate (**4**) in 20 mL CH_2Cl_2 were added and the mixture was stirred for 12 h. After extraction with 2 M aqueous HCl, H_2O and saturated aqueous Na_2CO_3, all volatiles were evaporated and the residue was treated with Et_2O. Remaining Et_3NHCl was separated and the filtrate concentrated to dryness. Yield: 47.6%; oil. ^{1}H NMR ($CDCl_3$): δ 7.36 (m, 5H, H_{aryl}), 6.26 (s, 1H, NH_{ala}), 5.79 (s, 1H, NH_{ser}), 5.43 (d, 1H, $^3J = 4$ Hz, CH_{ser}), 5.11 (s, 2H, C*H*$_2$OPh), 4.39 (m, 1H, CH_{ala}), 3.80 (s, 2H, CH_2Br), 3.74 (s, 3H, OCH_3), 1.41 (d, 3H, $^3J = 7.25$ Hz, CH_{3ala}). ^{13}C NMR ($CDCl_3$): δ 164.1 (s, *C*$OOCH_3$), 155.5 (s, CONH), 155.1 (s, CONH), 136.7, 128.6, 128.5, 128.1 (s, C_{ipso}, C_{ortho}, C_{meta}, C_{para}), 66.9 (s, CH_2O) 52.7 (s, CH_{ser}), 52. 4 (s, CH_3O), 49.5 (s, CH_{ala}), 32.9 (s, CH_2Br), 18.6 (s, CH_{3ala}). This compound was used in the synthesis of ZAlaSerphos (**3d**) as described above.

General synthesis for [RhCl(cod)(SerE)] complexes (8: SerE = ZSerPhos; 9: SerE = BocSerPhos; 11: SerE = ZSerArs). To a solution of 63 mg (0.13 mmol) $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ in 10 mL EtOH, a solution of 26 mmol ZSerphos **3a** (10.9 mg), or BocSerphos **3b** (10.1 mg) or ZSerArs **7** (12.1 mg) in 10 ml EtOH was slowly added at room. temp. under vigorous stirring. After the addition was complete, the mixture was stirred for 1 h and then several times shortly heated with a heat-gun. Subsequently, the solution was concentrated to about 10% of its initial volume. The formed precipitate was filtered off and recrystallized from acetonitrile to give bright yellow products.

*Chloro(η^4-1,5-cyclooctadiene)[R(S)-3-diphenylphosphanylmethyl-N-(carbobenzyloxy)serinate]rhodium(I) [RhCl(ZSerphos)(cod)] (**8**).* Yield: 93%; mp 138 °C. ^{1}H NMR (CD_3CN): δ 7.93 (m, 2H, H_{aryl}), 7.51–7.34 (m, 13H, H_{aryl}), 7.18 (d, 1H, $^3J = 7.45$ Hz,

NH), 5.41 (br, 4H, –CH=), 5.17 (m, 2H, OCH_2), 4.70 (m, 1H, CH), 3.72 (s, 3H, OCH_3), 2.98–2.90 (m, 2H, PCH_2), 2.26 (m, $–CH_2–$), 2.02 (m, $–CH_2–$). ^{13}C NMR (CD_3CN): δ 171.9 (s, $COOCH_3$), 155.8 (s, CONH), 136.8 (s, C_{ipso}), 134.5 (d, $^1J_{PC}$ = 12.1 Hz, C_{ipso}) 132.1 (d, $^4J_{PC}$ = 9.6 Hz, C_{ortho}), 130.8 (s, C_{ortho}), 130.1 (s, C_{meta}), 128.4 (s, C_{para}), 128.6 (s, C_{para}), 127.9 (d, $^3J_{PC}$ = 6.5 Hz, C_{meta}), 71.2 (br, $CH=CH$), 66.4 (s, CH_2O), 52.1 (s, CH_3), 51.6 (s, CH), 32.0 (br, CH_2 (cod)), 28.3 (d, $^1J_{PC}$ = 26.2 Hz, PCH_2). ^{31}P NMR (CD_3CN): δ 20.6 (d, $^1J_{RhP}$ = 151.7 Hz). IR (KBr pellet) [ν/cm^{-1}]: 3307 (s, NH str.), 2915, 2877 (s, CH str.), 1741 (s, C=O), 1707 (ss, (C=O) amide I), 1507 (ss, (N–H) amide II), 1430 (m), 1381, 1354, 1260, 1212, (ss), 1041 (s), 1028, 797, 757, 699. UV/VIS (thf) λ_{max}/nm (ε/l mol^{-1} cm^{-1}): 402.2 (2174), 279.1 (5042). Anal. Calc. for $C_{32}H_{36}ClNO_4PRh$ (667.96 g mol^{-1}): C: 57.54%, H: 5.43%, N: 2.09%, P: 4.64. Found: C: 57.3%, H: 5.4%, N: 2.3%, P: 4.6%.

