Functionalized Ether Derivatives of $HOCH_2C(CH_2PPh_2)_3$ and Related Tripod Ligands – Synthesis and Coordination Chemistry☆

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Neopentane-derived tripod ligands of the general type $HOCH_2C(CH_2PPh_2)(CH_2Y)(CH_2Z)$ (**1**; Y, Z = PPh_2, SR) are notoriously resistant to ether formation at their hydroxy group. Two routes have been found, which allow the transformation of **1** into ether functionalized tripod ligands $ROCH_2C(CH_2PPh_2)(CH_2Y)(CH_2Z)$ (Y = Z = PPh_2: **5**, Y = Z = SR: **8**). One of these strategies relies upon the η^3 coordination of **1** in **1**·$Mo(CO)_3$ (**2**). By this way the donor groups are efficiently protected and the steric encumbrance of the CH_2OH group at the backbone of the ligands is greatly reduced by fixing three arms of the neopentane scaffolding to the metal center. After deprotonation, reaction with electrophiles will produce the corresponding ether derivatives $ROCH_2C(CH_2PPh_2)(CH_2Z)_2$ (**3**). Mesylation of **2** leads to $MeSO_2OCH_2C(CH_2PPh_2)3{\cdot}Mo(CO)_3$ (**4**), which reacts with alkoxides to produce **3** in a sequence of reversed polarity. Ligands **5** [$ROCH_2C(CH_2PPh_2)_3$] are liberated from **3** by UV irridation of their solutions in the presence of pyridine *N*-oxide. Direct etherification of **1** is also possible in some cases after deprotonation of **1** by KO*t*Bu and subsequent reaction with an electrophile RX in the narrow temperature range between –10 and +20 °C. By this way, ω-methyl polyglycol ether functions are easily introduced resulting in $H_3C(OC_2H_4)_nOCH_2C(CH_2PPh_2)_3$ (**5g**, **h**).

Introduction

One of the properties of a ligand which has not been generally considered to be too important is its solubility in different solvents and the herewith introduced solubility of its coordination compounds. On the other hand it has been shown how solubility properties may considerably improve processes which rely on the catalytic activity of ligand-metal templates, one of the examples of even technical importance being the Rhone-Poulenc process.[1] In this case hydrophilic phosphane ligands are the reason for the advance.[2] Many other catalytic processes do in principle allow for this kind of modification[3], given that the ligand can be appropriately modified. Modifying ligands to enhance and specify solubility is thus of basic interest. Modifying ligands by attaching auxiliary groups, such as to allow the attachment of ligand-metal templates to a surface is another reason for putting more weight to the question of an appropriate functionalizability of a ligand.[3] Homogeneous processes may be transferred to heterogenous ones using this approach combining the advantages of both homogeneous and heterogeneous catalyses.[4] Modifying ligands such as to induce a self-assembly type of order in the phases derived from their coordination compounds is yet another point of interest in this topic.[5] The rapid development of chemical sensors[6] as well as of non-linear optical materials[7] will further increase the demand for ligands which do not only have the appropriate coordinative capabilities but do at the same time allow for easy-to-achieve modifications by additional functionalities in order to imprint the specific properties which are needed in each case to their coordination compounds.

As a consequence a well-thought-of strategy for designing a particular class of ligands will from the very beginning incorporate a functionality which may serve as a linker group such as to allow for all the modifications eventually needed. In a project concerned with the synthesis and application of tripod ligands $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ much work has been devoted to the problem of designing a convergent strategy to introduce different donor groups[8a][8b][8c][8d][8e][8f][8g][8h], even enantioselective procedures have been worked out.[9a][9b][9c] The problem of introducing a linker group at the backbone has, however, not yet been solved in a convergent way. Wherever syntheses of ligands modified in this sense had been reported, the modified groups were incorporated from the very beginning of the syntheses.[8k][8m] Even though with the synthesis of $HOCH_2C(CH_2X)(CH_2Y)(CH_2Z)$[8k] the alcohol function appears to naturally lend itself to further functionalization, the steric bulk of the neopentane system hitherto precluded the scope of this reaction. Only silylation and esterification[8k] leading to R_3Si- and $RCOO-$ derivatives had been found to work. And even with these reactions the protection of donor functions X, Y, Z like PR_2 was found to be necessary. The functionalizations thus introduced strongly limit the potential application of these ligands due to their sensitivity to hydrolysis. An ether functionality would be far more superior. Despite continued efforts[8k][8l] to achieve etherification of the hydroxymethyl group of these neopentane-based ligands definitive solutions of this problem have only now been found. We report here on methods which allow for this type of modification of tripod ligands and which are at the same time tolerant to a broad

