Synthesis of C_1-Symmetric Tripod Ligands Containing a P,P,N Donor Set – η^2-Coordination in d^8-Metal Complexes

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Dedicated to Professor Horst Kisch on the occasion of his 60th birthday

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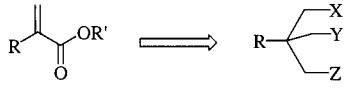
Tripod ligands $RC(CH_2X)(CH_2Y)(CH_2Z)$ (X, Y, Z = NR_2, PR_2) are accessible from α,β-unsaturated esters $R(=CH_2)COOR'$. The key steps in this synthetic approach are Michael additions of amines and phosphanes to produce $RCH(COOR')(CH_2X)$ (X = NR_2, PR_2) (**2** and **3**), followed by hydroxymethylation with paraformaldehyde to result in $RC(COOR')(CH_2OH)(CH_2X)$ (X = NR_2) (**4**). Standard transformations of this C_1-symmetric precursor allow for the synthesis of tripod ligands such as $PhC(CH_2pz)(CH_2PPh_2)(CH_2PMes)$ (**11**). Coordination of these ligands with d^8-metal ions [nickel(II), palladium(II), rhodium(I)] results in square-planar complexes with the chelate cycles in half-chair, twist-boat or boat conformations, depending on the specific substitution pattern. Coordination through two phosphane donors with the nitrogen donor acting as a dangling arm is generally preferred throughout. Detail preparative procedures and complete characterisation by analytical methods, including X-ray analysis of the coordination compounds, are given.

Introduction

While tripod ligands $CH_3C(CH_2PR_2)_3$ have been known for a long time,[1] the synthesis of chiral tripodal ligands $CH_3C(CH_2X)(CH_2Y)(CH_2Z)$ (X, Y, Z = donor groups) has only been developed in the last decade.[2,3] Different synthetic procedures were found to allow access to these compounds. It was observed, however, that the introduction of nitrogen donors in one or more of the X, Y, Z positions called for quite specific procedures, dependent both on the specific precursor and on the specific type of the NRR′ function to be introduced.[2b,2d,3g,3h,4] A general drawback of the strategies so far published for the synthesis of $RC(CH_2X)(CH_2Y)(CH_2Z)$ resides in the fact that there is no free choice of the kind of the group R fixed at the backbone of the tripodal ligand. Only ligands with R = H,[5] CH_3,[1–3] and CH_2OR'[6] are easily available by the published routes, while other functions such as benzyl, alkyl or alkenyl groups have to be introduced into appropriate ligand precursors by specific reactions,[7] which do not, however, in general allow for the consequent introduction of three different donor groups X, Y, and Z.

In search of a solution for both of these problems we studied α,β-unsaturated esters $RC(=CH_2)COOR'$ as potential precursors (see Scheme 1). We now report that the transformation of these precursors into tripod ligands is achieved with different kinds of groups R as well as different kinds of donor functions X, Y, Z including NRR′.

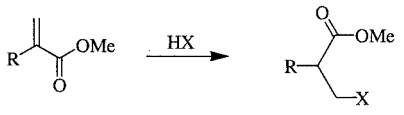


Scheme 1

Results and Discussion

Ligand Synthesis

α,β-Unsaturated esters $RC(=CH_2)COOR'$ are known to undergo 1,4-addition reactions with different types of HX compounds, including RR′NH[8] and R_2PH.[9] By applica-



1 **2, 3**

1a R = Ph
1b R = CH_3

2a R = Ph X = $N(CH_2)_5$
2b R = CH_3 X = NEt_2
2c R = CH_3 X = $N(CH_2)_5$
2d R = CH_3 X = pz
3 R = Ph X = PPh_2

Scheme 2

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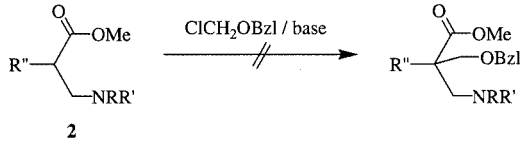
tion of this strategy, compounds **2** and **3** are obtained from compounds **1** in high yields (see Scheme 2 and Exp. Sect.).

The ester function in compounds **2** offers itself for transformation into a CH_2X' donor entity in later steps of the reaction. In order to obtain tripod ligands, an additional functionalisable CH_2X'' group has to be added to the central position of **2** in such a way that it forms the third "leg" of the desired tripod ligand. Hydroxymethylation is the obvious solution. Reactions of this type are generally quite efficient, but only in the absence of a CH_2NRR' substituent and with aldehyde or ketone functions, rather than an ester function as present in **2**.[10] Unactivated esters of the general type of framework as present in **2** – that is, disubstituted in the α,α′-position – are only rarely found to be suitable precursors for hydroxymethylation.[11] Hydroxymethylation is generally only successful if they are activated by an additional electron-withdrawing group, such as in malonic ester derivatives, and this type of reaction has accordingly been used as a key step for the construction of specific tripod ligands.[3d,7b,7c]

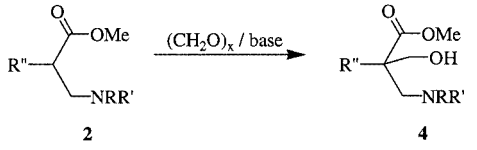
With compound **2**, however, it was found that even substitution under basic conditions by chloromethyl benzyl ether failed (see Scheme 3).



2

Scheme 3

While the direct introduction of a CH_2OH group in the form of formaldehyde or paraformaldehyde is reported to be less efficient[10,12] than the synthesis of its protected form by use of $ClCH_2OBzl$, it still proved possible to find suitable conditions for the synthesis of **4** from **2** by just this route (Scheme 4). The key to obtaining the necessary reactivity was the nature of the deprotonation of **2**; such deprotonation to afford the corresponding enolate is possible with NaH/DMF at 20 °C or LDA/THF at −70 °C. The choice of either one of these bases depends on the nature of R′′ and NRR′ in **2** (see Exp. Sect.), while KO*t*Bu was found to be ineffective in this kind of reaction.



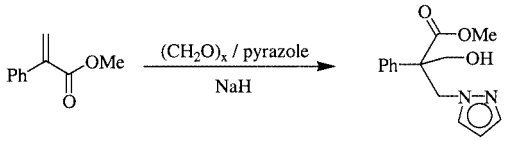
2 **4**

2a R" = Ph NRR' = $N(CH_2)_5$ **4a** R" = Ph NRR' = $N(CH_2)_5$
2b R" = CH_3 NRR' = NEt_2 **4b** R" = CH_3 NRR' = NEt_2
2c R" = CH_3 NRR' = $N(CH_2)_5$ **4c** R" = CH_3 NRR' = $N(CH_2)_5$

Scheme 4

The yields of the transformations of **2** into **4** are between 45 and 65% and correspond well to yields reported for the hydroxymethylation of RCH_2COR' by paraformaldehyde.[10]

In the case of **1a**, Michael addition and hydroxymethylation could be performed in a one-pot reaction with pyrazole as the HNRR′ reagent (see Scheme 5),[13] compound **4d** being obtained in 65% yield in this way. This type of one-pot reaction was, however, only successful with **1a** as the Michael acceptor and pyrazole as the Michael donor, and so only **4d** – and not **4a**–**4c** – is accessible by this simple route.

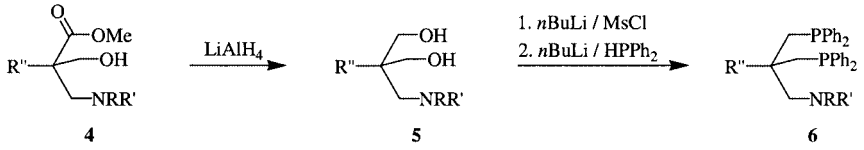


1a **4d**

Scheme 5

The compounds **2**–**4** have been fully characterised by elemental analysis, mass spectrometry and ^1H and ^{13}C NMR spectroscopy (see Tables 4, 6, 7 and Exp. Sect.).

Reduction of the ester function in **4** afforded the diols **5**, which – after activation by mesyl chloride – could be transformed into the diphosphanes **6** (see Scheme 6). These diphosphanes are tripod ligands containing two P and one N donor functions. Their identity was established by their elemental analyses, mass spectra and NMR spectra (see



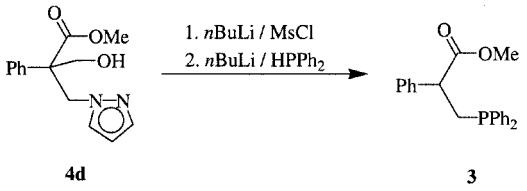
4 **5** **6**

4b R" = CH_3 NRR' = NEt_2 **5a** R" = CH_3 NRR' = NEt_2 **6a** R" = CH_3 NRR' = NEt_2
4d R" = Ph NRR' = pz **5b** R" = Ph NRR' = pz **6b** R" = Ph NRR' = pz

Scheme 6

Tables 5−7 and Exp. Sect.) and by the formation of tripod metal complexes (see Coordination Chemistry).

Since compounds **4** already contain three different functionalities, their transformation into chiral racemic tripod ligands should be possible. The activation of the OH group of **4** by mesyl chloride was found to be quite inefficient in this respect: either the yields were very low or, as in the case of **4d**, formal elimination of the CH_2pz group occurred, to give **3** as the main product (see Scheme 7).



