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Synthesis, coordination chemistry and polymerfixation of the tripod-ligand $HOC_6H_4CH_2C(CH_2PPh_2)_3$[1]

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Abstract

Starting from 4-methoxybenzylmalonic ester $MeOC_6H_4CH_2CH(COOEt)_2$, the synthesis of the tripod-ligand $HOC_6H_4CH_2C(CH_2PPh_2)_3$, **12**, functionalized with a phenolic group at its backbone, is achieved in a few steps. Ether derivatives of **12** show the normal coordination behavior of $RC(CH_2PPh_2)_3$. Thus $MeOC_6H_4CH_2C(CH_2PPh_2)_3$ forms the complexes $[\mathbf{7}\cdot Fe(NCMe)_3]$ $(BF_4)_2$ (**8**) and $\mathbf{7}\cdot Mo(CO)_3$ (**9**). The phenolate derived from **12** by deprotonation reacts with the CH_2Cl groups of Merrifield resin to form covalently polymer fixed **12** with high efficiency. The polymer bound tripod ligands undergo tripod typical coordination reactions. In addition to the usual spectroscopic and analytical techniques, X-ray analyses of derivatives of **12** as well as of **8** and **9** are used to identify the products.

Keywords: Polymer bound ligands; Functionalized tripod ligands; Molybdenum complexes; Iron complexes

1. Introduction

Neopentane based tripod-ligands $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ have a well documented and sometimes peculiar coordination chemistry which has quite some promises in the field of catalysis as well [1]. To make full use of their specific properties, a possibility to link these tripodal ligands to auxiliary groups of different types would be welcome. Only a few specialised syntheses leading to distinct derivatives $RCH_2C(CH_2PPh_2)_3$ species had been reported in the past ([2]b, h, j). It has recently been found [3] that the neopentane bound hydroxy group of tripod ligands $HOCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ may serve as a linker entity via ether formation under rather specialised conditions which avoid the attack of the neopentane bound donor groups X, Y, Z by the ether forming electrophile [3]. The sluggish reactivity of the neopentane system and the short spacer separating the OH group from its tertiary carbon atom preclude the application of this strategy for the fixation of neopentane based ligands on polymers. We report here on the synthesis of $HOC_6H_4CH_2C(CH_2PPh_2)_3$, **12** the phenolic hydroxy group of which is separated from the tertiary carbon atom by a benzyl type spacer. From malonic ester precursors ([2]a) **12** is obtained in five steps with a fair overall yield of 35%. It is shown that ethers derived from **12** have the full coordinating capability of the parent compound $CH_3C(CH_2PPh_2)_3$. Results of covalently fixing **12** to Merrifield resin are reported.

2. Results and discussion

To formally insert a phenyl-spacer into the backbone of $HOCH_2C(CH_2PPh_2)_3$, easily achieveable 4-methoxybenzyl-malonicester [4] is deprotonated with sodium hydride and alkylated with chloromethyl-benzylether [5] to form **1**. The diester **1** is transformed into the diol **2**

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[1] Dedicated to Professor Dr Hermann Irngartinger on the occasion of his 60th birthday.

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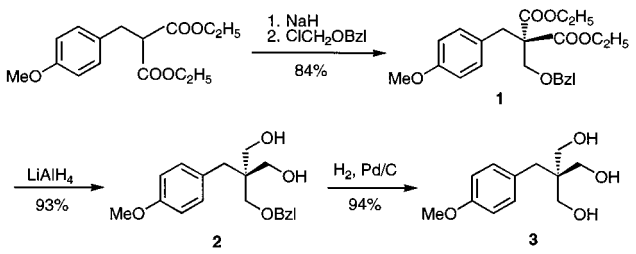


Scheme 1.

with $LiAlH_4$. Cleavage of the benzylether with hydrogen and Pd/C leads to the triol **3**, which can be activated either through chlorination or esterification (Scheme 1).

The CH_2OH groups in **3** are transformed into electrophilically activated centers by standard procedures (Scheme 2).

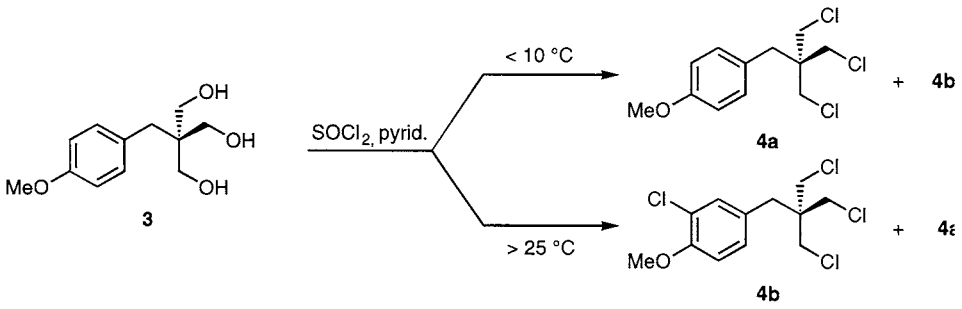
At temperatures above 10°C chlorination of the arene ring in the 3-position becomes a noticeable side reaction. Initially the reaction was performed at temperatures above 25°C resulting in an almost 1:1 mixture of **4a** and **4b**. It is not possible to separate **4a** and its ring-chlorinated derivative **4b** by chromatography.

Therefore the mixture was immediately subjected to phosphinilation in the hope that the resulting tripod ligands might be separable (Scheme 3). It was observed that under these conditions the methoxy function of **4b** is cleaved while as the experiments with **4a** (see below) show it is stable under these conditions when no *ortho* chlorine function is present. The phenolic hydroxy function of **5** resulting after hydrolytic workup increases the differentation of **5** and **7** such that pure **5** is obtained by crystallisation.