Chloro(η^4*-1,5-cyclooctadiene)[R(S)-3-diphenylphosphanylmethyl-N-(tert-butoxycarbonyl)serinate]rhodium(*I*) [RhCl(*^{Boc}*Serphos)(cod)] (**9**).* Yield: 62%; mp 105 °C. ^{1}H NMR ($CDCl_3$): δ 7.88 (m, 2H, H_{aryl}), 7.53–7.26 (m, 8H, H_{aryl}), 6.82 (d, 1H, ^3J = 7.14 Hz, NH), 5.54 (br, 2H, –CH=), 4.72 (m, 1H, CH), 4.24 (br, 2H, CH=), 3.73 (s, 3H, OCH_3), 3.18–3.03 (m, 2H, PCH_2), 2.43 (m, $–CH_2–$), 2.04 (m, $–CH_2–$), 1.52 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 172.1 (d, $^3J_{PC}$ = 13.1 Hz, $COOCH_3$), 155.5 (s, CONH), 134.5 (d, $^1J_{PC}$ = 11.8 Hz, C_{ipso}) 132.1 (d, $^4J_{PC}$ = 9.7 Hz, C_{ortho}), 129.6 (s, C_{para}), 128.2 (d, $^3J_{PC}$ = 8.2 Hz, C_{meta}), 104.5 (m, CH=), 78.4 (s, $C(CH_3)_3$), 70.5 (dd, $^1J_{RhC}$ = 53.7 Hz, $^2J_{CP}$ = 13.7 Hz, $CH=CH$), 66.4 (s, CH_2O), 52.2 (s, CH_3), 51.1 (s, CH), 32.9, 32.2, 30.5 (s, CH_2 (cod)), 29.1 (d, $^1J_{PC}$ = 26.1 Hz, PCH_2), 28.6 (s, CH_2 (cod)), 28.14 (s, $C(CH_3)_3$). -^{31}P NMR ($CDCl_3$): δ 20.8 (d, $^1J_{RhP}$ = 150.0 Hz). IR (KBr pellet) [ν/cm^{-1}]: 3296 (s, NH str.), 2962–2830 (s, CH str.), 1754 (ss, C=O), 1697 [ss, (C=O) amide I], 1504 [ss, N–H amide II], 1431 (m, P–C str.), 1362, 1258 (m, $P–CH_2$), 1214, (m), 1160 (s, C–O), 1096 (s), 1017, 801 (s, monosub. arene), 744 (s, monosub. arene), 691. UV/VIS (thf) λ_{max}/nm (ε/l mol^{-1} cm^{-1}): 400.1 (1681), 287.1 (5500). Anal. Calc. for $C_{29}H_{38}ClNO_4PRh$ (633.95 g mol^{-1}): C: 54.94%, H: 6.04%, N: 2.21%. Found: C: 54.3%, H: 5.97%, N: 2.3%.