Scheme 7

The mechanism of this reaction has not yet been studied, but $MePPh_2$ and $MeP(=O)Ph_2$ have been observed (^{31}P NMR, GC/MS) as accompanying products.

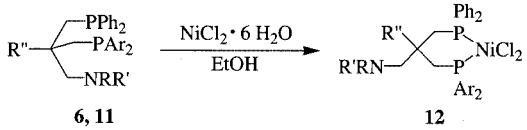
In contrast, activation by means of the Appel reaction[14] transformed **4** into **7** in fair yields (see Scheme 8). The direct substitution of the chloride function of **7** by diphenylphosphide was successful for **7a**, while with **7b**, with its pyrazolyl functionality, sluggish reactivity, and partial decomposition was observed. For **7a**, with its diethylamine function, a clear transformation into **8** (63% yield) was accomplished (see Scheme 8).

A more general route is based on the reduction of the ester group as the first step. The activation of the resulting alcohol function by mesyl chloride was followed by the substitution of the mesylate by diarylphosphide. The remaining chlorine function could then be substituted by a different diarylphoshide. The reaction sequence has been fully worked out for the transformation **7b** → **9** → **10** → **11** (see Scheme 9). The two phosphide substitution steps give yields normal for this type of process, with an overall yield of **11** of 35% based on **7b**. To avoid unwanted side reactions during these substitution steps (internal cyclization) the reaction temperatures have to be thoroughly controlled (see Exp. Sect., for elemental analysis, NMR spectra, and mass spectra of compounds **7−11**, see Tables 4−7).

Coordination Chemistry

Tripod ligands containing nitrogen and phosphorus donor functions in one and the same ligand are known to form tripodal coordination compounds. This has been demonstrated with $Mo(CO)_3$ as the coordinated entity.[3g,3h] With d^8-ions as the metal constituents, square-planar coordination of the metal ion is generally preferred and is exclusively observed for tripod ligands containing a P,P,N donor set.[4b,15] With this type of η^2-coordination of a tripod ligand containing different types of donor functions, it is not clear a priori which kinds of donor functions will be coordinated.

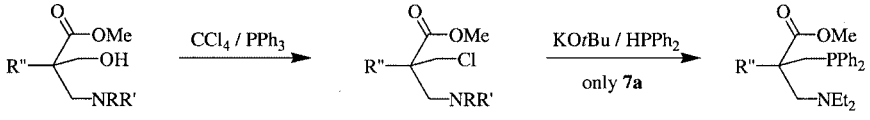
Compounds **6**, **8**, and **11** offer the opportunity to address this question. The coordination behaviour of this type of compounds with respect to nickel(II), palladium(II), and rhodium(I) was therefore analysed.



	R"	PAr_2	NRR'
6a	CH_3	PPh_2	NEt_2
6b	Ph	PPh_2	pz
11	Ph	$PMes_2$	pz

	R"	PAr_2	NRR'
12a	CH_3	PPh_2	NEt_2
12b	Ph	PPh_2	pz
12c	Ph	$PMes_2$	pz

Scheme 10

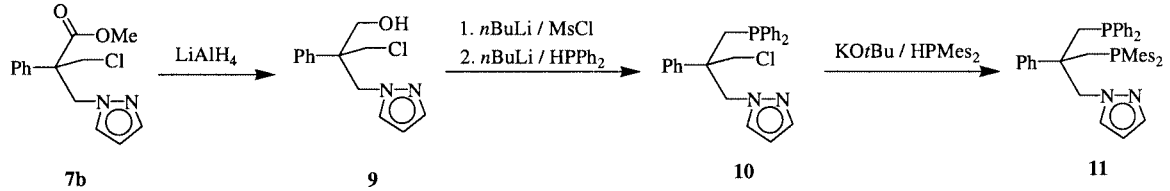


4b R" = CH_3 NRR' = NEt_2
4d R" = Ph NRR' = pz

7a R" = CH_3 NRR' = NEt_2
7b R" = Ph NRR' = pz

R" = CH_3

Scheme 8



Scheme 9

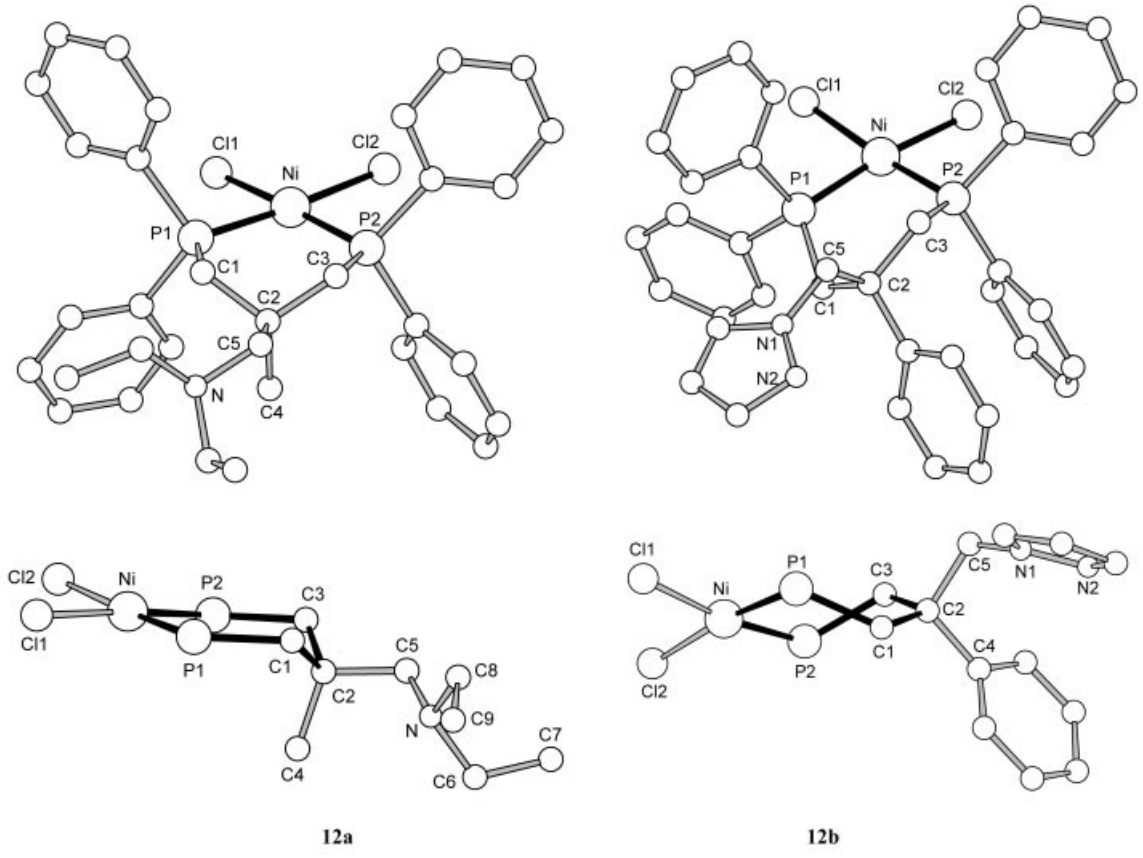


Figure 1. Two views of the X-ray structure of compound **12a** (left, half-chair conformation) and **12b** (right, twist-boat conformation); top: general view; bottom: view showing the conformation of the six-membered chelate cycle (phenyl groups are not shown for the sake of clarity)

Tripod ligands **6a**, **6b**, and **11** each contain a P,P,N donor set. Complexation with aqueous $NiCl_2$ resulted in orange to red, square-planar nickel(II) complexes **12** in which the two phosphane functions are coordinated exclusively while the nitrogen-functionalised "leg" is a dangling substituent (see Scheme 10). The same type of coordination behaviour has already been observed for other ligands of the type $RC(CH_2PPh_2)_2(CH_2X)$. Phosphorus coordination is preferred over coordination of ligand groups X such as NRR′, OH, OMe, and SR.[3e,16]

The structures of **12a** and **12b** as determined by X-ray crystallography are shown in Figure 1.

Interestingly, the conformations of the chelate cycles are different for the two compounds − being a half-chair form in **12a** and a twist-boat form in **12b** (see Table 1). The relative stability of these types of conformations has recently been analysed thoroughly.[17]

Compound **8** has three different potential donor substituents within the tripodal framework: coordination is conceivable for the PPh_2, the NEt_2 and the ester groups. Compound **8** was found to react with $(dme)NiCl_2$ to give a violet, paramagnetic compound, which − due to its insufficient crystallisation properties − could not be obtained in analytically pure form. In contrast, palladium(II), introduced by use of $(cod)PdCl_2$, and rhodium(I), introduced by use of $[(nbd)RhCl]_2$, give the readily crystallised, diamagnetic compounds **13** (yellow) and **14·PF$_6$** (orange) (Scheme 11).