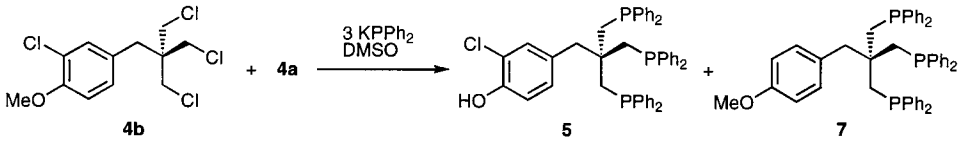
The structures of **5** and **7** have been determined by X-ray analyses (Fig. 1, Table 1). There is nothing special about individual distances and angles (Table 1). An interesting observation is made with respect to the torsion angles characterizing the conformations of four different tripod ligands of the general formula $RCH_2C(CH_2PPh_2)_3$. In all four cases studied so far (Table 1), the rotational positions of the four groups radiating from the central carbon atom C4 with respect to their rotation around the corresponding C4–CH_2 bonds is very much alike in so far as an almost staggered conformation is approached at any C–C bond (torsion angles around ± 60 and 180°, see Fig. 1, Table 1) [6]. In addition, the rotation of the aryl groups with respect to the C_{ipso}–C–(CH_2) bonds is very close to 90° for all compounds (Table 1). The fact that these parameters describing the conformation of the core of these compounds are invariant within a small angular range must mean that this conformation is almost exclusively determined by the inner molecular forces and does not strongly depend on the forces acting upon the molecules in their four different crystal environments.

The problem of side reactions as observed in the activation of **3** by $SOCl_2$ is completely avoided when **3** is activated by $PhSO_2Cl$, to form **6**. The reaction of **6** with $KPPh_2$ in DMSO results in a fair yield of the desired product **7** (Scheme 4).

Even though there can be no question that **7** will behave as a tripod ligand like other derivatives $RCH_2C(CH_2PPh_2)_3$ ([2]a, b) the coordination compounds **8** and **9** have been synthesized and fully characterized with the reason for this being that the structural information obtained by X-ray analysis of such compounds is highly valuable: in any attempt to derive the rules governing the conformational arrangement and flexibility of tripod-metal compounds [$RCH_2C(CH_2X)(CH_2Y)(CH_2Z)$]$ML_n$ one has to rely on a structural data base as broad as possible. Methods to extract the relevant information from such databases



Scheme 2.



Scheme 3.

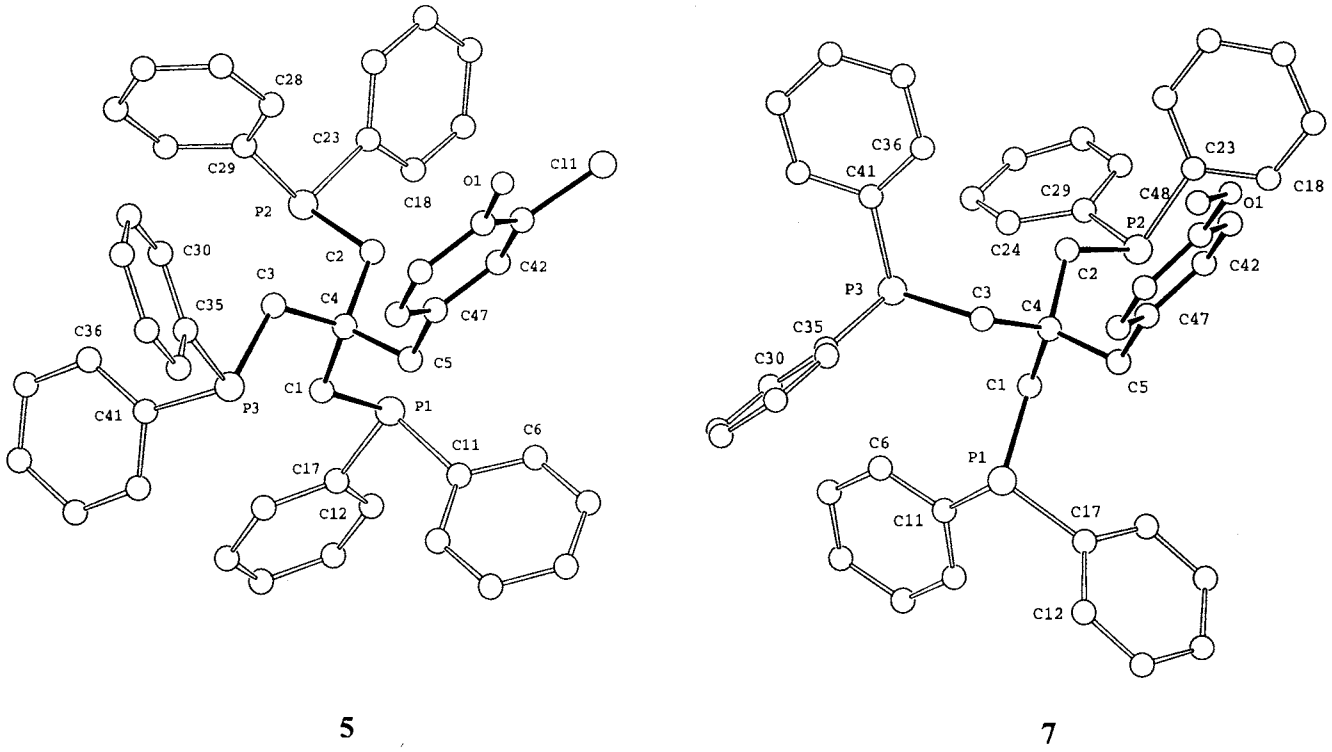


Fig. 1. Views of **5** and **7**.

Table 1
Selected bond lengths (pm) and angles (°) of the ligands $RCH_2C(CH_2PPh_2)_3$

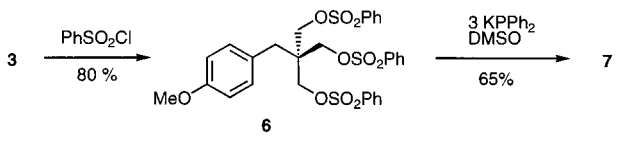
	5 R = 3-chloro-4-hydroxybenzyl	**7** R = 4-methoxybenzyl	R = phenyl ([2]b)	R = H ([1]i)
P–C(CH_2)	185.5(2)–186.2(2)	185.3(2)–186.3(2)	184.9(5)–185.2(4)	185.1(5)–185.9(6)
P–C(Ar)	183.4(5)–184.8(5)	181.9(5)–183.5(5)	183.8(5)–185.5(5)	183.8(5)–185.6(5)
C4–CH_2	153.8(3)–157.3(3)	154.5(3)–155.1(3)	154.9(6)–158.1(6)	153.6(7)–154.2(8)
C4–CH_2–P	115.0(4)–116.2(4)	116.2(4)–117.2(4)	115.2(3)–117.7(3)	114.7(4)–118.7(4)
C1–C4–C5–C_{ipso}	−173	−178	61	—
C4–C5–C_{ipso}–C_{ortho}	89	91	91	—
C5–C4–C1–P1	−71	61	174	−79
C5–C4–C2–P2	178	67	−63	−66
C5–C4–C3–P3	−60	−174	−68	−176

Estimated standard deviations of the least significant figures are given in parentheses.

have been developed [6] and the structures of **8** and **9** are helpful additions to these databases (Scheme 5).