Chloro(η^4*-1,5-cyclooctadiene)[R(S)-3-diphenylarsanylmethyl-N-(carbobenzyloxy)serinate]rhodium(*I*) [RhCl(*^{Z}*Serars)(cod)] (**11**).* Yield: 35.5%; mp 126 °C. ^{1}H NMR (CD_3CN): δ 7.70–7.66 (m, 2H, H_{aryl}), 7.49–7.2 (m, 13H, H_{aryl}), 6.98 (d, 1H, ^3J = 7.62 Hz, NH), 5.11 (dd, 2H, ^2J = 16.3 Hz, OCH_2), 4.59 (m, 1H, CH), 4.27 (s, 4H, –CH=), 3.68 (s, 3H, OCH_3), 2.89–2.77 (m, 2H, $AsCH_2$), 2.7 (m, $–CH_2–$), 1.86–1.79 (m, $–CH_2–$). ^{13}C NMR (CD_3CN): δ 172.4 (s, $COOCH_3$), 156.2 (s, CONH), 137.4 (s, C_{ipso}), 134.3 (s, C_{ipso}) 130.6 (s, C_{ortho}), 130.35 (s, C_{para}), 129.4 (s, C_{meta}), 128.9 (s, C_{ortho}), 128.5 (s, C_{para}), 128.3 (s, C_{meta}), 82.2 (br, $CH=CH$), 66.8 (s, CH_2O), 52.6 (s, CH_3), 52.1 (s, CH), 31.0 (s, CH_2 (cod)), 28.0 (s, $AsCH_2$). IR (KBr pellet) [ν/cm^{-1}]: 3272 (s, NH str.), 2911, 2872 (s, CH str.), 1743 (ss, C=O), 1710 (s, amide I, C=O), 1527 (s, amide II), 1431 (m), 1211 (ss), 1044, 1025, 734, 693. UV/VIS (thf) λ_{max}/nm (ε/l mol^{-1} cm^{-1}): 374.8 (1242), 277.1 (5000). Anal. Calc. for $C_{32}H_{36}AsClNO_4Rh$ (711.91 g mol^{-1}): C: 53.99%, H: 5.10%, N: 1.97%. Found: C: 47.5%, H: 5.14%, N: 1.3%.

Synthesis of chloro(η^4**-1,5-cyclooctadiene)[2-*R*(*S*)-2′-*S*(*R*)-(benzyloxycarbonylamino)propionylamino)-3-(diphenylphosphanyl)-methylpropionate]rhodium(I) [RhCl(cod)(**^{Z}**AlaSerphos)] (10).** To a solution of 80 mg $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (0.15 mmol) in 10 mL benzene, 160 mg ^{Z}AlaSerphos (**3d**) (0.31 mmol) in 10 mL benzene were added dropwise. The reaction mixture was stirrred for 1 h at room temp. and then all volatiles were evaporated. The residue was recrystallized from EtOH: yield: >95%; mp 108–110 °C. ^{1}H NMR (CD_2Cl_2): δ 8.46/8.16 (d, ^3J = 6.7/6.8 Hz, 1H, NH_{Ser}), 8.06/7.90 (m, 2H, H_{aryl}), 7.55–7.33 (m, 13H, H_{aryl}), 5.75/5.50 (br, NH_{Ala}), 5.57/5.31 (br, 4H, –CH=), 5.17/5.13 (s, 2H, OCH_2Ph), 4.84/4.70 (dddd, $^3J_{\alpha,\beta}$ = 2.8/3.0 Hz, $^3J_{\alpha,\beta'}$ = 13.0/12.0 Hz, $^3J_{\alpha,NH}$ = 6.7/6.8 Hz, $^3J_{\alpha,P}$ = —/8.8 Hz, 1H, CH_{Ser}), 4.60/4.09 (m, 1H, CH_{Ala}), 3.72/3.69 (s, 3H, OCH_3), 3.27/3.01 (ddd, $^2J_{\beta,P}$ = 6.6/3.8 Hz, $^3J_{\alpha,\beta}$ = 12.0/13.0 Hz, $^2J_{\beta,\beta'}$ = 14.7 Hz/—, 1H, CH_2P), 2.87/2.85 01 (ddd, $^2J_{\beta',P}$ = 12.2/14.2 Hz, $^3J_{\alpha,\beta'}$ = 3.0/2.8 Hz, $^2J_{\beta,\beta'}$ = 14.7 Hz/—, 1H, CH_2P), 2.45/2.09 (br, 4H, $–CH_2–$ (cod)), 2.34/1.90 (br, 4H, $–CH_2–$ (cod)), 1.49/1.44 (d, $^3J_{H,H}$ = 7.0/7.0 Hz, CH_{3Ala}). ^{13}C NMR (CD_2Cl_2): δ 173.0/172.5 (s, $COOCH_3$), 171.9/171.7 (s, CONH), 156.1/155.9 (s, CONH), 137.3/137.3 (s, C_{ipso}), 135.4/134.8 (d, $^1J_{P,C}$ = 12.3/12.3 Hz, C_{ipso}), 133.1/132.6 (d, $^2J_{P,C}$ = 9.9/9.9 Hz, C_{ortho}), 128.6/128.2 (d, $^3J_{P,C}$ = 7.0/7.0 Hz, C_{meta}), 131.5/131.1 (s, C_{ortho}), 130.7/130.7 (s, C_{meta}), 128.9/128.8 (s, C_{para}), 128.7/128.7 (s, C_{para}),73.3/72.2/71.5 (d, J = 13.5 Hz, CH (cod)), 66.9/66.9 (s, CH_2Ph), 58.5/58.5 (s, OCH_3), 51.0/51.0 (s, CH_{Ala}), 50.7/50.4 (s, CH_{Ser}), 33.5/33.2/32.7 (br, CH_2 (cod)), 29.1/28.7 (d, $^1J_{C,P}$ = 23.2/23.2 Hz, CH_2P), 20.1/19.7 (s, $CH_{3(Ala)}$). ^{31}P NMR (CD_2Cl_2) δ 20.3/18.4 (d, $^1J_{P,Rh}$ = 150.7/150.7 Hz). ^{103}Rh NMR (CD_2Cl_2) δ 372/365. IR (KBr pellet) [ν/cm^{-1}]: 3258 (s, NH str.), 1735 (ss, C=O), 1717 [ss, (C=O) amide I], 1509 [ss, (N–H) amide II]. Anal. Calc. for $C_{35}H_{41}ClN_2O_5PRh$ (739.05 g mol^{-1}): C: 56.88%, H: 5.59%, N: 3.79%. Found: C: 56.90%, H: 5.61%, N: 3.78%.