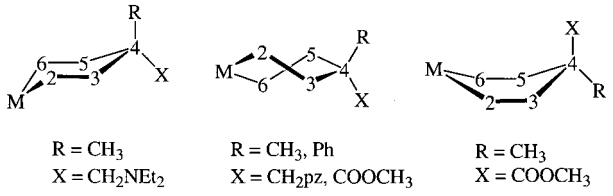
NMR (^1H, ^{13}C, ^{31}P) spectra of **13** reveal the expected resonances as sharp signals even at 30 °C (see Tables 4 and 6). The ethyl groups of the NEt_2 entity are diastereotopic, consistent with the proposed structure. Diastereotopic differentiation of the ethyl groups in **14·PF$_6$** is only observable below −30 °C (see Tables 4 and 6), while above this temperature some dynamic process gives rise to considerable broadening of the peaks such that the diastereotopic differentiation is no longer observable. The dynamic process is presumably due to a change in the conformation of the chelate cycle.[17,18]

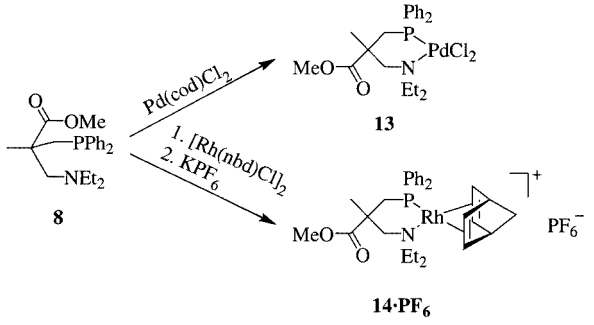
X-ray analysis of **13** establishes the square-planar coordination of the palladium atom and reveals that the chelate cycle has a twist-boat conformation (see Figure 2, Table 1). The X-ray structure of **14$^+$** similarly establishes the pseudo-square-planar coordination of the rhodium atom. The chelate cycle is found to have the unconventional boat form, with the sterically more demanding methoxycarbonyl group axial and the methyl group in the equatorial position (see Figure 2, Table 1). The methoxycarbonyl group is orientated such that the normal to its plane points toward the rhodium centre (see Figure 2). The distance between the

Table 1. Selected bond lengths [pm], bond angles [°] and torsion angles [°] of compounds **12a**, **12b**, **13**, and **14**

	12a [M = Ni][a]	**12b** [M = Ni][a]	**13** [M = Pd][a]	**14·PF$_6$** [M = Rh][a]
M−Cl	219.4(1); 221.6(1)	219.8(1); 219.9(1)	229.8(1)[b]; 239.1(1)[c]	–
M−P	215.8(1); 216.8(1)	215.1(1); 215.7(1)	221.8(1)	228.8(1)
M−N	–	–	213.8(1)	223.8(2)
M−C	–	–	–	210.7(2)[b]; 212.3(2)[b] 223.4(2)[c]; 224.0(2)[c]
P1−M−P2/N	96.1(1)	91.8(1)	93.5(1)	91.1(1)
Cl1−M−Cl2	92.1(1)	94.5(1)	89.9(1)	–
P1−M−Cl1	85.9(1)	87.4(1)	85.6(1)	–
P2/N−M−Cl2	86.2(1)	87.6(1)	92.4(1)	–
P1−M−Cl2	175.1(1)	170.9(1)	167.1(1)	–
P2/N−M−Cl1	176.3(1)	172.4(1)	172.9(1)	–
Chelate cycle[d]	half-chair (2,6 = P)	λ-twist boat (2,6 = P)	λ-twist boat (2 = P, 6 = N)	boat (2 = P, 6 = N)
M−2−3−4	+44.1(4)	+67.9(2)	+59.6(3)	+13.3(2)
2−3−4−5	−72.2(5)	−35.3(2)	−30.8(3)	−74.0(2)
3−4−5−6	+67.2(5)	−30.0(2)	−40.1(4)	+64.2(2)
4−5−6−M	−36.9(4)	+65.0(2)	+71.0(3)	+7.6(2)
5−6−M−2	+8.4(2)	−25.4(1)	−27.6(2)	−48.8(2)
6−M−2−3	−10.8(2)	−25.8(1)	−25.7(1)	+34.7(2)
3−2−6−5	−2.3	−47.7	−51.3	−8.3

[a] Standard deviations in units of the least significant digit are given in each case. [b] *trans* to N. [c] *trans* to P. [d] A consistent numbering scheme (torsion angles) for all the compounds as depicted below is used for the sake of easier comparison:





Scheme 11

rhodium atom and the carboxy group (Rh−O: 348.7 pm and 350.2 pm) is too large to be interpreted in terms of any direct bonding between these partners while it is short enough for some type of secondary interaction to be assumed (see Table 2).

Boat conformations as observed for **14**$^+$ have not yet been found in crystal structures of rhodium complexes with six-membered phosphorus-containing saturated chelate cycles, while their inherent relative stability in some cases has been indicated by a thorough molecular dynamics analysis.[17b] With the dynamic behaviour of six-membered phosphorus-containing saturated chelate cycles in mind,[17,18] equilibria between different ring conformations are the most probable explanation for the temperature dependence of the behaviour of the NMR spectra of **14·PF$_6$**.

Conclusion

It has been shown that α,β-unsaturated esters RC(=CH_2)COOR′ may serve as starting materials for the synthesis of tripod ligands RC(CH_2X)(CH_2Y)(CH_2Z). The procedure allows for the incorporation of different types of substituents R in the backbone and also allows the introduction of donor functions X = NR_2 in the presence of different potential phosphorus donor functions (Y, Z).

Ligands of this type − containing a P,P,N donor set − coordinate to d^8-metal ions through their two phosphorus donor groups, resulting in a square-planar coordination with the amine function acting as a dangling arm.

Ligands containing a P,N,O donor set (O = part of a carboxy group) form complexes in which P,N donors serve as ligands in six-membered chelate cycles. For the d^8-metal ions Pd^{II} and Rh^{I} the coordination is square-planar. The O donor is not involved in direct bonding to the metal atom but may engage in secondary interaction with it.

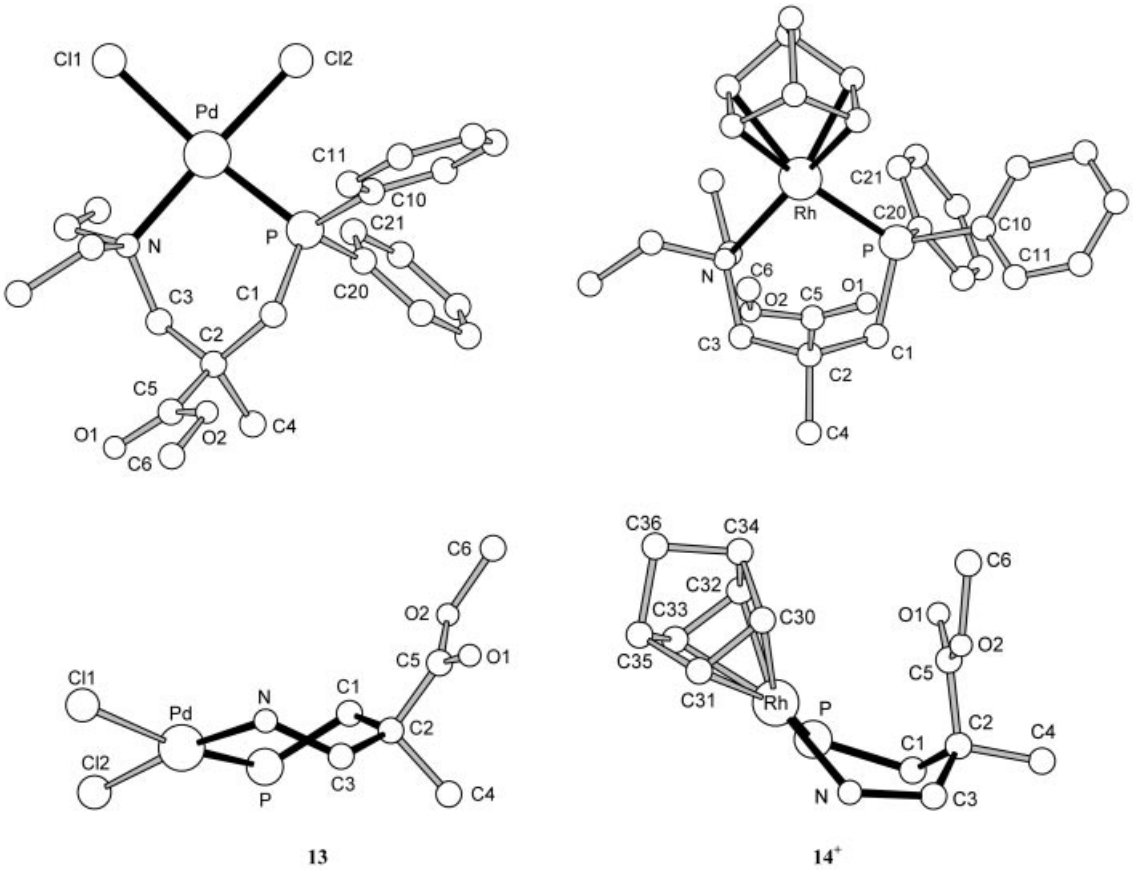


Figure 2. Two views of the X-ray structure of compound **13** (left, twist-boat conformation) and the cation **14**$^+$ (right, boat conformation); top: general view; bottom: view showing the conformation of the six-membered chelate cycle (phenyl groups are not shown for the sake of clarity)

Table 2. Selected bond lengths [pm], bond angles [°] and torsion angles [°] of the ester groups in compounds **13** and **14**

	13 [M = Pd][a]	**14**·PF_6 [M = Rh][a]
C5−O1 (C=O)	119.9(4)	120.0(3)
C5−O2 (C−O)	134.6(4)	133.7(3)
C6−O2 (C−O)	145.8(4)	145.1(3)
M−C5	485.4	313.9
M−O1	559.2	348.7
M−O2	533.3	350.2
C2−C5−O1	124.6(3)	123.9(2)
C2−C5−O2	111.6(3)	112.6(2)
O1−C5−O2	123.6(3)	123.3(2)
C6−O2−C5	116.7(3)	116.6(2)
C6−O2−C5−O1	−3.4(5)	+3.5(3)
C6−O2−C5−C2	−0.1(3)	−8.7(2)

[a] Standard deviations in units of the least significant digit are given in each case.