Compound **8** is prepared in analogy to the synthesis of other $[(tripod)Fe(NCMe)_3]^{2+}$ species ([2]b–f) from $[Fe(NCMe)_6]^{2+}$ [7]. Compound **9** was likewise obtained by applying the standard procedure ([2]f–i) starting from $(NCMe)_3Mo(CO)_3$ [8].

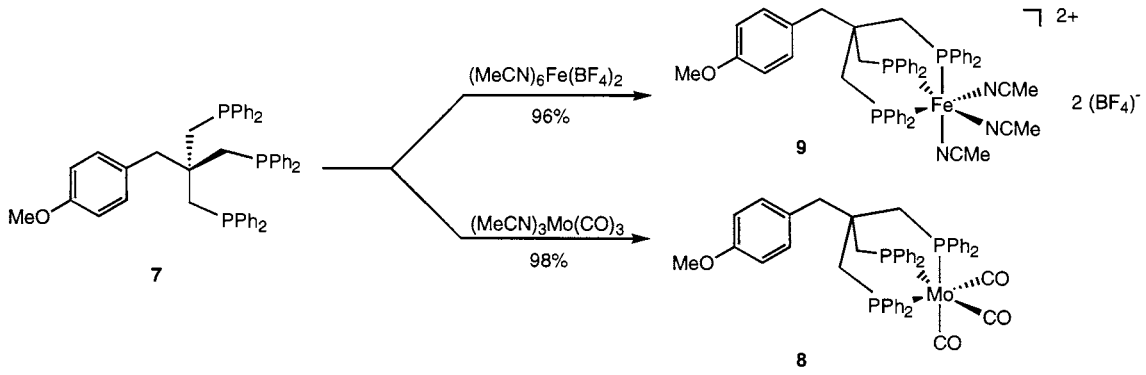
Both compounds are obtained in excellent yields, the local C_3 symmetry of the $Fe(NCMe)_3$ as well as of the



Scheme 4.

$Mo(CO)_3$ chromophores is evident from the ν(CN)- and ν(CO)-IR data, respectively (experimental part). NMR data as well as elemental analysis prove the assigned constitutions which are further corroborated by X-ray analyses (Table 2, Fig. 2).

Both compounds show the expected idealized octahedral geometry with the tripod ligand occupying one face of the octahedron (Fig. 2). The distances and angles (Table 2) are well within the range known for other $[(tripod)Fe(NCMe)_3]$ compounds ([2]b–f). The torsional arrangements of the chelate scaffolding are different with **8** showing one large torsion around 35° and two medium torsions around 17° while **9** has three large torsion angles (Table 2) and is comparable in this respect to $[\{PhCH_2C(CH_2PPh_2)_3\}Fe(NCMe)_3]^{2+}$ ([2]c).



Scheme 5.

Refering to the torsion angles characterizing the rotational positions of the phenyl groups ($Q–P_i–C_j–C_k$, Table 2) it is observed that there is one PPh_2 group at P1 in each of the compounds which has both its phenyl rings in an orientation almost parallel to the idealized C_3 axes of the molecules (Fig. 2, Table 2). With respect to the PPh_2 group showing the small torsion angles the sectors occupied by the benzyl group at the bridgehead carbon are different in compounds **8** and **9** (Fig. 2). In each case however one of the P bonded phenyl groups in this occupied sector has a low torsion angle (Fig. 2).

Taken together the structural examples given show that an alkoxy function in the *para* position of the benzyl substituent at the bridgehead carbon of the chelate cage does not strongly influence neither the coordination capability nor the conformational behavior of the ligands. This is a favorable observation with respect to the idea of using a phenolic group at the backbone of tripod ligands as a linker group.

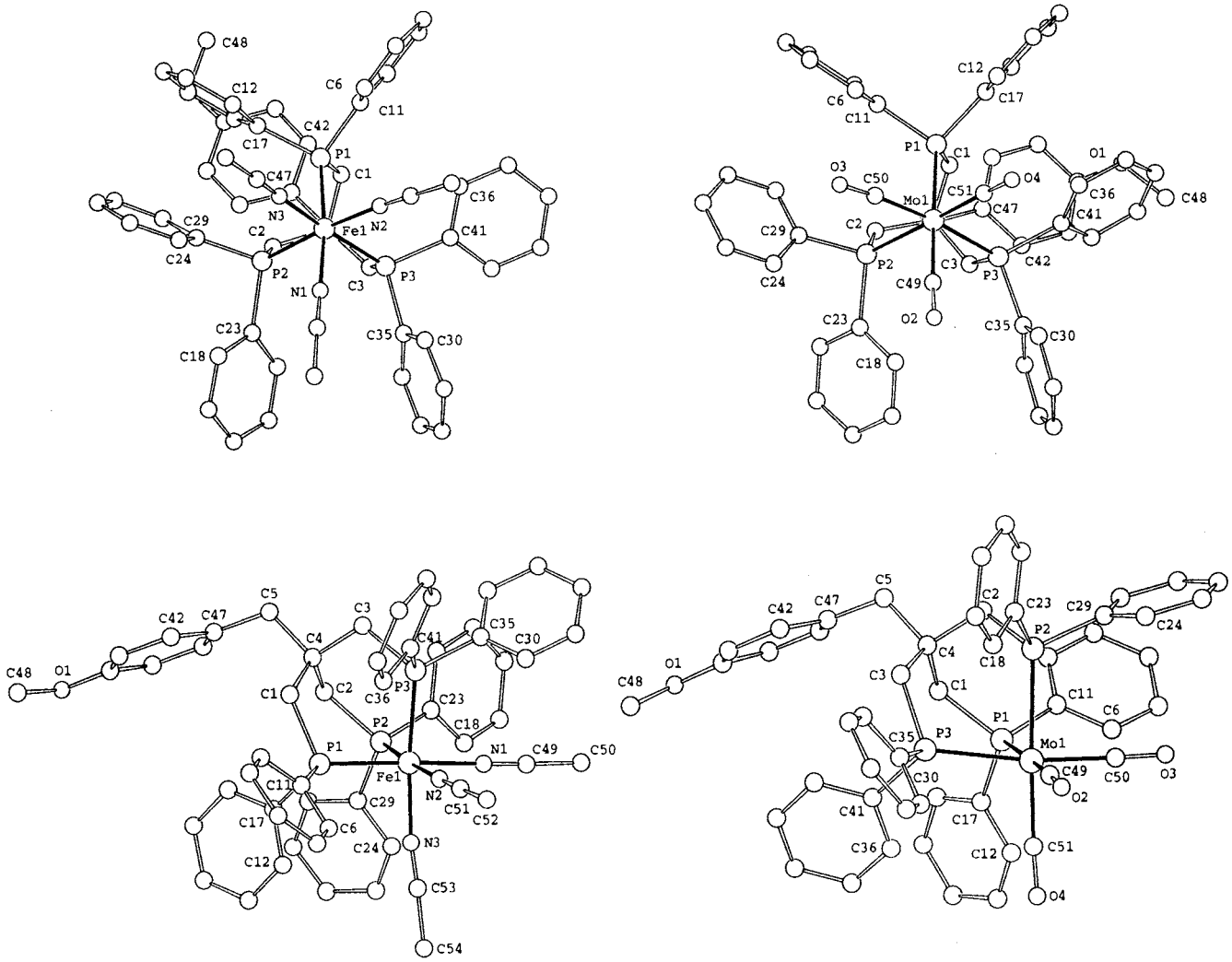
For the synthesized ligands of this type the approach described for the transformation of **1** to **4** was further elaborated. The methoxy group of **4a** is transformed into the phenolic hydroxy group of **10** with Me_3SiI as the activating reagent. **10** is obtained as a colorless microcrystalline solid whose properties conform in all points to its constitution as given. A further proof of its identity is the straightforward transformation of **10** into the ether **11** which is obtained as a colorless oil and is as well fully characterized by all usual spectroscopic and analytical techniques. The ease with which **10** undergoes etherification is in stark contrast to the difficulties opposing the etherification of $HOCH_2C(CH_2Cl)_3$ ([2]h) which are in part due to intermolecular cyclization reactions. The phenyl spacer in **10** does not allow for this type of intramolecular reaction. An intermolecular reaction by condensation of CH_2Cl groups with phenoxy-groups which might in principle be a problem is not observed under the applied conditions (Scheme 6).