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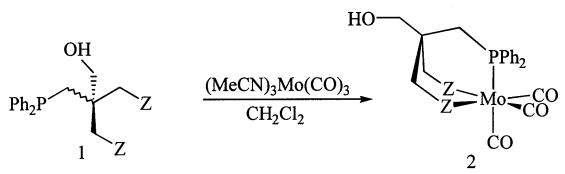
range of functionalities in the auxiliary group as well as in the donor set of the ligands.

Results and Discussion

Modification of Coordinated Ligands

There are two main reasons for the failure of the transformation of the CH_2OH group in $HOCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ into an ether function: one of them being the sluggish reactivity of the neopentane system[10] and the other one being inherent in the sensitivity of the donor groups to electrophilic attack.[8k][8l] This second impediment may in part be overcome by appropriate protection of the donor groups e.g. adduct formation of PR_2 donors with borane to give protected PR_2-BH_3 entities which are less prone to electrophilic attack. A strategy which solves both problems at the same time may be envisaged in η^3-coordinating all three donor groups to one metal center. This should protect the donor groups and should at the same time reduce the steric crowding around the CH_2OH group at the neopentane framework with this steric crowding being the main reason for the reduced reactivity of neopentane derivatives.[10] It is observed that the tricarbonylmolybdenum fragment serves as an efficient template in this sense. Tripod tricarbonylmolybdenum complexes are easily accesible and remarkably stable.[8i][8k][8l] Thus, ligands **1** are transformed into their $Mo(CO)_3$ derivatives **2** (Scheme 1) with excellent yields (Experimental Section).

Scheme 1



1a: Z = PPh_2
1b: Z = SBzl

2a: Z = PPh_2
2b: Z = SBzl

Their ν(CO) IR spectra (Experimental Section) are in accord with the C_3 symmetry of the $Mo(CO)_3$ chromophore which is somewhat disturbed by the two different donor functions in **2b** so that the E band is split into two discernable components. The NMR data (Tables 1 and 2, Experimental Section) are in full accord with the assigned constitution. Compound **2a** is deprotonated at the alcohol function by KO*t*Bu (Scheme 2). The potassium alkoxide thus obtained reacts with various electrophiles to produce the corresponding ethers **3**. The infrared and ^{31}P-NMR spectra (Experimental Section) as well as the ^{13}C- and ^{1}H-NMR data (Tables 1 and 2) are in full accord with the structures. Compounds **3** are obtained as analytically pure pale yellow microcrystalline solids, the structures of **3a** and **3b** have been determined by X-ray crystallography.[16]

While the above procedure relies upon transforming the CH_2OH function of **2a** into a nuleophilic group, a method

Table 1. ^{1}H-NMR data of **1b**, **2b**, **7**, **8a**, **8b**, **9a**, and **9b**