The conformations of the six-membered chelate cycles comprise the conventional half-chair and twist-boat forms as well as the unconventional boat form.

Experimental Section

General Remarks: All manipulations involving phosphanes were carried out under argon by use of standard Schlenk techniques. All solvents were dried by standard methods[19] and distilled under argon. The solvents $CDCl_3$ and CD_2Cl_2 used for NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4 Å molecular sieves. NMR: Bruker Advance DPX 200 at 200.12 MHz (^{1}H); 50.323 MHz (^{13}C{^{1}H}); 81.015 MHz (^{31}P{^{1}H}); T = 303 K unless stated otherwise; chemical shifts (δ) with respect to $CDCl_3$ (^{1}H: δ = 7.27; ^{13}C: δ = 77.0 ppm) and CD_2Cl_2 (^{1}H: δ = 5.32 ppm; ^{13}C: δ = 53.5 ppm) as internal standards. ^{31}P chemical shifts (δ) with respect to 85% H_3PO_4 (^{31}P: δ = 0 ppm) as external standard. FT-IR: Biorad Excalibur FTS 3000 spectrophotometer (samples in solutions between CaF_2 windows). MS: Finnigan MAT 8230. EI (70 eV). FAB (xenon; matrix: 4-nitrobenzyl alcohol). Melting points: Gallenkamp MFB-595010; uncorrected values. Elemental analyses: Microanalytical Laboratory of the Organic-Chemical Institute, University of Heidelberg.

Crystallographic Structure Determinations: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil, and fixed to a glass capillary. The measurements were carried out with an Enraf−Nonius Kappa CCD diffractometer, with graphite-monochromated Mo-K_α radiation used throughout.

Table 3. Crystallographic data of compounds **12a**, **12b**, **13**, and **14**

Compound	**12a**	**12b**	**13**	**14·PF$_6$**
Empirical formula (without solvate)	$C_{33}H_{39}Cl_2NNiP_2$	$C_{37}H_{34}Cl_2N_2NiP_2$	$C_{22}H_{30}Cl_2NO_2PPd$	$C_{29}H_{38}F_6NO_2P_2Rh$
Formula mass [g/mol]	641.2	698.2	548.8	711.5
Solvate	1 CH_2Cl_2; 0.5H_2O	–	–	–
Crystal size [mm]	0.15×0.15×0.05	0.10×0.10×0.10	0.10×0.02×0.02	0.20×0.20×0.15
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	$Pca2_1$ (no. 29)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$Pcba$ (no. 61)
Lattice constants:				
a [pm]	2153.9 (4)	1075.6 (2)	1252.3 (3)	2218.7 (4)
b [pm]	1124.4 (2)	1900.5 (4)	1383.4 (3)	1621.6 (3)
c [pm]	1411.8 (3)	1642.5 (3)	1354.3 (3)	1625.7 (3)
β [°]	90	97.54 (3)	92.85 (3)	90
V [10^6·pm^3]	3419 (1)	3328 (1)	2343 (1)	5849 (1)
Z	4	4	4	8
d_X [g·cm^{-3}]	1.426	1.393	1.558	1.616
T [K]	200	200	293	200
Scan range [°]	3.6 ≤ 2θ ≤ 54.9	3.3 ≤ 2θ ≤ 54.0	4.2 ≤ 2θ ≤ 60.2	3.7 ≤ 2θ ≤ 55.8
Method	ω-scan, Δω = 1.0°	ω-scan, Δω =1.0°	ω-scan, Δω =1.0°	ω-scan, Δω =1.0°
Scan speed	30 sec/frame	5 sec/frame	10 sec/frame	10 sec/frame
No. of measured reflections	7860	14564	11921	13968
No. of unique reflections	7544	7251	6845	6966
No. of observed reflections	6782	6095	4985	5451
Observation criterion	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$
No. of param. refined	348	400	257	409
Resid. el. dens. [10^{-6}e·pm^{-3}]	1.42	0.72	0.89	0.40
R_1/R_w [%] (refinement on F^2)	6.6/15.2	3.7/10.3	4.6/11.4	3.4/8.5

Table 4. Chemical shifts (δ values), integrals [x H], and coupling constants J in the ^{1}H NMR spectra of **4**, **7**, **8**, **13**, and **14**

No.[a]	CH_2N [2 H]	CH_2X [2 H]	OCH_3 [3 H]	C_qCH_3 [3 H]	OH [1 H]	Aryl-H	Others
4a[b]	2.84 d, 3.49 d, $^2J_{H,H}$ = 13.9	4.40 br. s, X = OH	3.70 s	–	6.49 br. s	7.29 m [5 H]	1.38–1.45 m, 1.54 br. s, 2.42–2.69 m [10 H], piperidine-H
4b[b]	2.49 d, 3.02 d, $^2J_{H,H}$ = 14.0	3.61 d, 3.81 d, $^2J_{H,H}$ = 11.3, X = OH	3.63 s	1.04 s	5.44 br. s	–	0.93 t, 2.40–2.60 m [10 H], $^3J_{H,H}$ = 7.1, NEt_2
4c[b]	2.41 d, 3.02 d, $^2J_{H,H}$ = 13.8	3.68 d, 3.91 d, $^2J_{H,H}$ = 11.0, X = OH	3.70 s	1.07 s	5.55 br. s	–	1.36–1.42 m, 1.49–1.52 m, 2.38–2.54 m [10 H], piperidine-H
4d[b]	4.61 d, 5.02 d, $^2J_{H,H}$ = 14.4	3.93 d, 4.17 d, $^2J_{H,H}$ = 12.2, X = OH	3.74 s	–	4.61 br. s	7.33–7.39 m [5 H]	6.22 t, 7.31 d, 7.55 d [3 H], $^3J_{H,H}$ = 2.0, pyrazole-H
7a[b]	2.64 d, 2.73 d, $^2J_{H,H}$ = 14.2	3.69 d, 3.79 d, $^2J_{H,H}$ = 10.8, X = Cl	3.70 s	1.25 s	–	–	0.95 t, 2.53 q [10 H], $^3J_{H,H}$ = 7.1, NEt_2
7b[b]	4.80 d, 5.13 d, $^2J_{H,H}$ = 14.1	4.06 d, 4.34 d, $^2J_{H,H}$ = 10.9, X = Cl	3.81 s	–	–	7.07–7.11 m [2 H], 7.35–7.38 m [3 H]	6.12 t, 6.99 d, 7.52 d [3 H], $^3J_{H,H}$ = 2.0, pyrazole-H
8[b]	2.67 d, 2.85 d, $^2J_{H,H}$ = 13.7	2.35 d, 2.50–2.66 m, $^2J_{H,H}$ = 10.8, X = PPh_2	3.49 s	1.25 s	–	7.35–7.51 m [10 H]	0.97t, 2.50–2.66m [10 H], $^3J_{H,H}$ = 7.1, NEt_2
13[c]	2.77 d, 2.99 d, $^2J_{H,H}$ = 14.3	2.43 d, 3.20 d, $^2J_{H,H}$ = 16.0, X = PPh_2	3.74 s	1.04 s	–	7.45–7.73 m [8 H], 8.13–8.24 m [2 H]	1.44 t, 1.75 t, 2.70–4.30 m [10 H], $^3J_{H,H}$ = 7.1, NEt_2
14[c] [d]	2.26 d, 3.50 d, $^2J_{H,H}$ = 14.7	2.47 d, 3.33 d, $^2J_{H,H}$ = 15.7, X = PPh_2	4.09 s	1.43 s	–	7.32–7.63 m [8 H], 7.86–7.95 m [2 H]	1.03 t, 1.62 t, 2.05–3.10 m [10 H], $^3J_{H,H}$ = 7.1, NEt_2 1.53 br. s,[e] 2.83 br. s,[f] 3.71 br. s,[f] 3.77 br. s,[g] 4.00 br. s,[g] 5.20 br. s,[f] 5.32 br. s,[f] [8 H], norbornadiene-H

[a] s = singlet, d = doublet, t = triplet, m = multiplet, br. s = broad signal; coupling constants in Hz. [b] Solvent $CHCl_3$. [c] Solvent CH_2Cl_2. [d] Measuring temperature −40 °C. [e] CH_2 group. [f] Olefinic CH group. [g] Bridgehead CH group.