Synthesis of (η^4**-1,5-cyclooctadiene)[*R*(*S*)-3-diphenylphosphanemethyl-*N*-(carbobenzyloxy)serinate)rhodium(I) hexafluorophosphate [Rh(cod)(**κ^2**-^{Z}Serphos)]PF$_6$ (12).** 0.31 g [RhCl(cod)-(^{Z}Serphos)] **10** (0.46 mmol) was dissolved in 30 mL benzene. To this yellow solution, 148 mg $[Ag(MeCN)_2]PF_6$ (0.46 mmol) was added under exclusion of light. After 1 h stirring at room temp., the formed precipitate (AgCl) was filtered off and the filtrate was slowly concentrated to dryness dried under vacuum to give a yellow solid. Yield: 97%; mp 74 °C. ^{1}H NMR ($CDCl_3$): δ 7.93–7.34 (m, 15H, H_{aryl}), 6.26 (d, 1H, ^3J = 8.2 Hz, NH), 5.37 (br, 2H, –CH=), 5.01 (m, 2H, OCH_2), 4.84 (m, 1H, CH), 4.33 (br, 2H, –CH=), 3.85 (s, 3H, OCH_3), 3.23–2.80 (m, 2H, PCH_2), 2.47 (m, $–CH_2–$), 2.08 (m, $–CH_2–$). ^{13}C NMR ($CDCl_3$): δ 171.9 (s, $COOCH_3$), 158.5 (s, CONH), 136.3 (d, $^1J_{PC}$ = 10.1 Hz, C_{ipso}), 134.5 (s, C_{ipso}), 133.7 (d, $^4J_{PC}$ = 12.4 Hz, C_{ortho}), 131.8 (s, C_{ortho}), 131.7 (s, C_{meta}), 130.98 (s, C_{para}), 129.1 (s, C_{para}), 128.8 (d, $^3J_{PC}$ = 6.8 Hz, C_{meta}), 108.5 (m, $CH=CH$), 71.3 (br, $CH=CH$), 68.3 (s, CH_2O), 53.9 (s, CH_3), 52.55 (s, CH), 31.9 (br, CH_2 (cod)), 27.5 (d, $^1J_{PC}$ = 26.8 Hz, PCH_2). ^{31}P NMR ($CDCl_3$): δ 25.7 (d, $^1J_{PRh}$ = 148.5 Hz, $RhPCH_2$), −143.0 (sept, $^1J_{PF}$ = 713 Hz, PF_6^-). IR (KBr pellet) [ν/cm^{-1}]: 3384 (br, NH str.), 2918, 2876 (s, CH str.), 1725 (s, C=O), 1623 (ss, amide I), 1432 (m), 1382, 1259, 1218, 1096 (s), 1026, 839 (ss, PF str.), 695. Anal. Calc. for $C_{29}H_{38}F_6NO_4P_2Rh$ (777.48): C: 49.43%, H: 4.67%, N: 1.8%. Found: C: 50.4%, H: 4.9%, N: 2.0%.