^{1}H NMR[a]	CH_2P	CH_2SBzl	CH_2OR	SCH_2Ph	R	H aromat.
1b, R = H	2.35, d, 2 H, 4.4[b]	2.66, s, 4 H	3.52, s, 2 H	3.62, s, 4 H	–	7.57–7.18, m, 20 H
2b, R = H	2.50, bs, 2 H	2.35, bs, 4 H	3.11, bs, 2 H	3.98 3.83, 2d, 4 H, 13.5[c]	–	7.57–7.18, m, 20 H
7, R = CH_2	–	2.93, s, 4 H	4.33, s, 2 H	3.73, s, 2 H	–	7.36–7.30, m, 10 H
8a, R = Me	2.41, d, 2 H, 4.0[b]	2.81 2.74, 2d, 4 H, 12.7[c]	3.25, s, 2 H	3.68, s, 4 H	3.03, s, 3 H	7.53–7.25, m, 20 H
8b, R = Et	2.44, d, 2 H, 3.8[b]	2.81, s, 4 H	3.35, s, 2 H	3.71, s, 4 H	3.22, q, 2 H, 6.9[d] 1.09, t, 3 H, 6.9[d]	7.58–7.27, m, 20 H
9a, R = Me	2.43, d, 2 H, 7.4[b]	2.39, s, 4 H	2.98, d, 2 H, 1.0[e]	3.68, s, 4 H	3.27, s, 3 H	7.53–7.25, m, 20 H
9b, R = Et	2.46–2.40, m, 2 H	2.40, s, 4 H	3.03, s, 2 H	4.00 3.93, 2d, 4 H, 15.0[c]	3.40, q, 2 H, 6.9[d] 1.17, t, 3 H, 6.9[d]	7.90–7.34, m, 20 H

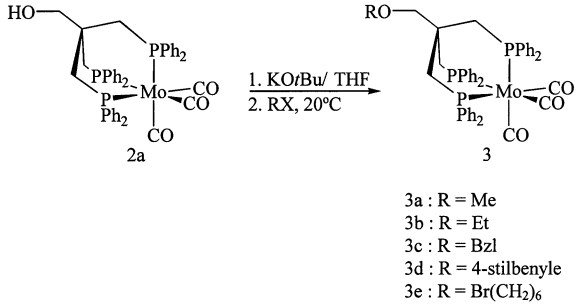
[a] **1b, 7** and **8** in $CDCl_3$, **2b** in [D_8]THF, **9** in CD_2Cl_2. – [b] $^2J_{HP}$. – [c] $^2J_{HH}$. – [d] $^3J_{HH}$. – [e] $^4J_{HP}$ in Hz.

Table 2. ^{13}C-NMR data of **1b**, **2b**, **7**, **8a**, **8b**, **9a**, and **9b**

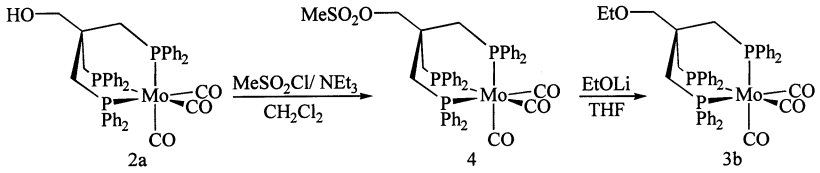
^{13}C NMR[a]	CH_2P	CH_2SBzl	CH_2OR	SCH_2Ph	C_qCH_2O	R	CO	C aromat.
1b, R = H	34.1, d, 15.5[c]	38.0, d, 10.1[d]	66.6, d, 8.3[d]	37.4, s	43.8, d, 10.9[e]	–	–	137.9–126.8, m
2b, R = H	31.5, d, 12.9[c]	36.5, d, 4.6[d]	73.5, d, 9.2[d]	48.8, d, 5.5[d]	43.5, d, 4.6[e]	–	223.4, d, 8.3[f], 220.3, d, 34.9[g]	139.6–128.4, m
7, R = CH_2	–	37.5–37.3, 2s[b]	79.8, s	37.5–37.3,2s[b]	43.6, s	–	–	137.9–126.9, 4s
8a, R = Me	35.0, d, 17.0[c]	38.7, d, 10.3[d]	76.0, d, 8.4[d]	38.3, s	44.0, d, 13.4[e]	58.7, s	–	139.8–127.4, m
8b, R = Et	35.0, d, 16.9[c]	38.7, d, 10.3[d]	73.6, d, 8.7[d]	38.3, s	44.0, d, 13.3[e]	66.6, s; 15.5, s	–	140.0–127.3, m
9a, R = Me	31.5, d, 11.7[c]	35.9, d, 4.4[d]	82.1, d, 8.8[d]	48.3, d, 5.8[d]	42.1, d, 5.5[e]	59.5, s	223.4, m	138.1–128.4, m
9b, R = Et	31.5, d, 12.0[c]	35.8, d, 4.2[d]	81.1, d, 9.2[d]	48.2, d, 5.8[d]	42.2, d, 5.2[e]	67.3, s; 15.1, s	223.3, d, 9.0[f], 220.1, d, 35.0[g]	138.1–128.4, m

[a] **1b**, **7** and **8** in $CDCl_3$, **2b** in [D_8]THF, **9** in CD_2Cl_2. – [b] Assignment not unambigously possible. – [c] $^1J_{CP}$. – [d] $^3J_{CP}$. – [e] $^2J_{CP}$. – [f] $CO_{cis\text{-}P}$. – [g] $CO_{trans\text{-}P}$.