The reluctance to cyclysation reactions of the phenolate ion obtained from **10** by treatment with KO^{t}Bu is a pre-requisite for the successful transformation of **10** to the tripod ligand **12**.

Table 2
Selected bond lenghts [pm] and angles [°] of **8** and **9**[a]

[b]	**8**	**9**	[b]	**8**	**9**	[c]	**8**	**9**	[d]
M–P1	227.6(1)	253.6(2)	P1–M–P2	91.7(4)	83.1(1)	C4–C1–P1–M	34.6	27.7	36.6
M–P2	227.1(1)	252.6(2)	P1–M–P3	85.6(4)	81.6(1)	C4–C2–P2–M	16.3	30.6	35.5
M–P3	225.0(1)	250.8(2)	P2–M–P3	90.4(4)	84.8(1)	C4–C3–P3–M	18.1	39.7	27.8
M–L1	195.1(3)	198.2(7)	L1–M–L2	85.9(1)	85.1(3)	Q–P1–C11–C6	−5	−2	7
M–L2	195.6(3)	197.8(7)	L1–M–L3	86.7(1)	83.9(3)	Q–P1–C17–C12	8	−1	−9
M–L3	196.3(3)	197.6(7)	L2–M–L3	84.2(1)	90.6(3)	Q–P2–C23–C18	41	−56	−27
			C4–C5–C47	116.5(3)	116.8(5)	Q–P2–C29–C24	−10	−45	−43
			C44–O1–C48	116.8(3)	116.8(6)	Q–P3–C35–C30	−22	−13	−5
						Q–P3–C41–C36	−74	−33	89
						C4–C5–C47–C42	97	88	75
						C43–C44–O1–C48	2	−10	—

[a] Estimated standard deviations of the least significant figures are given in parentheses.
[b] The designators L1 are used to characterize the carbon or nitrogen atoms of the co-ligands. M specifies the metal center in each case.
[c] Q specifies the end point of a vector attached to the corresponding phosphorous center which points towards the observer with respect to the projections of the compounds onto the P3 planes as given in Fig. 2 (top). The vector is vertical to the P3 plane.
[d] This column refers to the corresponding values for $[\{PhCH_2C(CH_2PPh_2)_3\}Fe(NCMe)_3]^{2+}$ ([2]c).



8 **9**

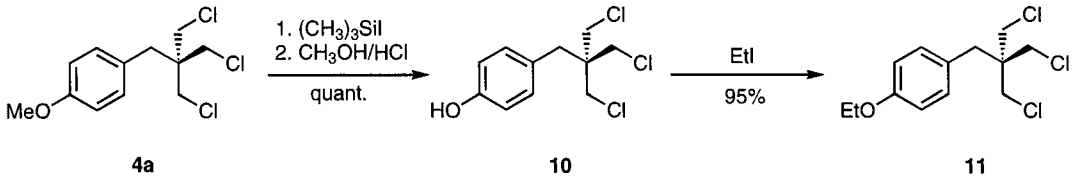
Fig. 2. Two views of the structures of **8** and **9**. Top view: projection onto the P3 plane.

Deprotonation of **10** by KO^{t}Bu and consequent reaction with three equivalents of $KPPh_2$ in DMSO leads to a fair yield of **12**. As a raw product, **12** is a colorless oil which slowly transforms into a microcrystalline colorless powder when its solution in Et_2O is mixed with PE40/60 in an ultrasonic bath over a few hours. As an alternative way to obtain analytically pure **12** chromatography on silica gel has been found to work. The Et_2O/PE40/60 fraction containing **12** leaves the compound as a microcrystalline colorless powder after evaporation (Scheme 7).

The sequence of reactions from **1** to **12**, as described, implies six steps altogether. Even though, the overall yield of **12** amounts to over 35%.

As a first test to validate the utility of the phenyl spacer in **12** with respect to the problem of covalently anchoring hydroxy-functionalized tripod-ligands on a polymer the reaction of **12** with a CH_2Cl-functionalized polystyrene resin of the Merrifield type was analysed. From the reactivity reported for $HOCH_2C(CH_2PR_2)_3$ ([2]f, h) it is evident that this type of hydroxy functionalized tripod-ligand could not be covalently fixed to a CH_2Cl-functionalized resin, because of the intermolecular cyclization reactions which are characteristic of this type of compound under the conditions of etherification ([2]h). Nevertheless a series of experiments was done with the $HOCH_2$-group of $HOCH_2C(CH_2PR_3)_3$ or the $ClCH_2$-group of $ClCH_2C(CH_2PR_2)_3$ as potential precursors with respect to polymer fixation [9]. The ^{31}P resonances of the products obtained were however, exclusively observed at $\delta = +30$, indicating that phosphorus instead of oxygen had been attacked as the nucleophilic center [10]. Success in polymer fixation was achieved with **12** as the tripod constituent.