The data were processed with the standard Nonius software,[20] and the calculations were performed with the SHELXT PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.[21] Graphical handling of the structural data during solution and refinement was performed with XMPA.[22] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix, least-squares calculations. Data relating to the structure determinations are collected in Table 3. Figures 1 and 2 were prepared with WinRay-32.[23] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-191480 to -191483. Copies of the data can be obtained free of charge

Table 5. Chemical shifts (δ values), integrals [*x* H] and coupling constants *J* in the ^{1}H NMR spectra of **5**, **6**, and **9**−**12**

No.[a]	CH_2N [2 H]	CH_2X	CH_2Y	C_qCH_3 [3 H]	OH [2 H]	Aryl-H	Others
5a[b]	2.52 s	3.58 pt [4 H], $^2J_{H,H}$ = 11.3, X = Y = OH		0.79 s	4.97 br. s	−	1.03 t, 2.54 q [10 H], $^3J_{H,H}$ = 7.1, NEt_2
5b[b]	4.72 s	3.90 br. s [4 H], X = Y = OH		−	2.30−3.10 br. s	7.28−7.44 m [5 H]	6.19 t, 7.09 d, 7.55 d [3 H] $^3J_{H,H}$ = 2.0 pyrazole-H
6a[b]	2.54 s	2.45 m [4 H], X = Y = PPh_2		0.98 s	−	7.33−7.50 m [20 H]	0.99 t, 2.64 q [10 H], $^3J_{H,H}$ = 7.0, NEt_2
6b[b]	5.04 s	2.81 d, 2.97 d [4 H], $^2J_{H,H}$ = 14.3, X = Y = PPh_2		−	−	6.86−7.01 m [5 H], 7.17−7.34 m [20 H]	6.06 t, 6.90 d, 7.49 d [3 H], $^3J_{H,H}$ = 2.0, pyrazole-H
9[b]	4.56 d, 4.65 d, $^2J_{H,H}$ = 14.3	3.75 d, 3.94 d [2 H], $^2J_{H,H}$ = 12.0, X = OH	3.80 d, 3.97 d [2 H], $^2J_{H,H}$ = 11.5, Y = Cl	−	4.31 br. s [1H]	7.28−7.39 m [5 H]	6.19 t, 7.15 d, 7.53 d [3 H], $^3J_{H,H}$ = 2.0, pyrazole-H
10[b]	4.57 d, 4.96 d, $^2J_{H,H}$ = 14.0	2.79 br. s [2 H], X = PPh_2	4.07 d, 4.24 d [2 H], $^2J_{H,H}$ = 11.5, Y = Cl	−	−	7.14−7.35 m [15 H]	6.14 t, 7.09 d, 7.53 d [3 H], $^3J_{H,H}$ = 2.0, pyrazole-H
11[b]	4.95 br. s	2.85 d, 2.95 d [2 H], $^2J_{H,H}$ = 14.4, X = PPh_2	3.09 d, 3.36 d [2 H], $^2J_{H,H}$ = 14.4, Y = $PMes_2$	−	−	6.57−6.60 m [4 H], 6.77−7.37 m [15 H]	2.18 br. s [18 H], aryl-CH_3, 6.01 t, 6.77−7.37 m, 7.49 d [3 H], $^3J_{H,H}$ = 2.0, pyrazole-H
12a[c]	2.15 s	2.22 d, 3.80 br. s [4 H], $^2J_{H,H}$ = 15.2, X = Y = PPh_2		0.27 s	−	7.40−7.73 m [16 H], 8.48−8.51 m [4 H]	0.91 t, 2.49 q [10 H], $^3J_{H,H}$ = 7.0, NEt_2
12b[c]	3.87 s	2.74 d, 2.99 d [4 H], $^2J_{H,H}$ = 15.1, X = Y = PPh_2		−	−	6.81−7.13 m [5 H], 7.40−8.20 m [20 H]	5.91 t, 6.40 d, 7.33−7.67 m [3 H], $^3J_{H,H}$ = 2.0, pyrazole-H

[a] s = singlet, d = doublet, t = triplet, m = multiplet, br. s = broad signal, pt = pseudo-triplet; coupling constants in Hz. [b] Solvent $CHCl_3$. [c] Solvent CH_2Cl_2.

on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Materials: Silica gel (Kieselgel 32−63 μm, ICN Biomedicals GmbH) used for chromatography was degassed at 1 mbar for 24 h and saturated with argon. A solution of *n*BuLi in hexane (2.5 M) was used for deprotonations. $HPPh_2$,[24] $HPMes_2$[25] and methyl 2-phenylacrylate (**1a**)[26] were prepared according to or by adaptation of literature procedures. All other chemicals were obtained from commercial suppliers and used without further purification. Boiling range of the petroleum ether used: 40−60 °C. For ^{1}H NMR data see Tables 4 and 5, for ^{13}C NMR data see Table 6, and for analytical data see Table 7.

Ligand Syntheses

General Procedure for the Synthesis of 2: The α,β-unsaturated ester **1a** or **1b** (0.5 mol) was mixed with the secondary amine (1.1 equiv.), and hydroquinone (1.0 g) in the case of **1b**. The solution was heated and, after cooling, the crude product was distilled under reduced pressure through a 15-cm Vigreux column, yielding the β-amino esters **2** as colourless liquids.

Methyl 2-Phenyl-3-(1-piperidino)propanoate (2a): Starting materials: **1a**, piperidine. The mixture was heated to 70 °C for 1 h. Yield: 103.8 g (0.42 mol, 84%), b.p. 84 °C (0.1 mbar). ^{1}H NMR ($CDCl_3$): δ = 1.43−2.61 ppm (m, 10 H, piperidine-H), 2.50−2.61 (m, 1 H, CH_2N), 3.21 (dd, $^2J_{H,H}$ = 12.6, $^3J_{H,H}$ = 10.2 Hz, 1 H, CH_2N), 3.71 (s, 3 H, OCH_3), 3.90 (dd, $^3J_{H,H}$ = 4.6, $^3J_{H,H}$ = 10.2 Hz, 1 H, PhC*H*), 7.31−7.35 (m, 5 H, aromat. H). ^{13}C NMR ($CDCl_3$): δ = 24.8 ppm, 26.5, 55.0 (3 × s, piperidine-C), 50.4 (s, Ph*C*H), 52.3 (s, OCH_3), 62.9 (s, CH_2N), 127.7−138.3 (m, aromat. C), 174.4 (s, C=O).

Methyl 3-(Diethylamino)-2-methylpropanoate (2b): Starting materials: **1b**, diethylamine. The mixture was heated under reflux for 72 h. Yield: 41.6 g (0.24 mol, 48%), b.p. 29 °C (0.2 mbar). ^{1}H NMR ($CDCl_3$): δ = 0.93 ppm (t, 6 H, NCH_2CH_3, $^3J_{H,H}$ = 7.0 Hz), 1.08 (d, 3 H, $CHCH_3$, $^3J_{H,H}$ = 7.1 Hz), 2.30 (dd, $^2J_{H,H}$ = 12.7, $^3J_{H,H}$ = 6.3 Hz, 1 H, CH_2NEt), 2.34 (q, $^3J_{H,H}$ = 7.0 Hz, 4 H, NCH_2CH_3,), 2.50−2.73 (m, 2 H, $CHCH_3$ and CH_2NEt), 3.62 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ = 12.3 ppm (s, NCH_2CH_3), 15.8 (s, $CHCH_3$), 39.4 (s, $CHCH_3$), 47.8 (s, NCH_2CH_3), 51.7 (s, OCH_3), 57.3 (s, CH_2NEt), 177.0 (s, C=O).

Methyl 2-Methyl-3-(1-piperidino)propanoate (2c): Starting materials: **1b**, piperidine. The mixture was heated to 90 °C for 6 h. Yield: 76.0 g (0.41 mol, 82%), b.p. 54 °C (0.2 mbar). ^{1}H NMR ($CDCl_3$): δ = 1.10 ppm (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, $CHCH_3$), 1.35−2.33 (m, 10 H, piperidine-H), 2.21 (dd, $^2J_{H,H}$ = 12.3, $^3J_{H,H}$ = 6.3 Hz, 1 H, CH_2N), 2.53 (dd, $^2J_{H,H}$ = 12.3, $^3J_{H,H}$ = 8.3 Hz, 1 H, CH_2N), 2.62 (sext, 1 H, $^3J_{H,H}$ = 7.1 Hz, $CHCH_3$), 3.63 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ = 16.0 ppm (s, $CHCH_3$), 24.8, 26.3, 55.0 (3 × s, piperidine-C), 38.3 (s, $CHCH_3$), 51.7 (s, OCH_3), 62.7 (s, CH_2N), 177.0 (s, C=O).

Methyl 2-Methyl-3-(1-pyrazolyl)propanoate (2d): Starting materials: **1b**, pyrazole. The mixture was heated under reflux for 60 h. Yield: 68.4 g (0.41 mol, 82%), b.p. 48 °C (0.2 mbar). ^{1}H NMR ($CDCl_3$): δ = 1.07 ppm (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, $CHCH_3$), 3.02 (sext, 1 H, $^3J_{H,H}$ = 7.1 Hz, $CHCH_3$), 3.57 (s, 3 H, OCH_3), 4.08 (dd, $^2J_{H,H}$ = 13.7, $^3J_{H,H}$ = 6.5 Hz, 1 H, CH_2N), 4.34 (dd, $^2J_{H,H}$ = 13.7, $^3J_{H,H}$ = 7.5 Hz, 1 H, CH_2N), 6.11, 7.30, 7.40 (t, 2×d, 3 H, $^3J_{H,H}$ = 2.0 Hz, pyrazole-H). ^{13}C NMR ($CDCl_3$): δ = 15.1 ppm (s, $CHCH_3$), 41.0 (s, $CHCH_3$), 52.2 (s, OCH_3), 54.5 (s, CH_2N), 105.6, 130.2, 140.0 (3 × s, pyrazole-C), 174.9 (s, C=O). For further analytical data of **2a**−**2d**, see Table 7.