Synthesis of (η^4**-1,5-cyclooctadiene)-[2-*R*(*S*)-2′-*S*(*R*)-(benzyloxycarbonylamino)propionylamino)-3-(diphenylphosphanyl)methylpropionate]rhodium(I) hexafluorophosphate [Rh(cod)(**κ^2**-^{Z}AlaSerphos)]-PF$_6$ (13).** 42 mg [RhCl(cod)(^{Z}AlaSerphos)] **10** (0.06 mmol) were dissolved in 5 mL benzene and 23 mg $TlPF_6$ (1.1 eq.)

were added. The reaction mixture was treated for 15 min under ultra-sonication and subsequently the precipitate (TlCl) was removed by filtration. The clear filtrate was evaporated under vacuum to give **13** as a yellow solid in quantitative yield. ^{1}H NMR (CD_2Cl_2): δ 8.24/8.10 (d, ^{3}J = 7.1/7.1 Hz, 1H, NH_{Ser}), 8.04–7.12 (m, 15H, H_{aryl}), 5.76/5.73 (m, 1H, CH_{Ser}), 5.47/5.33 (br, 2H, –CH=), 5.10/5.08 (s, 2H, OCH_2Ph), 5.14/4.90 (d, 6.6/5.9 Hz, 1H, NH_{Ala}), 4.04/3.75 (m, 1H, CH_{Ala}), 4.00/3.97 (s, 3H, OCH_3), 3.41/3.35 (br, 2H, –CH= *trans* to P), 3.21/3.16 (br, 2H, –CH= *trans* to O), 3.05/2.95 (m, 2H, CH_2P), 2.70–1.90 (br, 8H, CH_2 (cod)), 0.82/0.75 (d, ^{3}J = 7.3/7.0 Hz, 3H, CH_{3Ala}). ^{13}C NMR (CD_2Cl_2): δ 179.4/179.3 (br, $C_{Ala}ONH$), 169.3/169.1 (d, $^{3}J_{CP}$ = 17.2/18.3 Hz, $C_{Ser}ONH$), 156.3/156.3 (s, $C{=}O_{cbz}$), 136.1/136.1 (s, C_{ipso}), 134.7/134.4 (d, $^{2}J_{PC}$ = 13.0/13.3 Hz, C_{ortho}), 129.6/129.4 (d, $^{1}J_{PC}$ = 11.1/7.5 Hz, C_{ipso}), 136–126 (C_{aryl}), 110.1/109.5 (m (br), CH (cod) *trans* to P), 71.0/69.9 (m (br), CH (cod) *trans* to O), 67.3/67.2 (s, OCH_2Ph), 54.3/54.3 (s, OCH_3), 52.9/52.9 (s, CH_{Ser}), 51.8/51.2 (s, CH_{Ala}), 35.0/35.4 (m, CH_2P), 34.0/32.1/28.7/27.1 (CH_2 (cod)), 15.9/15.9 (s, $CH_{3(Ala)}$). ^{31}P NMR (CD_2Cl_2): δ 27.9/27.9 (d, $^{1}J_{PRh}$ = 151.8 Hz, PPh_2), −144.4 (sept, $^{1}J_{PF}$ = 712 Hz, PF_6^-). ^{103}Rh NMR (CD_2Cl_2): δ 426/413. IR [ν/cm^{-1}]: 3330 (s, NH str.), 1723 (ss, C=O), 1613 (ss, (C=O) amide I). Anal. Calc. for $C_{35}H_{41}F_6N_2O_5P_2Rh$ (848.55 g mol^{-1}): C: 49.54%, H: 4.87%, N: 3.30%. Found: C: 49.67%, H: 4.88%, N: 3.29%.