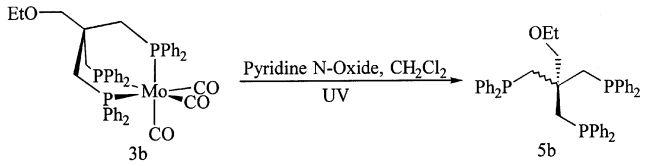
Scheme 2



Scheme 3



Scheme 4



inverting the polarity by mesylation of the hydroxy group is also possible.

2a, when treated with an excess of mesyl chloride in the presence of NEt_3 (Scheme 3), gives the mesylate **4** which after chromatography is obtained analytically pure as a pale yellow microcrystalline solid (Experimental Section; Tables 4 and 5). The mesylate **4** reacts with LiOEt to give **3b** albeit in lower yields as compared to the yields obtained using the above procedure based on an inverted polarity. The procedure starting from **4** was therefore not further generalized. It should be noted that the free ligand $HOCH_2C(CH_2PPh_2)(CH_2Y)(CH_2Z)$ can not be mesylated[11] and even a change of the reaction conditions as described later did not work with mesyl chloride.

In order to make the above procedure useful for the synthesis of the corresponding free ligands decoordination of the $Mo(CO)_3$ template in **3** is necessary. An especially useful approach for this purpose has been developed by H. A. Mayer et al.[12], who found that tripod ligands containing P-donor functions may be decoordinated from their $Mo(CO)_3$ complexes by irridating their CH_2Cl_2 solutions in the presence of pyridine *N*-oxide. With **3b** as an example this procedure was shown to work equally well for the class of tripod ligands which are of concern in this paper. **3b** liberates the tripod ligand **5b** (Scheme 4).

The ligand has to be purified by chromatography since even under these specialized conditions oxidation at the phosphorus atoms is a minor side reaction. **5b** is obtained as an analytically pure colorless viscous material, the identity of which is evident from the ^{31}P-NMR and analytical data (Experimental Section) as well as from ^1H- and ^{13}C-NMR results (Tables 4 and 5).

Modification of Free Ligands

It had been shown that ether formation from **1a** is not possible under standard Williamson conditions.[8k] Neither change of the solvent nor change of the counter ion (Na^+, Li^+) was found to be a remedy in this situation[8k], nor did BH_3 protection of the phosphane donors cause a positive change. Lacking reactivity or quaternization at the phosphorus atoms were the seemingly unavoidable problems.[8k][11] We found now that **1a** after deprotonation with KO*t*Bu in THF does react with various electrophiles at temperatures below 20°C to give the corresponding ethers (Scheme 5).

Scheme 5

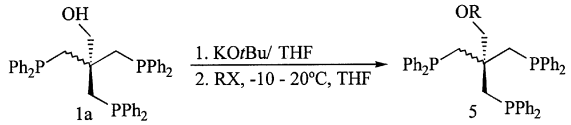


Table 3. Alkylation reagents RX and yields for the reaction of **1a** to **5a–h**

	R	X	Yield (%)
5a	Me	I	72
5b	Et	I	69
5c	$CH_3[CH_2]_9$	OTs	33
5d	$CH_3[CH_2]_{21}$	OTs	44
5e	$H_2C{=}CH[CH_2]_9$	OTs	38
5f	$Cl[CH_2]_6$	OTs	52
5g	$Me[OC_2H_4]_3$	OTs	53
5h	$Me[OC_2H_4]_n$, $n = 4-13$	OTs	[a]

[a] Yield cannot be determined due to separation problems of **5h** from the starting compounds.