Methyl 3-(Diphenylphosphanyl)-2-phenylpropanoate (3): Compound **1a** (1.62 g, 10 mmol) and diphenylphosphane (1.86 g, 10 mmol) were dissolved in DMF (30 mL). NaH (60% dispersion in mineral oil, 200 mg, 5 mmol) was added, and the reaction mixture was stirred at 25 °C for 18 h and then quenched by addition of deoxygenated water (10 mL). The product was extracted with diethyl

Table 6. Chemical shifts (δ values) and coupling constants J in the $^{13}C\{^1H\}$ NMR spectra of **4**−**14**

No.[a]	CH_2N	CH_2X	CH_2Y	OCH_3	C_qCH_3	C_qCH_3	C=O	Aryl-C	Others
4a[b]	66.9	67.4, X = OH	−	52.6	55.3	−	174.8	126.4−140.4 m	24.1, 26.8, 56.9, piperidine-C
4b[b]	61.0	68.8, X = OH	−	52.1	47.8	20.8	176.9	−	11.7, 48.4, NEt_2
4c[b]	66.2	69.1, X = OH	−	52.2	47.6	21.0	176.8	−	24.1, 26.7, 56.8, piperidine-C
4d[b]	55.5	63.2, X = OH	−	52.9	58.3	−	173.7	126.9−138.9 m	105.8, 131.9, 140.0, pyrazole-C
5a[b]	62.4	68.8, X = Y = OH		−	40.1	19.9	−	−	12.1, 49.3, NEt_2
5b[b]	55.0	66.4, X = Y = OH		−	50.0		−	127.0−140.7 m	105.8, 131.7, 139.8, pyrazole-C
6a[b]	65.5 t, $^3J_{C,P}$ = 7.7	40.2 dd, X = Y = PPh_2, $^1J_{C,P}$ = 15.5; $^3J_{C,P}$ = 8.7		−	41.0 t, $^2J_{C,P}$ = 12.5	26.6 t, $^3J_{C,P}$ = 9.7	−	128.6−141.0 m	12.3, 49.0, NEt_2
6b[b]	59.5 t, $^3J_{C,P}$ = 11.7	39.1 dd, X = Y = PPh_2, $^1J_{C,P}$ = 18.5; $^3J_{C,P}$ = 10.2		−	46.5 t, $^2J_{C,P}$ = 16.2	−	−	126.9−142.0 m	105.3, 131.3, 139.3, pyrazole-C
7a[b]	59.7	49.5, X = Cl	−	52.1	49.7	19.9	175.5	−	12.1, 48.4, NEt_2
7b[b]	54.3	46.6, X = Cl	−	53.2	57.6	−	172.5	126.5−137.9 m	105.7, 131.4, 140.5, pyrazole-C
8[b]	64.3 d, $^3J_{C,P}$ = 9.1	37.6 d, X = PPh_2, $^1J_{C,P}$ = 15.6	−	51.7	48.2 d, $^2J_{C,P}$ = 13.2	22.5 d, $^3J_{C,P}$ = 11.1	177.3	128.7−140.2 m	12.1, 48.5, NEt_2
9[b]	55.8	65.6, X = OH	47.9, Y = Cl	−	50.3	−	−	127.1−139.8 m	106.0, 131.8, 140.1, pyrazole-C
10[b]	57.8 d, $^3J_{C,P}$ = 9.1	38.0 d, X = PPh_2, $^1J_{C,P}$ = 18.1	49.5 d, Y = Cl, $^3J_{C,P}$ = 14.6	−	48.2 d, $^2J_{C,P}$ = 16.1	−	−	127.3−140.2 m	105.6, 131.2, 140.2, pyrazole-C
11[b]	59.8 t, $^3J_{C,P}$ = 11.5	40.9 dd, X = PPh_2, $^1J_{C,P}$ = 16.5, $^3J_{C,P}$ = 8.7	34.7 dd ,Y = $PMes_2$, $^1J_{C,P}$ = 21.0, $^3J_{C,P}$ = 10.1	−	47.9 t, $^2J_{C,P}$ = 20.1	−	−	127.3−140.2 m	21.1 d, $^5J_{C,P}$ = 2.8, *p*-CH_3, 23.2 d, 23.8 d, $^3J_{C,P}$ = 14.5, *o*-CH_3, 105.2, 130.5, 139.2, pyrazole-C
12a[c]	70.4	34.7 br. s, X = Y = PPh_2		−	40.4	24.8	−	128.5−138.6 m	12.1, 49.3, NEt_2
12b[c]	62.9	30.6 br. s, X = Y = PPh_2		−	45.6	−	−	127.2−140.6 m	105.1, 131.2, 139.7, pyrazole-C
13[c]	60.8 d, $^3J_{C,P}$ = 10.7	28.8 d, X = PPh_2, $^1J_{C,P}$ = 26.9	−	53.4	44.5 br. s	28.1 br. s	175.8	128.6−135.9 m	11.7, 13.4, 55.3, 57.9, NEt_2
14[d]	67.2 br. s	32.8 d, X = PPh_2, $^1J_{C,P}$ = 23.9	−	53.7	50.2 br. s	28.3 d, $^3J_{C,P}$ = 14.7	176.1 d, $^3J_{C,P}$ = 4.5	129.2−134.0 m	7.4, 16.0, 52.4, 54.9, NEt_2, 51.8 br. s,[e] 52.2 br. s,[e] 54.9 br. s,[f] 61.1 br. s,[f], 66.7 br. s,[g], 94.6 br. s,[f] 94.7 br. s,[f] norbornadiene-C

[a] All signals are singlets unless otherwise stated; d = doublet, dd = doublet of doublet, t = triplet, m = multiplet, br. s = broad signal; coupling constants in Hz. [b] Solvent $CHCl_3$. [c] Solvent CH_2Cl_2. [d] Measuring temperature −40 °C. [e] Bridgehead CH group. [f] Olefinic CH group. [g] CH_2 group.

ether (4 × 20-mL portions), the organic portion was separated, and solvent was removed in vacuo. The resulting viscous oil was purified by chromatography on silica gel with petroleum ether/diethyl ether (6:1; R_f = 0.43) as eluent to afford **3** (2.30 g, 6.6 mmol, 66%) as a colourless oil. ^1H NMR ($CDCl_3$): δ = 2.59 ppm (d, $^2J_{H,H}$ = 13.6 Hz, 1 H, CH_2P), 2.96 (d, $^2J_{H,H}$ = 13.6 Hz, 1 H, CH_2P), 3.60−3.71 (m, 1 H, PhC*H*), 3.66 (s, 3 H, OCH_3), 7.33−7.48 (m, 15 H, aromat. H). ^{13}C NMR ($CDCl_3$): δ = 33.2 ppm (d, $^1J_{C,P}$ = 14.7 Hz, CH_2P), 49.0 (d, $^2J_{C,P}$ = 19.3 Hz, Ph*C*H), 52.5 (s, OCH_3), 127.9−139.8 (m, aromat. C), 174.3 (d, $^3J_{C,P}$ = 4.6 Hz, C=O). ^{31}P NMR ($CDCl_3$): δ = −20.9 (s). For further analytical data, see Table 7.

Methyl 3-Hydroxy-2-phenyl-2-[(1-piperidino)methyl]propanoate (4a): Compound **2a** (5.00 g, 20 mmol) and paraformaldehyde (2.70 g) were suspended in DMF (100 mL). Upon addition of NaH (60% dispersion in mineral oil, 900 mg) to the cooled (0 °C) suspension, the reaction mixture became clear within minutes. The reaction mixture was allowed to warm up to 25 °C and was stirred for 18 h. The reaction was quenched by the addition of brine (150 mL). The aqueous phase was extracted with diethyl ether (4 × 100-mL portions). The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated by rotary evaporation. The resulting viscous oil was purified by chromatography on silica gel with petroleum ether/diethyl ether (1:1; R_f = 0.39, strong tailing) as eluent to afford **4a** (3.60 g, 13.0 mmol, 65%) as a viscous fluid. For analytical data see Tables 4, 6 and 7.