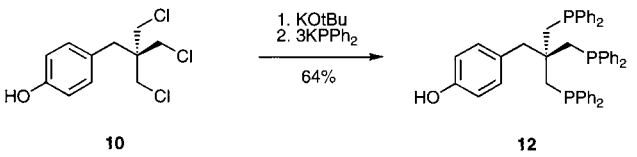
To incorporate **12** into the polymer the resin-granulate as commercially available was allowed to swell in



Scheme 6.

o-dichlorobenzene. A total of 1.4 equivalents (with respect to the CH_2Cl-groups of the polymer) of **12** and correspondingly 1.4 equivalents of sodium hydride were added to the suspension of the gel and the mixture was heated to 70°C for a period of 5 days. After evaporation of the solvent and extensive washing the resulting powder was dried to constant weight. The increase in weight was in accord with results obtained by microanalytic determination of the phosphorous content of the powder. With 3.9% phosphorous found, ca. 60% of the reactive groups must have been linked to the ligand [11]. The ^{31}P-NMR signal characteristic for the ligand loaded resin is found at $\delta = -27.7$ for the gel prepared from it by swelling in *o*-dichlorobenzene. The value of the observed chemical shift is thus identical to the one observed for the free precursor **12**. There are no other ^{31}P-NMR signals in the spectrum of the gel which clearly proves that no quarternization by electrophilic attack at the phosphorous centers had occurred. Phosphonium salts if they were formed would lead to resonances at around $\delta = +30$ ([2]f). In order to directly visualize the covalent linkage between the tripod ligand and the resin, the latter was subjected to conditions under which $[(tripod)Fe(NCMe)_3]^{2+}$ ([2]c) and $[(tripod)Co(catecholate)]^{+}$ ([1]h) complexes are obtained from free tripod ligands in solution. Under these conditions the polymer changed its color to the colors characteristic of these types of tripod-complexes. The covalent fixation of these chromophoric groups was probed by trying to extract the colored tripod-metal complexes with THF or methylene chloride. Even over a period of days no colored compounds were extracted into these solvents, and the color of the polymer remained unchanged.

Taken together, these observations show that the phenolate linker group as present in **12** is efficient in the covalent fixation of tripod ligands on appropriately functionalized polymers.



Scheme 7.

3. Experimental

3.1. General

All manipulations were carried out under an argon atmosphere by means of standard Schlenk techniques. All solvents were dried by standard methods and destilled under argon. The $CDCl_3$, CD_2Cl_2 and $[D_8]$THF used for the NMR spectroscopic measurements were degassed by three successive 'freeze-pump-thaw' cycles and dried over 4-Å molecular sieves. The silica gel (Kieselgel z.A. 0.06–0.2 mm, J.T. Baker Chemicals B.V.) used for chromatography was degassed at 1 mbar for 24 h and saturated with argon. NMR: Bruker Avance DPX 200 at 200.13 MHz (^{1}H), 50.323 MHz ($^{13}C\{^1H\}$), 81.015 MHz ($^{31}P\{^1H\}$); chemical shifts (δ) with respect to $CDCl_3$ (^{1}H: $\delta = 7.27$, ^{13}C: $\delta = 77.0$), CD_2Cl_2 (^{1}H: $\delta = 5.32$, ^{13}C: $\delta = 53.5$) and $[D_8]$THF (^{1}H: $\delta = 3.58$, ^{13}C: $\delta = 67.7$) as internal standards, and with respect to 85% H_3PO_4 (^{31}P: $\delta = 0$) as external standard. IR: Bruker FT-IR IFS-66; CaF_2 cells. MS: Finnigan MAT 8400; FAB: Nibeol (4-nitrobenzyl alcohol) or TEA (triethanol amine) matrices, respectively; EI: 70 eV. Elemental analyses: microanalytical laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. Melting points: Gallenkamp MFB-595 010; melting points were not corrected. All other chemicals were commercially obtained and used without further purification.

3.2. Preparation of *1*

Sodium-hydride (11.3 g; 470 mmol) was suspended in THF (600 ml) at 0°C. The mixture was warmed to room temperature and 4-methoxybenzyl-malonic-acid-diethylester (120.0 g; 430 mmol), dissolved in THF (100 ml) was added dropwise. The mixture was stirred until no more hydrogen evolved (2.5 h). Chloromethylbenzylether (67 g; 430 mmol) dissolved in THF (50 ml) was added and the mixture was refluxed for 3 h. The turbid-white mixture was allowed to cool to 25°C and was hydrolized with aqueous NH_4Cl (5%) and ice. The aqueous phase was extracted with diethylether (2 × 100 ml). The combined organic phases were washed with water (100 ml) and dried ($MgSO_4$). After removal of the solvent 153 g crude product remained as a colorless

Table 3
^{1}H-NMR data of **3**, **4a**, **6**, **7**, **10**, **11** and **12**

[a]	RO	*p*-ArCH_2C	CCH_2X	X	Aromatic H
3, R = Me; X = OH	3.75, s, 3H	2.64, s, 2H	3.47, d, 6H, [4.9]	—	6.79–7.20, m, 4H
4a, R = Me; X = Cl	3.81, s, 3H	2.77, s, 2H	3.50, s, 6H	—	6.86–7.31, m, 4H
6, R = Me; X = OSO_2Ph	3.78, bs, 3H	2.61, s, 2H	3.78, m, 6H	7.5–7.9, m, 15H	6.62–6.84, m, 4H
7, R = Me; X = PPh_2	3.78, s, 3H	2.86, s, 2H	2.38, s, 6H	7.25–7.37, bm, 30H	6.76–7.10, m, 4H
10, R = H; X = Cl	5.03, s, 1H	2.77, s, 2H	3.48, s, 6H	—	6.79–7.26, m, 4H
11, R = Et; X = Cl	1.44, t, 3H, [7.0] 4.03, m, 2H	2.78, s, 2H	3.48, s, 6H	—	6.89–7.26, m, 4H
12, R = H; X = PPh_2	—	2.83, s, 2H	2.35, s, 6H	7.24, bm, 30H	7.90–7.34, m, 20H

[a] In $CDCl_3$ solution at 25°C; δ values; $^2J_{HH}$ coupling constants in Hz.