The relative rates of ether formation or quaternization at the phosphorus atoms are different enough under these conditions to impede the extensive formation of quaternization products. As minor side products the phosphonium salts are separated by chromatography from the products **5** and the ligands **5** are obtained in fair yields by this procedure. They are colorless viscous oils in general; only **5a** could be obtained as a microcrystalline solid by recrystallization from CH_2Cl_2. The compounds **5a–5g** are obtained in an analytically pure state; the polyoxyethylene derivative **5h** is not completely separated from the starting materials.

Table 4. ^{1}H-NMR data of **2**, **3**, **4**, and **5**

^{1}H NMR [a]	CH_2P	CH_2OR	R	H aromat.
2a, R = H	2.30, br. s, 6H	3.56, br. s, 2 H	–	7.00−7.40, m, 30 H
3a, R = Me	2.31, br. s, 6H	3.28, br. s, 2 H	3.48, s, 3H	7.44−7.05, m, 30 H
3b, R = Et	2.35, br. s, 6H	3.36, br. s, 2 H	3.63, q, 2 H, 7.0[c]; 1.31, t, 3 H, 7.0[c]	7.43−7.06, m, 30 H
3c, R = Bzl	2.37, br. s, 6H	3.45, br. s, 2 H	4.66, s, 2H	7.37−7.05, m, 30 H
3d, R = 4-stilbenyl	2.36, br. s, 6H	3.44, br. s, 2 H	4.66, s, 2H	7.61−7.06, m, 41 H
3e, R = Br[CH_2]$_6$	2.32, br. s, 6H	3.32, br. s, 2 H	3.55, t, 6.3[c], CH_2O; 3.42, t, 6.7[c], CH_2Br; 1.89−1.50, m, 8 H, $CH_2CH_2CH_2$	7.37−7.04, m, 30 H
4, R = CH_3SO_2	2.32, br. s, 6H	4.11, br. s, 2 H	3.11, s, 3H	7.35−7.06, m, 30 H
5a, R = Me	2.61, d, 6 H, 2.6[b]	3.06, s, 2 H	2.51, s, 3H	7.27−7.43, m, 30 H
5b, R = Et	2.52, d, 6 H, 2.4[b]	3.11, s, 2 H	0.7, t, 3 H, 6.9[c]; 2.62, q, 2 H, 7.0[c]	7.26−7.40, m, 30 H
5c, R = CH_3[CH_2]$_9$	2.68, d, 6 H, 2.5[b]	3.11, s, 2 H	1.0, t, 3 H, 5.6[c]; 1.1−1.5, m, 16 H	7.90−7.34, m, 30 H
5d, R = CH_3[CH_2]$_{21}$	2.55, d, 6 H, 2.4[b]	3.16, s, 2 H	0.94−3.39, m, 45 H; 3.39, m, 2 H	7.27−7.60, m, 30 H
5e, R = H_2C=CH[CH_2]$_9$	2.63, d, 6 H, 2.3[b]	3.21, s, 2 H	1.1−1.6, m, 14 H; 2.11, m, 2H; 2.73, m, 2H; 5.04, m, 2 H; 5.92, m, 2 H	7.29−7.44, m, 30 H
5f, R = Cl[CH_2]$_6$	2.59, d, 6 H, 2.6[b]	3.21, s, 2 H	1−1.5, m, 6H; 1.7, q, 2 H, 6.8[c]; 2.73, t, 2 H, 6.0[c]; 3.50, t, 2 H, 6.8[c]	7.28−7.45, m, 30 H
5g, R = Me[OC_2H_4]$_3$	2.55, d, 6 H, 2.5[b]	2.86, s, 2 H	2.86, m,2H; 3.18, m, 4 H; 3.37, s, 3H; 3.51−3.56, m, 8 H	7.25−7.37, m, 30 H
5i, R = NC[CH_2]$_6$	2.56, d, 6 H, 2.6[b]	3.21, s, 2 H	1.1−1.6, m, 10 H; 2.22, t, 2 H, 7.0[c]; 2.71, m, 2 H	7.27−7.39, m, 30 H
5j, R = HOOC[CH_2]$_6$	2.57, d, 6 H, 2.4[b]	3.18, s, 2 H	1.1−1.5, m, 8 H; 2.32, m, 2H; 2.71, m, 2 H	7.27−7.40, m, 30 H
5k, R = HOH_2C[CH_2]$_6$	2.56, d, 6 H, 2.6[b]	3.21, s, 2 H	1.1−1.6, m, 10 H; 2.22, m, 2H; 2.70, m, 2 H	7.27−7.39, m, 30 H