Synthesis of acetonitrile(η^4-1,5-cyclooctadiene)[*R*(*S*)-3-diphenylphosphanemethyl-*N*-(carbobenzyloxy)serinate)rhodium(I) hexafluorophosphate [Rh(cod)(^{Z}Serphos)]PF_6 (14). To a solution of 0.31 g [RhCl(cod)(^{Z}Serphos)] **8** (0.46 mmol) in 30 mL acetonitrile a solution of 148 mg $[Ag(MeCN)_2]PF_6$ (0.46 mmol) in 10 mL acetonitrile was added under exclusion of light. After 1 h stirring at room temp., the white precipitate (AgCl) was removed by filtration and the clear filtrate was concentrated under vacuum. The yellow oily residue was washed twice with small amounts of *n*-hexane and than dried in vacuum to give a yellow solid. Yield: 67%. ^{1}H NMR ($CDCl_3$): δ 7.93–7.32 (m, 15H, H_{aryl}), 7.08 (br, 1H, NH), 5.47 (br, 2H, –CH=), 5.21 (m, 2H, OCH_2), 4.77 (m, 1H, CH), 4.23 (br, 2H, –CH=), 3.75 (s, 3H, OCH_3), 3.17–2.88 (m, 2H, PCH_2), 2.48–1.75 (m, 8H, $–CH_2–$), 2.01 (s, 3H, CH_3CN). ^{13}C NMR ($CDCl_3$): δ 171.8 (d, $^{3}J_{PC}$ = 13.1 Hz, $COOCH_3$), 156.5 (s, ONH), 136.05 (s, C_{ipso}), 134.4 (d, $^{1}J_{PC}$ = 11.6 Hz, C_{ipso}), 132.0 (d, $^{4}J_{PC}$ = 9.44 Hz, C_{ortho}), 130.6 (s, C_{ortho}), 129.9 (s, C_{meta}), 128.3 (d, $^{3}J_{PC}$ = 5.4 Hz, C_{meta}), 128.1 (s, C_{para}),127.6 (s, C_{para}), 117 (N), 104.9 (m, *C*H=*C*H), 71.0 (br, *C*H=*C*H), 66.7 (s, CH_2O), 52.5 (s, CH_3), 51.34 (s, CH), 32.8, 32.1, 30.56 (br, CH_2 (cod)), 29.1 (d, $^{1}J_{PC}$ = 26.5 Hz, CPH_2), 28.27 (br, CH_2 (cod)) 1.73 (s, CH_3CN). ^{31}P NMR ($CDCl_3$): δ 20.4 (d, $^{1}J_{PRh}$ = 149.4 Hz, $RhPCH_2$), −143.0 (sept, $^{1}J_{PF}$ = 711 Hz, PF_6^-). IR (KBr pellet) [ν/cm^{-1}]: 3400 (br, NH str.), 2951, 2877 (s, CH str.), 1727 (s, C=O), 1708 (ss, amide I), 1503 (s, amide II), 1430 (m), 1381, 1258, 1094 (s), 1027, 800 (s, PF str), 695.

X-Ray crystallography (see Table 6)

Single crystals were selected in an argon filled glovebox. The data were collected on a Picker four-circle, Stoe upgraded, diffractometer (**8**, **9**) and a Siemens CCD (**10**, **11**) diffractometer. For **8** and **9** an experimental absorption correction (integration from crystal shape) was performed. For **10** and **11**, an absorption correction was

Table 6 Details concerning the data collection and refinement of the structures of **8**, **9**, **10** and **11**