Table 4
^{13}C-NMR data of **3**, **4a**, **6**, **7**, **10**, **11** and **12**

[a]	RO	*p*-ArCH_2C	CCH_2X	*X*	*C* quart.	Aromatic *C*
3, R = Me; X = OH	55.6, s	65.9, s	35.4, m, (8.8)	—	44.6, m	113–159, m
4a, R = Me; X = Cl	55.0, s	45.5, s	34.2, s, 6H	—	45.2, m	114–159, m
6, R = Me; X = OSO_2Ph	55.6, s	33.5, m	67.5, s	114–135, m	43.4, m	114–159, m
7, R = Me; X = PPh_2	55.0, s	42.7, m	39.8, m, (7.7)	113–139, m	42.6, m	113–157, m
10, R = H; X = Cl	—	45.5, s	34.2, s	—	45.2, m	114–155, m
11, R = Et; X = Cl	14.6, s; 63.2, s	45.5, s	34.3, m	—	45.3, m	114—158, m
12, R = H; X = PPh_2	—	45.5, s	38.8, m	114–139, m	45.6, m	114–153, m

[a] In $CDCl_3$ solution at 25°C; δ values; $^1J_{CP}$ couplings constants in Hz.

Table 5
Crystal data and structural analysis results for **5**, **7**, **8** and **9**

Compound	**5**	**7**	**8**	**9**
Formula	$C_{47}H_{42}OClP_3$	$C_{48}H_{45}OP_3$	$C_{54}H_{54}N_3OP_3B_2F_8Fe$	$C_{51}H_{45}O_4P_3Mo$
Molecular mass (g mol^{-1})	751.2	730.8	1083	910.7
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group (no.)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P2_1/c$ (14)
a (pm)	1053.7 (3)	1908.7 (3)	1454.7 (3)	1007.0 (2)
b (pm)	1392.5 (3)	2039.9 (3)	1496.1 (3)	2523.6 (4)
c (pm)	1474.5 (3)	1030.9 (3)	1587.6 (2)	1848.8 (3)
α (°)	104.24 (2)	90.000 (0)	115.66 (1)	90.000 (0)
β (°)	104.89 (1)	89.16 (1)	114.76 (1)	102.51 (0)
γ (°)	96.92 (2)	90.000 (0)	72.45 (1)	90.000 (0)
Cell volume (10^6 pm^3)	1992	4013	2798	4587
Molecular units/cell	2	4	2	4
$D_{calc.}$ (g cm^{-3})	1.252	1.209	1.384	1.449
Temperature (K)	200	298	200	200
No. of reflections for cell parameter refinement	31	29	30	31
Scan range (°)	$4.1<2\theta<46.0$	$4.0<2\theta<46.0$	$3.5<2\theta<49.0$	$4.1<2\theta<48.0$
Scan speed (° min^{-1}) ω-scan	14.0	10.0	12.0	10.0
No. of reflections measured	5853	5766	9515	7629
No. of unique reflections	5502	5577	9101	7180
No. of reflections observed ($I>2\sigma$)	4535	2554	6780	4750
No. of parameters refined	477	472	779	566
residual electron density (10^{-6} e pm^{-3})	0.29	0.25	0.65	0.69
R_1/R_w (%) (refinement on F^2)	3.8/11.2	7.3/17.7	5.2/15.8	7.3/15.9

oil which was purified by column chromatography on silica gel (20 cm, Ø = 4 cm). The fraction eluted with a mixture of petrol ether 40/60/diethylether (3:1, TLC control: $R_f = 0.50$) gave **1** as a colorless oil. ^{1}H-NMR ($CDCl_3$): $\delta = 1.25$ (t, $J = 7.5$ Hz, 6 H, CCH_3), 3.36 (s, 2H, ArCH_2), 3.72 (s, 2 H, CCH_2OBzl), 3.77 (s, 3 H, CH_3O), 4.20 (q, $J = 7.5$ Hz, 4 H, O$CH_2$$CH_3$), 6.79–7.35 (m, 9 H, *H* aromatic). $C_{23}H_{28}O_6$ (400.2): Anal. Calc. C

68.98, H 7.05; found C 69.15, H 7.24. MS (EI); m/z (%): 400 (4) [M^+], 91 (100) [$C_7H_7^+$].

3.3. Preparation of **2**

$LiAlH_4$ (30 g; 790 mmol) was suspended in diethylether (400 ml) at 0°C. A solution of crude **1** (153 g; 380 mmol) in diethylether (200 ml) was added dropwise. After the addition the mixture was stirred at 40°C for 4 h. The mixture was allowed to cool to 25°C and hydrolized by slow addition of water (30 ml), 15% aqueous NaOH (30 ml) and water (90 ml) subsequently. It was separated by filtration from hydrolization products which were further extracted by a Soxhlet-apparatus with diethylether. The combined organic phases were dried ($MgSO_4$) and the solvent was removed in vacuo. A total of 122 g of crude product remained as a colorless oil which was purified by column chromatography on silica gel (20 cm, Ø = 4 cm). The fraction eluted with diethylether (TLC control: $R_f = 0.54$) gave **2** as a colorless oil. ^{1}H-NMR ($CDCl_3$): $\delta = 2.69$ (bs, 2 H, CCH_2O), 3.18 (m, 2 H, OH), 3.39 (s, 2 H, $ArCH_2$), 3.68 (m, 4 H, CH_2OH), 3.82 (s, 3 H, CH_3O), 4.53 (s, 2 H, OCH_2Ar), 6.8-7.4 (m, 9 H, H aromatic). ^{13}C-NMR ($CDCl_3$): $\delta = 35.4$ (m, $J = 8.8$ Hz, CH_2P), 44.6 (m, C quart.), 55.6 (s, CH_3O), 65.9 (s, CH_2), 113–158 (m, C aromatic). $C_{19}H_{24}O_4$ (316.4): Anal. Calc. C 72.13, H 7.65; found C 71.91, H 7.73. MS(EI); m/z (%): 316 (10) [M^+], 121 (100) [$C_8H_9^+$].