Methyl 2-(Diethylaminomethyl)-3-hydroxy-2-methylpropanoate (4b): A solution of lithium diisopropylamide[27] (110 mmol) in THF (100 mL) was added at −78 °C to a suspension of **2b** (17.3 g, 100 mmol) and paraformaldehyde (10.5 g, 350 mmol) in THF (200 mL). The mixture was stirred for 1 h at −78 °C and then for 4 h at 25 °C, quenched by the addition of water (50 mL) and partitioned between diethyl ether and water. The aqueous layer was extracted with diethyl ether (3 × 50 mL), and the combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated by rotary evaporation. Distillation of the residue under reduced press-

Table 7. Analytical data of **2**−**14**

No.	Formula	*M* [g/mol]	MS[a] *m*/*z* (%)	$C_{calcd.}/C_{found}$	$H_{calcd.}/H_{found}$	$Cl_{calcd.}/Cl_{found}$	$N_{calcd.}/N_{found}$	$P_{calcd.}/P_{found}$
2a	$C_{15}H_{21}NO_2$	247.3	246 (10), 98 (100)	72.84/72.89	8.56/8.45		5.66/5.59	
2b	$C_9H_{19}NO_2$	173.3	173 (19), 158 (22), 86 (100), 58 (61)	62.39/62.28	11.05/10.90		8.08/8.04	
2c	$C_{10}H_{19}NO_2$	185.3	184 (28), 154 (13), 98 (100), 84 (46), 70 (86), 59 (62), 55 (92)	64.83/64.54	10.34/10.34		7.56/7.55	
2d	$C_8H_{12}N_2O_2$	168.2	168 (36), 137 (18), 109 (67), 81 (100), 69 (45)	57.13/57.14	7.19/7.25		16.66/n.d.	
3	$C_{22}H_{21}O_2P$	348.4	348 (37), 333 (86), 262 (57), 201 (100), 183 (70)	75.85/75.73	6.08/6.08			8.89/n.d.
4a	$C_{16}H_{23}NO_3$	277.4	278 (1), 276 (1), 98 (100)	69.29/69.50	8.36/8.57		5.05/4.83	
4b	$C_{10}H_{21}NO_3$	203.3	203 (1), 86 (100), 58 (16)	59.09/59.37	10.41/10.54		6.89/6.81	
4c	$C_{11}H_{21}NO_3$	215.3	215 (2), 98 (100), 84 (10), 55 (14)	61.37/61.44	9.83/9.74		6.51/6.55	
4d	$C_{14}H_{16}N_2O_3$	260.3	260 (38), 243 (13), 230 (70), 162 (100), 144 (74), 103 (65), 91 (28), 81 (66)	64.60/64.82	6.20/6.42		10.76/10.33	
5a	$C_9H_{21}NO_2$	175.3	175 (2), 86 (100), 58 (15)	61.67/n.d.	12.08/n.d.		7.99/n.d.	
5b	$C_{13}H_{16}N_2O_2$	232.3	232 (3), 184 (75), 144 (100), 134 (37), 103 (55), 91 (51), 81 (80), 77 (52), 69 (38)	67.22/67.43	6.94/7.03		12.06/11.81	
6a	$C_{33}H_{39}NP_2$	511.6	511 (7), 434 (10), 183 (16), 86 (100)	77.47/77.47	7.68/7.84		2.74/2.77	12.11/n.d.
6b	$C_{37}H_{34}N_2P_2$	568.6	568 (12), 491 (100), 383 (10), 301 (14), 262 (17), 183 (20)	78.15/77.54	6.03/6.03		4.93/4.94	10.89/n.d.
7a	$C_{10}H_{20}ClNO_2$	221.7	221 (10), 86 (100), 58 (50)	54.17/53.79	9.09/9.13	15.99/n.d.	6.32/6.33	
7b	$C_{14}H_{15}ClN_2O_2$	278.7	278 (100), 243 (47), 211 (11)	60.33/60.30	5.42/5.45	12.72/12.69	10.05/9.91	
8	$C_{22}H_{30}NO_2P$	371.5	371 (2), 183 (13), 86 (100)	71.14/70.89	8.14/8.30		3.77/3.75	8.34/n.d.
9	$C_{13}H_{15}ClN_2O$	250.7	251 (6), 220 (22), 215 (100), 185 (91), 152 (72), 115 (73), 103 (75), 91 (62), 81 (80), 77 (52)	62.28/62.41	6.03/6.31	14.14/n.d.	11.17/10.65	
10	$C_{25}H_{24}ClN_2P$	418.9	418 (15), 383 (22), 315 (74), 301 (47), 262 (58), 183 (100)	71.68/72.20	5.77/5.89	8.46/8.11	6.69/6.57	7.39/7.67
11	$C_{43}H_{46}N_2P_2$	652.8	653 (45), 533 (100)	79.12/78.89	7.10/7.20		4.29/4.25	9.49/n.d.
12a	$C_{33}H_{39}Cl_2NNiP_2$	641.2	604 (100), 569 (15), 511 (58), 434 (45)	61.81/59.68	6.13/6.52	11.06/n.d.	2.18/2.08	9.66/n.d.
12b	$C_{37}H_{34}Cl_2N_2NiP_2$	698.2	696 (7), 661 (100), 626 (16), 491 (26), 411 (21)	63.65/63.22	4.91/5.15	10.16/9.58	4.01/4.05	8.87/8.70
12c	$C_{43}H_{46}Cl_2N_2NiP_2$	782.4	745 (43), 709 (15), 575 (11), 533 (62), 525 (10), 441 (100)	63.34[b]/63.14	5.74[b]/6.04	12.89[b]/n.d.	3.40[b]/3.36	7.51[b]/n.d.
13	$C_{22}H_{30}Cl_2NO_2PPd$	548.8	512 (100), 477 (59), 370 (71)	48.15/48.18	5.51/5.51	12.92/12.82	2.55/2.61	5.64/5.78
14·PF$_6$	$C_{29}H_{38}F_6NO_2P_2Rh$	711.5	566 (100), 479 (13), 388 (30)	48.96/48.69	5.38/5.39		1.97/2.02	8.71/8.76

[a] Compounds **2**−**11**: EI-MS; compounds **12**−**14**: FAB-MS. [b] Calculated for **12c**·0.5CH_2Cl_2.

ure afforded **4b** (8.8 g, 43 mmol, 43%) as a colourless liquid, b.p. 62 °C (0.2 mbar). For analytical data, see Tables 4, 6 and 7.

Methyl 3-Hydroxy-2-methyl-2-[(1-piperidino)methyl]propanoate (4c): Starting material: **2c** (18.5 g, 100 mmol). This compound was prepared analogously to **4b**. Yield: 11.1 g (51.6 mmol, 52%), b.p. 99 °C (0.2 mbar). For analytical data, see Tables 4, 6 and 7.

Methyl 3-Hydroxy-2-phenyl-2-[(1-pyrazolyl)methyl]propanoate (4d): Pyrazole (5.10 g, 75 mmol) was deprotonated at 0 °C with sodium hydride (1.00 g, 25 mmol, 60% dispersion in mineral oil) in DMF (50 mL). This solution was slowly added at 0 °C to a mixture of **1a** (8.14 g, 50 mmol) and paraformaldehyde (4.50 g, 150 mmol) in DMF (50 mL). When a clear, colourless solution had formed, the reaction mixture was stirred at 25 °C for 1 h. The reaction was quenched by the addition of brine (150 mL), and the aqueous phase was extracted with diethyl ether (4 × 100-mL portions). The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated by rotary evaporation. The resulting viscous oil was purified by chromatography on silica gel with petroleum ether/diethyl ether (1:3; R_f = 0.42) as eluent to afford **4d** (8.10 g, 31.0 mmol, 62%) as a colourless oil. For analytical data, see Tables 4, 6 and 7.

General Procedure for the Synthesis of 5 and 9: A solution of the substituted ester (**4** or **7b**; 20 mmol) in THF (50 mL) was slowly added at 25 °C to a stirred suspension of $LiAlH_4$ (30 mmol per OH group) in THF (200 mL). The mixture was stirred for 15 h and hydrolysed by dropwise addition of water. The precipitate was filtered off and washed five times with ethyl acetate. The combined organic phases were dried with $MgSO_4$ and the solvents were evaporated to dryness to yield the corresponding alcohols.

2-(Diethylaminomethyl)-2-methylpropane-1,3-diol (5a): Starting material: **4b**. Yield: 3.45 g (19.7 mmol, 99%) of a viscous oil.

2-Phenyl-2-[(1-pyrazolyl)methyl]propane-1,3-diol (5b): Starting material: **4d**. Yield: 4.52 g (19.5 mmol, 97%) of a microcrystalline powder, m.p. 86 °C.

2-(Chloromethyl)-2-phenyl-3-(1-pyrazolyl)propan-1-ol (9): Starting material: **7b**. Yield: 4.81 g (19.2 mmol, 96%) of a microcrystalline powder. For further analytical data of **5a**, **5b**, and **9**, see Tables 5−7.

General Procedure for the Synthesis of 6 and 10: The substituted alcohol (**5** or **9**; 10.0 mmol, 1 equivalent) in THF (50 mL) was deprotonated at −30 °C with *n*BuLi (1.2 equiv. per OH group). The resulting solution was then allowed to warm to 25 °C, stirred for 30 min and subsequently recooled to −30 °C. Methanesulfonyl chloride (1.2 equiv. per OH group) was then added slowly, and the reaction mixture was stirred at 0 °C for 2 h. In a separate vessel diphenylphosphane (1.2 equiv. per OH group) in THF (50 mL) was deprotonated with *n*BuLi (1.2 equiv. per OH group). The resulting red lithium diphenylphosphide solution was added to the reaction mixture at −30 °C. After the mixture had been stirred for 15 h at 25 °C, all volatiles were removed in vacuo. The remaining residue was purified by chromatography on silica gel.