	8	**9**	**10**	**11**
Formula	$C_{32}H_{36}ClNO_4PRh$	$C_{29}H_{38}ClN_1O_4PRh{\cdot}0.5CH_3CN$	$C_{35}H_{40}ClN_2O_5PRh$	$C_{32}H_{36}AsClNO_4Rh$
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	8	4	2	1
T/K	293(2)	293(2)	293(2)	293(2)
D_c/g cm^{-3}	1.428	1.391	1.301	1.511
a/Å	21.339(2)	15.575(8)	10.7543(3)	8.3011(2)
b/Å	30.582(2)	10.255(5)	11.7575(2)	9.7422(3)
c/Å	9.520(5)	19.57(1)	16.8367(4)	10.7146(3)
α/°	90	90	104.312(1)	87.201(1)
β/°	90.55(5)	90.06(4)	91.873(1)	76.277(1)
γ/°	90	90	112.649(1)	68.507(1)
V/Å^3	6212(7)	3126(3)	1884.17(8)	782.54(4)
μ/mm^{-1}	6.015	5.965	0.606	1.716
Crystal size/mm	0.2 × 0.1× 0.1	0.2 × 0.15 × 0.1	0.2 × 0.1 × 0.1	1.0 × 0.6 × 0.4
Radiation (λ/Å)	Cu-Kα; graphite monochromator (1.54178)		Mo-Kα; graphite monochromator (0.71073)	
2θ range/°	$4.14 \le 2\theta \le 85.00$	$5.68 \le 2\theta \le 99.96$	$2.52 \le 2\theta \le 56.56$	$3.92 \le 2\theta \le 65.40$
Index ranges, hkl	−18 to 18, 0 to 26, 0 to 8	−15 to 11, 0 to 10, 0 to 19	−14 to 13, −12 to 15, −22 to 17	−11 to 12, −14 to 13, −15 to 8
No. of rflns total	4357	2998	15731	8075
No. of unique rflns	4357	2998	9127	6090
No. of parameters/restraints	649/0	356/0	433/0	361/3
R_1 (rflns $I > 2\sigma(I)$)	0.0440	0.0445	0.0557	0.0423
wR_2 (all data)	0.1216	0.1193	0.1714	0.1076
Max., min. residual electron density/e Å^{-3}	0.563, −0.406	1.002, −0.553	1.301, −0.766	1.068, −1.015

applied using the program SADABS. The structures were solved by direct methods, all non-hydrogen atoms were refined against F^2 (G. M. Sheldrick, SHELXL-97, Göttingen, 1993, 1997) with anisotropic temperature factors while the hydrogen atoms were constrained using a riding model.

The asymmetric unit of **9** contains half a molecule of acetonitrile, disordered over two positions which were refined with an occupancy factor of 0.5 for each site. Two diastereotopic molecules were found in the elementary cell of **10**. While the racemic SerPhos residue fulfils the symmetry properties of the centrosymmetric space group, this is not the case for the alanine. Hence the methyl group of the alanine was found on two different positions and was refined as a disordered group with an occupancy factor of 0.5 for each site.

CCDC reference numbers 178294, 178295, 283233 and 283234.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512653c

References

1 A. Agarkov, S. J. Greenfield, T. Ohishi, S. E. Collibee and S. R. Gilbertson, *J. Org. Chem.*, 2004, **69**, 8077. For a review, see: S. R. Gilbertson, *Prog. Inorg. Chem.*, 2001, **50**, 433.

2 See, for example: *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 2002.

3 For experimentally determined binding constants, see: (*a*) C. M. Haar, S. P. Nolan, W. J. Marshall, K. G. Molloy, A. Prock and W. P. Giering, *Organometallics*, 1999, **18**, 474; (*b*) D. C. Smith, Jr., C. M. Haar, E. D. Stevens and S. P. Nolan, *Organometallics*, 2000, **19**, 1427.

4 See, for example: (*a*) H. Park and T. V. RajanBabu, *J. Am. Chem. Soc.*, 2001, **124**, 734, and references therein; (*b*) T. V. RajanBabu, T. A. Ayers and A. L. Casalnuovo, *J. Am. Chem. Soc.*, 1994, **116**, 4101; (*c*) A. Kumar, G. Oehme, J. P. Roque, M. Schwarze and R. Selke, *Angew. Chem.*, 1994, **106**, 2272; A. Kumar, G. Oehme, J. P. Roque, M. Schwarze and R. Selke, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2197; (*d*) R. Selke, *J. Organomet. Chem.*, 1989, **370**, 249; (*e*) R. Selke, *J. Organomet. Chem.*, 1989, **370**, 241; (*f*) V. Šunjić, I. Habuš and G. Snatzke, *J. Organomet. Chem.*, 1989, **370**, 295; (*g*) V. A. Pavlov, E. I. Klabunovskii, Y. T. Struchkov, A. A. Voloboev and A. I. Yanovsky, *J. Mol. Catal.*, 1988, **44**, 217.