3.4. Preparation of **3**

Crude **2** (23.4 g; 77.4 mmol) and 4 g of Pd/C (10%) were suspended in ethanol (350 ml). The mixture was kept under an atmosphere of hydrogen and stirred for 2 days at 20°C. The progress of the reaction was monitored by TLC. The mixture was filtered over silicagel and the solvent was removed in vacuo. A total of 16.4 g crude product was obtained as a viscous oil which was purified by column chromatography on silica gel (20 cm, Ø = 4 cm). The fraction eluted with diethylether (TLC control: $R_f = 0.19$) gave **3** as a highly viscous colorless oil. $C_{12}H_{18}O_4$ (226.3): Anal. calc. C 63.71, H 7.96; found C 63.29, H 8.91. MS(EI); m/z (%): 226 (10) [M^+], 121 (100) [$C_8H_9^+$]. (For ^{1}H- and ^{13}C-NMR data see Tables 3 and 4).

3.5. Preparation of **4a**

A solution of **3** (10.0 g; 44 mmol) in 11 ml pyridine was cooled to 0°C. Thionylchloride (18 g; 150 mmol) was added slowly by a syringe. The temperature of the mixture was kept below 10°C. After addition the mixture was refluxed for 3 h, allowed to cool to 25°C, hydrolized by water (8 ml) and extracted with dichloromethane (3 × 20 ml). The combined organic phases were filtered over 3 cm silica gel covered with 2 cm $MgSO_4$. The filtrate was concentrated and the resulting residue was chromatographed on silica gel (15 cm, Ø = 4 cm). The fraction eluted by a mixture of petrolether 40/60/diethylether (3:1, TLC control: $R_f = 0.66$) gave 13 g **4a** as a colorless solid (m.p. 52°C) in a 67% yield. Traces of **4b** were contained in the product as was evidenced by mass spectroscopy (weak signal at m/z 316). $C_{12}H_{15}OCl_3$ (281.6): Anal. Calc. C 51.13, H 5.33; found C 51.15, H 5.44; MS(EI); m/z (%): 281 (11) [M^+], 121 (100) [$C_8H_9O^+$]. (For ^{1}H- and ^{13}C-NMR data see Tables 3 and 4).

3.6. Preparation of **5**

When the reaction intended to give **4a** was run at 70°C the product contained an appreciable amount of **4b**. A solution of this product mixture (1.4 g) in DMSO (5 ml) was added to a solution of potassiumdiphenylphosphide (4.5 g; 20 mmol) in DMSO (34 ml) and the mixture was refluxed for 3 h at 120°C. The solvent was removed in vacuo and the sticky grey residue was washed with 50 ml H_2O by stirring 16 h. The remnants were dissolved in diethylether and dried with $MgSO_4$. Removing the solvent in vacuo and washing five times with 20 ml of petrol ether 40/60 gave the crude product as a viscous colorless oil or a sticky colorless powder. Crystals suitable for X-ray analysis were obtained by slowly evaporating a solution of **5** in petrolether40/60/diethylether within several days. ^{1}H-NMR ($CDCl_3$): $\delta = 2.4$ (s, 6 H, CH_2P), 2.86 (s, 2 H, $ArCH_2$), 6.8–7.4 (m, 33 H, H aromatic). ^{13}C-NMR ($CDCl_3$): $\delta = 39.7$ (m, CH_2P), 43.3 (m, $ArCH_2$), 45.2 (m, C quart), 128–150 (m, C aromatic). $C_{47}H_{42}OClP_3$ (750.4): Anal. Calc. C 75.23, H 5.60; found C 74.92, H 5.53. MS(FAB); m/z (%): 750 (8) [M^+], 673 (100); 585 (11). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = -28.8$ (s).

3.7. Preparation of **6**

A solution of **3** (10.0 g; 43 mmol) in 60 ml pyridine was cooled to 8°C. Benzenesulfonylchloride (27.3 g; 155 mmol) was added by a funnel. The mixture was stirred for 1 day and poured into a mixture of 100 ml water, 200 ml methanol and 80 ml concentrated HCl. A viscous oil separated, which solidified after several days. Recrystallisation from ethanol (50 ml) gave 22.8 g of **6** as a white powder (m.p. 105°C) in 80% yield. $C_{30}H_{30}O_{10}S_3$ (646.8): Anal. Calc. C 55.71, H 4.68; found C 55.62, H 4.63. MS(EI); m/z (%): 646 (22) [M^+], 121 (100) [$C_8H_9O^+$]. (For ^{1}H- and ^{13}C-NMR data see Tables 3 and 4).

3.8. Preparation of **7**

A solution of diphenylphosphane (7.8 g; 42 mmol) in

40 ml dimethylsulfoxide was deprotonated with KO^{t}Bu in an ice bath. After stirring for 1 h **6**, (8 g; 12.4 mmol) diluted in 15 ml dimethylsulfoxide, was added and the mixture was refluxed for 3 h. After removing the solvent in vacuo the procedure of washing and drying followed the recipe for **5**. Further purification was performed by column chromatography on silica gel (20 cm, Ø = 4 cm). The fraction eluted with a mixture of petrol ether 40/60/diethylether (10:1, TLC control: $R_f = 0.25$) gave 5.6 g **7** as a white solid (m.p. 141°C) in 63% yield. $C_{48}H_{45}OP_3$ (730): Anal. Calc. C 78.90, H 6.16; found C 78.50, H 6.38; MS(FAB); *m/z* (%): 730 (32) [M^+], 653 (100) [M^+-Ph]. $^{31}P\{^1H\}$-NMR (CD_2Cl_2): $\delta = -28.1$ (s). (For ^{1}H-and ^{13}C-NMR data see Tables 3 and 4).

3.9. Preparation of **8**

$[Fe(CH_3CN)_6](BF_4)_2$ (357 mg; 0.75 mmol) was added to a solution of **7** (548 mg; 0.75 mmol) in acetonitrile (30 ml). The color of the mixture immediately turned red. After stirring for 1 h at room temperature the solvent was removed in vacuo. The red residue was washed several times with diethylether. After drying in vacuo 856 mg of **8** were obtained as a red powder in 96% yield. Crystals suitable for X-ray analysis were obtained by diffusion of diethylether into a solution of **8** in CH_2Cl_2 within 2 days. ^{1}H-NMR ($CDCl_3$): $\delta = 2.37$ (bs, 9 H, C*H*$_3$CN), 2.73 (bs, 6 H, C*H*$_2$P), 3.3 (bs, 2 H, ArC*H*$_2$), 4.0 (bs, 3 H, C*H*$_3$O), 7.2–7.4 (m, 34 H, *H* aromatic). ^{13}C-NMR ($CDCl_3$): $\delta = 37.7$ (m, *C*H$_2$P), 42.6 (m, *C* quart), 126–155 (m, *C* aromatic). $C_{54}H_{54}N_3OP_3FeB_2F_8$ (1083): Anal Calc. C 59.87, H 5.02, N 3.88; found C 56.54, H 5.18, N 4.33. (with the analytical equipment used, carbon values tend to be found too low in the presence of boron); MS(FAB); *m/z* (%): 1041 (6) [M^+–MeCN], 731 (100). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): $\delta = 29.43$ (s). IR (KBr): ν(CN) = 2324 cm^{-1} (w), 2288 cm^{-1} (m).