[a] **3** and **4** in CD_2Cl_2, **2** and **5** in $CDCl_3$. – [b] $^2J_{HP}$ – [c] $^3J_{HH}$ in Hz.

Table 5. ^{13}C-NMR data of **3**, **4**, and **5**

^{13}C NMR[a]	CH_2P	CH_2OR	C_qCH_2OR	R	C aromat.	CO
3a, R = Me	32.9−32.4, m	87.5, q, 9.8[b]	42.8, q, 6.4[c]	60.8, s	139.9−129.6, m	[e]
3b, R = Et	31.6−31.1, m	84.1, q, 9.8[b]	41.6, q, 6.4[c]	67.4, s; 15.4, s	139.6−128.4, m	221.7−221.2, m
3c, R = Bzl	31.5−31.0, m	83.6, q, 9.5[b]	41.6, q, 6.4[c]	73.7, s	139.4−127.9, m	221.6−221.1, m
3d, R = 4-stilbenyl	31.5−31.0, m	83.5, q, 9.5[b]	41.6, q, 6.6[c]	73.4, s	139.4−126.8, m	221.6−221.0, m
3e, R = Br[CH_2]$_6$	31.5−31.0, m	84.3, q, 9.6[b]	41.6, q, 6.5[c]	71.7, 34.5, 33.3, 30.0, 28.4, 26.0, 6s	139.5−128.3, m	221.8−221.1, m
4, R = CH_3SO_2	32,2−31.7, m	80.8, q, 10.1[b]	42.4, q, 7.4[c]	39.5, s	139.8−129.8, m	[e]
5a, R = Me	37.8, d, 8.9[d]	78.36, s	42.4, m	57.3, s	139.7−128.0, m	–
5b, R = Et	37.5, m, 8.0[d]	85.4, s	42.5, m	14.4, s; 65.3, s	138.9−128.1, m	–
5c, R = CH_3[CH_2]$_9$	38.5, m, 9.0[d]	71.1, s	43.1, m	14.7, s; 23.2−32.4, m,	140.5−128.7, m	–
5e, R = H_2C=CH[CH_2]$_9$	38.5, d, 8.5[d]	71.0, s	43.2, m	26.5−34.3, m; 77.2, m; 114.6, s; 139.7, s	140.5−128.6, m	–
5f, R = Cl[CH_2]$_6$	35.3, m	66.1, s	40.1, m	21.0−28.3, m; 65.7, s	138.8−124.0, m	–
5g, R = Me[OC_2H_4]$_3$	37.7, d, 8.8[d]	71.7, s	42.6, m	58.8, s; 69.6−71.7, m	139.6−128.0, m	–
5i, R = NC[CH_2]$_6$	38.3, m			18.0−25.0, m	140.1−128.7, m	–
5j, R = HOOC[CH_2]$_6$	38.4, d, 9[d]	70.8, s	43.2, m	25.1−34.6, m, 179.8, s	140.6 − 128.7, m	–
5k, R = HOH_2C[CH_2]$_6$	38.3, m			18.0−25.0, m	140.1−128.7, m	

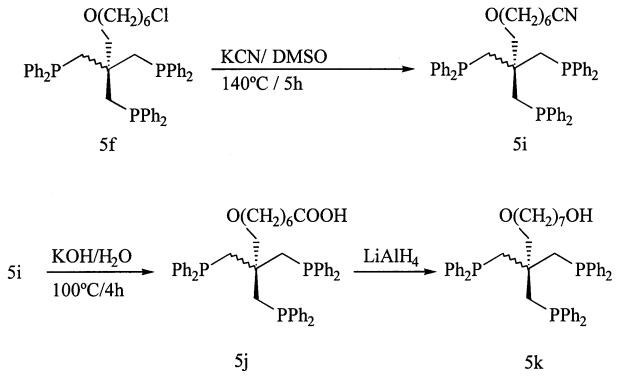
[a] **3** and **4** in CD_2Cl_2, **5** in $CDCl_3$. – [b] $^3J_{CP}$ – [c] $^2J_{CP}$ – [d] $^1J_{CP}$ in Hz. – [e] Due to worse solubility not observed.