{2,2-Bis[(diphenylphosphanyl)methyl]propyl}diethylamine (6a): Starting material: **5a**. Yield: 3.34 g (6.5 mmol, 65%) of a viscous oil, R_f = 0.43 (petroleum ether/diethyl ether, 3:1). ^{31}P NMR ($CDCl_3$): δ = −27.1 ppm (s).

1-{2,2-Bis[(diphenylphosphanyl)methyl]-2-phenylethyl}-1*H*-pyrazole (6b): Starting material: **5b**. Yield: 3.91 g (6.9 mmol, 69%) of a microcrystalline powder, R_f = 0.65 (petroleum ether/diethyl ether/CH_2Cl_2, 2:1:1), m.p. 145 °C. ^{31}P NMR ($CDCl_3$): δ = −26.8 ppm (s).

1-[2-(Chloromethyl)-3-(diphenylphosphanyl)-2-phenylpropyl]-1*H*-pyrazole (10): Starting material: **9**. Yield: 2.32 g (5.5 mmol, 55%) of a microcrystalline powder, R_f = 0.43 (petroleum ether/diethyl ether, 3:1), m.p. 119 °C. ^{31}P NMR ($CDCl_3$): δ = −26.9 ppm (s). For further analytical data of **6a**, **6b**, and **10**, see Tables 5−7.

General Procedure for the Synthesis of 7: A solution of anhydrous PPh_3 (15.7 g, 60 mmol) in CCl_4 (80 mL) was heated under reflux for 90 min, during which the colour of the solution changed from colourless to light red. The substituted β-hydroxy ester **4** (30 mmol), dissolved in CCl_4 (30 mL), was added rapidly to the boiling reaction mixture from a dropping funnel. The solution discoloured immediately and a brown precipitate of $O{=}PPh_3$ was formed. The mixture was heated under reflux for another 12 h and afterwards cooled to 25 °C. The precipitate was filtered off and washed five times with diethyl ether. The combined organic solutions were concentrated by rotary evaporation.

Methyl 2-(Chloromethyl)-3-(diethylamino)-2-methylpropanoate (7a): Starting material: **4b**. Kugelrohr distillation of the residue under reduced pressure afforded **7a** (7.3 g, 32.9 mmol, 55%) as a viscous oil, b.p. 100 °C (0.2 mbar).

Methyl 3-Chloro-2-phenyl-2-[(1-pyrazolyl)methyl]propanoate (7b): Starting material: **4d**. The remaining residue was purified by chromatography on silica gel with petroleum ether/diethyl ether (2:1; R_f = 0.53) as eluent to afford **7b** (9.4 g, 33.7 mmol, 56%) as a colourless powder, m.p. 100 °C. For analytical data of **7a** and **7b**, see Tables 4, 6 and 7.

General Procedure for the Synthesis of 8 and 11: The substituted alkyl chloride (**7b** or **10**; 10 mmol, 1 equiv.) was dissolved in DMSO (25 mL). In a separate vessel, diarylphosphane (1.2 equiv.) in DMSO (40 mL) was deprotonated at 25 °C with KO*t*Bu (1.2 equiv.). The resulting red potassium diarylphosphide solution was stirred for 20 min and then added dropwise to the solution of the alkyl chloride. The reaction mixture was stirred for 15 h and hydrolysed by dropwise addition of water (50 mL). The aqueous phase was extracted with diethyl ether (4 × 40-mL portions). The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvents were evaporated to dryness. The remaining residue was purified by chromatography on silica gel.

Methyl 3-(Diethylamino)-2-[(diphenylphosphanyl)methyl]-2-methylpropanoate (8): Starting material: **7b**. Yield: 2.32 g (6.3 mmol, 63%) of a viscous oil, R_f = 0.43 (petroleum ether/diethyl ether, 3:1). FT-IR (CH_2Cl_2): $\tilde{\nu}$ = 1726 cm^{-1} vs (CO), 1434 m (PPh). ^{31}P NMR ($CDCl_3$): δ = −24.3 ppm (s).

1-{2-[(Dimesitylphosphanyl)methyl]-3-(diphenylphosphanyl)-2-phenylpropyl}-1*H*-pyrazole (11): Starting material: **10**. Yield: 2.32 g (6.3 mmol, 63%) of a microcrystalline powder, R_f = 0.47 (petroleum ether/diethyl ether, 4:1), m.p. 120 °C. ^{31}P NMR ($CDCl_3$): δ = −34.1 ppm (d, $^4J_{P,P}$ = 10 Hz, $PMes_2$), −26.1 (d, $^4J_{P,P}$ = 10 Hz, PPh_2). For further analytical data of **8** and **11**, see Tables 5−7.

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General Procedure for the Synthesis of 12: A solution of the respective tripod ligand (1.05 mmol) in ethanol (10 mL, with some THF added to increase the solubility if necessary) was added rapidly to a solution of $NiCl_2{\cdot}6H_2O$ (1.0 mmol, 240 mg) in ethanol (10 mL). The colour of the reaction mixture immediately changed to red and within a few minutes the nickel complexes precipitated. After the mixture had been stirred at 25 °C for 1 h, the precipitate was fil-

tered, washed with diethyl ether (3 × 10-mL portions), and dried in vacuo.

[(6a-κ²*P*)NiCl₂] (12a): Starting material: **6a**. Recrystallisation from CH_2Cl_2/diethyl ether afforded **12a** (525 mg, 0.82 mmol, 82%) in the form of red crystals suitable for X-ray structure analysis, m.p. 212 °C (decomposition). ^{31}P NMR (CD_2Cl_2, −40 °C): δ = 10.7 ppm (s).

[(6b-κ²*P*)NiCl₂] (12b): Starting material: **6b**. Recrystallisation from CH_2Cl_2/diethyl ether afforded **12b** (650 mg, 0.93 mmol, 93%) in the form of red crystals suitable for X-ray structure analysis, m.p. 248 °C (decomposition). ^{31}P NMR (CD_2Cl_2, −40 °C): δ = 15.6 ppm (s).

[(11-κ²*P*)NiCl₂] (12c): Starting material: **11**. Removal of the solvent afforded **12c** (585 mg, 0.75 mmol, 75%) in the form of an orange, microcrystalline solid. ^{1}H NMR and ^{13}C NMR: no sharp signals could be detected, due to a dynamic process. ^{31}P NMR (CD_2Cl_2, −40 °C): δ = −4.5 ppm (d, $^2J_{P,P}$ = 95 Hz, $PMes_2$), 4.0 (d, $^2J_{P,P}$ = 95 Hz, PPh_2).

For crystallographic data of **12a** and **12b**, see Table 3; for further analytical data of **12a**−**12c**, see Tables 5−7.

[(8-κ²*N*,*P*)PdCl₂] (13): A solution of ligand **8** (210 mg, 0.5 mmol) in ethanol (15 mL) was added rapidly to a suspension of (η⁴-cod)$PdCl_2$ (145 mg, 0.5 mmol) in ethanol (10 mL). Within a few minutes the yellow reaction mixture became clear. After the mixture had been stirred at 25 °C for 12 h, all volatiles were removed in vacuo. The residual yellow solid was washed with diethyl ether (3 × 10-mL portions) and dried in vacuo. Recrystallisation from CH_2Cl_2/diethyl ether afforded **13** (180 mg, 0.33 mmol, 66%) in the form of yellow crystals suitable for X-ray structure analysis. FT-IR (CH_2Cl_2): $\tilde{\nu}$ = 1732 cm^{-1} vs (CO), 1438 m (PPh). ^{31}P NMR (CD_2Cl_2): δ = 19.6 ppm (s). For crystallographic data, see Table 3; for further analytical data, see Tables 4, 6 and 7.

[(8-κ²*N*,*P*)(η⁴-nbd)Rh]PF₆ (14·PF₆): [(η⁴-nbd)RhCl]$_2$ (230 mg, 0.5 mmol) was dissolved in acetone (5 mL). In a second flask, potassium hexafluorophosphate (195 mg, 1.05 mmol) was dissolved in acetone (5 mL, 0.1 mL of water added). This solution was added to the orange rhodium(I) solution. A colourless KCl precipitate formed over 5 min, while the colour of the reaction mixture faded. A solution of ligand **8** (370 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) was then added. After the mixture had been stirred at 25 °C for 1 h, all volatiles were removed in vacuo. The residue was taken up in acetone (20 mL) and dried with $MgSO_4$. The insoluble KCl was removed by filtering the solution through Kieselguhr. Removal of the solvent in vacuo and recrystallisation from CH_2Cl_2/diethyl ether afforded **14·PF₆** (640 mg, 0.9 mmol, 90%) in the form of orange crystals suitable for X-ray structure analysis, m.p. 203 °C (decomposition). FT-IR (CH_2Cl_2): $\tilde{\nu}$ = 1725 cm^{-1} vs (CO), 1437 m (PPh). ^{31}P NMR (CD_2Cl_2): δ = −144.2 ppm (sept, $^1J_{P,F}$ = 711 Hz, PF_6^-), 29.8 (d, $^1J_{Rh,P}$ = 174 Hz, PPh_2). For crystallographic data, see Table 3; for further analytical data, see Tables 4, 6 and 7.

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