3.10. Preparation of **9**

$(CH_3CN)_3Mo(CO)_3$ (144 mg; 0.47 mmol) was added to a solution of **7** (316 mg; 0.43 mmol) in CH_2Cl_2 (70 ml). After stirring for 16 h at room temperature, 15 ml petrol ether 40/60 was added to the mixture. The mixture was filtered over 2 cm silica gel and the solvent was removed in vacuo. A total of 385 mg of **9** was obtained as a pale yellow powder in 98% yield. Crystals suitable for X-ray analysis were obtained by diffusion of diethylether into a solution of **9** in CH_2Cl_2 within several days. ^{1}H-NMR ($CDCl_3$): $\delta = 2.32$ (s, 6 H, C*H*$_2$P), 2.86 (s, 2 H, ArC*H*$_2$), 3.78 (s, 3 H, C*H*$_3$O), 6.7–7.4 (m, 34 H, *H* aromatic). ^{13}C-NMR ($CDCl_3$): $\delta = 37.5$ (m, *C*H$_2$P), 41.2 (m, *C* quart), 53.4 (s, *C*H$_3$O), 111–157 (m, *C* aromatic). $C_{51}H_{45}O_4P_3Mo$ (910.7): Anal. Calc. C 67.26, H 4.98; found C 64.88, H 4.94. (with the analytical equipment used, carbon values tend to be found too low in the presence of boron or molybdenum); MS(FAB); *m/z* (%): 912 (18) [M^+], 825 (12) [M^+–3CO], 307 (100). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): $\delta = 16.1$ (s). IR (CH_2Cl_2): ν(CO) = 1932 cm^{-1} (s), 1832 cm^{-1} (s).

3.11. Preparation of **10**

4a (10 g; 35 mmol) was mixed with $(CH_3)_3SiI$ (12.5 g; 50 mmol) at room temperature and stirred for 5 days under an inert atmosphere and was hydrolized with methanol/hydrochloric acid (10 ml). The mixture was stirred for 1 day. Volatile constituents were removed in vacuo, the brown residue was dissolved in methylene chloride. Filtering over silica gel gave a colorless solution which after removing the solvent in vacuo left **10** as a colorless solid. Further purification was performed by column chromatography on silica gel (20 cm, Ø = 4 cm). The fraction eluted with a mixture of petrol ether 40/60/diethylether (3:1, TLC control: $R_f = 0.30$) gave 9.5 g **10** as a colorless solid (m.p. 68°C) in quantitative yield. $C_{11}H_{13}O_3Cl_3$ (267.6): Anal. Calc. C, 49.37; H, 4.86; found C, 48.87; H, 4.87. MS(EI); *m/z* (%): 266 (19) [M^+]; 107 (100) [$C_7H_7O^+$]. (For ^{1}H- and ^{13}C-NMR data see Tables 3 and 4).

3.12. Preparation of **11**

10 (230 mg; 0.86 mmol) was dissolved in THF (20 ml) and deprotonated with KO^{t}Bu (100 mg; 0.89 mmol) at 0°C. Iodoethane (536 mg; 3.61 mmol) was added and the mixture was warmed to room temperature. The turbid mixture was stirred for 1 h, the solvent was removed and the residue dissolved in CH_2Cl_2 (5 ml). The solution was filtered over silicagel and dried in vacuo. Further purification was performed by column chromatography on silica gel (20 cm, Ø = 4 cm). The fraction eluted with a mixture of petrol ether 40/60/diethylether (3:1, TLC control: $R_f = 0.73$) gave 233 mg **11** as a colorless oil in 92% yield. $C_{13}H_{17}OCl_3$ (295.7): Anal. Calc. C 52.82, H 5.80; found C 52.31, H 5.71. MS(FAB); *m/z* (%): 294 (40) [M^+], 135 (100) [$C_9H_{11}O^+$], 107 (96) [$C_7H_7O^+$]. (For ^{1}H- and ^{13}C-NMR data see Tables 3 and 4).

3.13. Preparation of **12**

To a solution formed by deprotonating diphenylphosphane (23 g; 123 mmol) in 30 ml DMSO by KO^{t}Bu (13.8 g; 123 mmol) at 0°C a solution of **10** (11 g; 41.2 mmol) was added in one portion and the mixture was refluxed for 3 h at 120°C. After removing the solvent in vacuo the procedure of washing and drying followed the recipe for **5**. Further purification

was performed by column chromatography on silica gel (20 cm, $\varnothing = 4$ cm). The fraction eluted with a mixture of petrol ether 40/60/diethylether (1:1, TLC control: $R_f = 0.40$) gave 18.9 g **12** as a white solid (m.p. 140°C) in 64% yield. $C_{47}H_{43}OP_3$ (716.8): Anal. Calc. C 78.76, H 6.05; found C 77.73, H 6.46. MS(EI); m/z (%): 716 (12) [M^+], 639 (100) [$M^+ - Ph$]. $^{31}P\{^1H\}$-NMR (CD_2Cl_2): $\delta = -28.8$ (s). (For ^1H- and ^{13}C-NMR data see Tables 3 and 4).

3.14. X-ray structure determinations

The measurements for **5, 7, 8, 9** were carried out on a Siemens P4 Diffractometer with graphite-monochromated Mo–K_α radiation. The intensities of three check reflections (measured every 100 reflections) remained constant throughout the data collections, thus indicating crystal and electronic stability. All calculations were performed using the SHELXT PLUS software package. Structures were solved by direct methods with the SHELXS-86 ([12]a) program and refined with the SHELX93 program ([12]b). Graphical handling of the data was done using XPMA [13]. Absorption corrections (ψ scan, $\Delta\psi = 10°$) were applied to the data. The structures were refined in fully anisotropic models by a full-matrix least-squares calculation. Hydrogen atoms were introduced at calculated positions.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-408094 for **5**, CSD-407838 for **7**, CSD-407837 for **8**, and CSD-407836 for **9** (Table 5).

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