The presence of different chain lengths in the product **5h** is evident from the mass spectra (Experimental Section) as well as from individual chromatographic bands for the major congeners of the mixture of oligomers acting as the auxiliary groups in **5h**. All compounds **5** show their ^{31}P resonances as a singlett at $\delta \approx -28$ (Experimental Section) as usual for the CH_2PPh_2 groups in tripod ligands.[8l] The ^{1}H-NMR spectra of **5a−5g** (Table 4) show the signals of all the chemically different groups of **5** in the correct integral ratio and with the expected J_{CP} couplings. The ^{13}C-NMR data (Table 5) are equally conclusive as to the constitution of the compounds.

It is observed that while iodide as a leaving group of the electrophile used to form the ether linkage works well in MeI and also in EtI as the electrophilic components, it is not apt for the introduction of components which contain longer chain alkyl constituents (**5e−5f**). In these cases, presumably by the elimination of HI, no products **5** are obtained. Using tosylate instead of iodide as the leaving group allows for the introduction of long-chain residues (**5c−5f**). These residues may well contain ω-olefinic functionalities (e.g. **5f**). The monomethylpolyoxyethylene function (**5g**, **5h**) may as well be introduced, with the corresponding tosylates which are themselves easily obtained from the commercial alcohols.[13] With the tris(oxyethylene) building block, which is commercially available as its analytically pure alcohol derivative **5g**, is formed correspondingly. The distribution characterizing the polymer mixture Me(OC_2H_4)$_n$OH

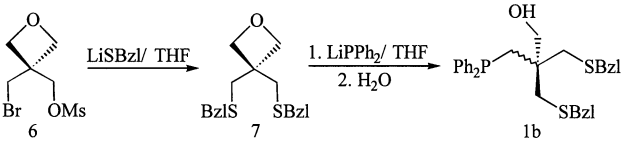
leads to a corresponding distribution of chain lengths in the product. The spread of compounds **5a**−**5h** shows that lipophilizing as well as hydrophilizing (**5g**, **h**) auxiliary groups may equally well be introduced by the above procedure. Examples **5e**, **5f** show that ω functionalization of alkyl chains is tolerated by the synthetic procedure, while further functionalization of the terminal double bond in **5e** has not yet been analyzed. Substitution of the chlorine function in **5f** has been investigated: **5f** in DMSO reacts with an excess of KCN to give the nitrile derivative **5i** which lends itself to a variety of further transformations (Scheme 6).

Scheme 6



In order to test whether the reaction conditions just described would also work when other donor groups besides phosphanes are present in hydroxy-functionalized ligands of type **1** the mixed-donor set ligand **1b** was synthesized.

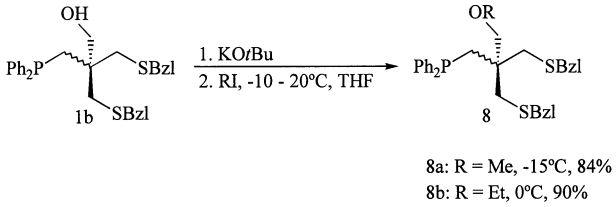
Scheme 7



The functionalized oxetane **6** was transformed into **7** by reaction with LiSBzl. In a consequent step the oxetane ring in **6** was nucleophilically opened by $LiPPh_2$ (Scheme 7). After workup, **1b** was obtained as a colorless oil of moderate viscosity. The sequence of reactions used to form **1b** from the functionalized oxetane **6** had already been successfully applied in several principally analogous cases.[8a][8b][8c][8d][8l] It corresponds to an entry into the chemistry of hydroxy-functionalized tripod ligands which is of rather broad scope. While **6** has already been described[8g] compounds **7** and **1b** have been unknown and have therefore been fully characterized by elemental analysis, mass spectrometry and ^{31}P-NMR data where appropriate (Experimental Section) as well as by ^{1}H- and ^{13}C-NMR data (Tables 1 and 2).