5 See, for example: S. R. Gilbertson, S. E. Collibee and A. Agarkov, *J. Am. Chem. Soc.*, 2000, **122**, 6522, and references therein.

6 G. Xu and S. R. Gilbertson, *Tetrahedron Lett.*, 2002, **43**, 2811.

7 (*a*) S. R. Gilbertson and X. Wang, *Tetrahedron*, 1999, **55**, 11609; (*b*) S. R. Gilbertson and X. Wang, *Tetrahedron Lett.*, 1996, **37**, 6475.

8 (*a*) I. Grassert, K. Schinkowski, D. Vollhardt and G. Oehme, *Chirality*, 1998, **10**, 754; (*b*) I. Grassert, V. Vill and G. Oehme, *J. Mol. Catal. A, Chem.*, 1997, **116**, 231.

9 S. R. Gilbertson, G. Chen, J. Kao, A. Beatty and C. F. Campana, *J. Org. Chem.*, 1997, **62**, 5557.

10 (*a*) C. Meyer, H. Grützmacher and H. Pritzkow, *Angew. Chem.*, 1997, **109**, 2576; C. Meyer, H. Grützmacher and H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2471; (*b*) H. Grützmacher, C. Meyer, S. Boulmaâz, H. Schönberg, S. Deblon, J. Liedtke, S. Loss and M. Wörle, *Phosphorus Sulfur Silicon*, 1999, **114**, 465.

11 D. J. Brauer, K. W. Kottsieger, S. Schenk and O. Stelzer, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1151.

12 S. J. Greenfield and S. R. Gilbertson, *Synthesis*, 2001, **15**, 2337.

13 See, for example: (*a*) H. J. Dyson and P. Wright, *Annu. Rev. Biophys. Chem.*, 1991, **20**, 519; (*b*) M. Williamson and J. P. Waltho, *Chem. Soc. Rev.*, 1992, 227; (*c*) C. Altona, R. Francke, R. De Haen, J. Ippel, G. Daalmans, A. Hoekzema and J. Van Wijk, *Magn. Reson. Chem.*, 1994, **32**, 670; (*d*) A. C. Wang and A. Bax, *J. Am. Chem. Soc.*, 1996, **118**, 2483, and references therein.

14 (*a*) K. Wüthrich, *NMR of Proteins and Nucleic Acids*, Wiley, New York, 1986; (*b*) V. Bystrov, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1976, **10**, 41.

15 Shifts by 50–100 cm^{-1} for ν(C=O) to lower wavenumbers and downfield (high frequency) shifts by ≈7 ppm of the ^{13}C resonance of the coordinating amide group in P,C=O ligands were reported: (*a*) S. Sjövall, L. Kloo, A. Nikitidis and C. Anderson, *Organometallics*, 1998, **17**, 579; (*b*) M. Kuriyama, K. Nagai, K.-i. Yamada, Y. Miwa, T. Taga and K. Tomioka, *J. Am. Chem. Soc.*, 2002, **124**, 8932.

16 Alternatively one may speculate that the alanine residue is even more fluxional in **10** and the sharper NMR lines stem from averaged signals even at low temperature.

17 D. Savithri, C. Leumann and R. Scheffold, *Helv. Chim. Acta*, 1996, **79**, 288.

18 M. Monsigny, D. Delay and M. Vaculik, *Carbohydr. Res.*, 1977, **59**, 589.

19 D. Theodoropoulos, I. Schwartz and R. Walter, *Biochemistry*, 1967, **6**, 3927.

20 T. H. Lemmen, G. V. Goeden, J. C. Huffman, R. L. Geerts and K. G. Caulton, *Inorg. Chem.*, 1990, **29**, 3680.

21 M. Santamaria, T. Maina, U. Mazzi and M. Nicolini, *Inorg. Chim. Acta*, 1995, **240**, 291.