The hydroxy function in **1b** is indeed transformed into an ether functionality under the conditions which have been found to be productive in the transformation of **1a**−**5** (Scheme 8). Compounds **8** are colorless oils which are unequivocally characterized by their analytical and spectroscopic data (Experimental Section; Tables 1 and 2).

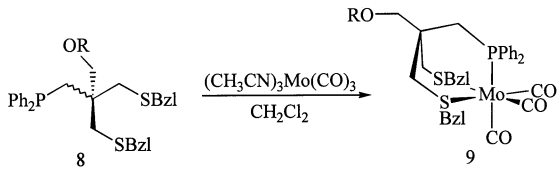
Scheme 8



8a: R = Me, -15°C, 84%
8b: R = Et, 0°C, 90%

Compounds **8** contain three different ligand functionalities in principle (PPh_2, SBzl, OR). If they undergo η^3 coordination, different possibilities with respect to the formation of isomers exist in principle. It is observed that with the "soft" template $Mo(CO)_3$ only the P- and S-donor functions coordinate.

Scheme 9



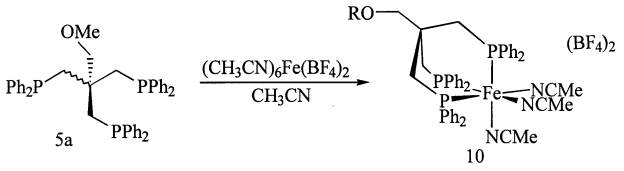
8a: R = Me
8b: R = Et

9a: R = Me
9b: R = Et

Upon reaction of **8** with $(CH_3CN)_3Mo(CO)_3$[14] the derivatives **9** are formed which contain the ligand in an η^3 coordination mediated by the two SBzl functions and the PPh_2 group (Scheme 9). Compounds **9** are microcrystalline yellow solids which are fully characterized with their analytic and spectroscopic data (Experimental Section; Tables 1 and 2). In compounds **9** as in compound **2b** two sets of carbonyl groups are expected. The ^{13}C-NMR resonances clearly distinguish between these two sets: the CO group *trans* to the phosphorus donor shows a large $^2J_{CP}$ coupling constant: (**2b**: 34.9 Hz; **9b**: 35.0 Hz) while the two carbonyl groups *cis* to the phosphorus atom are characterized by coupling constants of around 9 Hz (Table 2). The idealized symmetry of the $Mo(CO)_3$ entity is thus disturbed and as described for **2b** the ν(CO)-IR E bands of **9a** and **9b** are split into two distinct components (Experimental Section). The diastereotopicity of some of the CH_2 groups in **9** is only occasionally resolved in their ^{1}H-NMR (Table 1). The same statement applies for the diastereotopic differentation of some of the CH_2 groups in **8**, **1b**, and **2b** (Table 1). While with the selective coordination of P and S donors in **9** and the consequent exclusion of the OR donor from coordination, no problems arise with respect to the formation of a mixture of isomers it might well be that a template less soft than $Mo(CO)_3$ might change the situation. To test this hypothesis **5a** containing three phosphorus and one oxygen

donors was treated with $[Fe(CH_3CN)_6](BF_4)_2$[8l][8m][8n][8o] (Scheme 10).

Scheme 10



The propensity of the starting material to form tris(acetonitrile)iron cations had already been demonstrated.[8l][8m][8n][8o] With **5** as the ligand compound **10** is obtained as the only product. No signs of oxygen coordination are thus observed even when the less soft metal center Fe^{II} as compared to Mo^0 in **9** is coordinated. **10** is fully characterized by the usual analytical and spectroscopic techniques (Experimental Section).

Experimental Section

General: All manipulations were carried out under argon 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 (^1H), 50.323 MHz ($^{13}C\{^1H\}$), 81.015 MHz ($^{31}P\{^1H\}$)); chemical shifts (δ) in ppm with respect to $CDCl_3$ (^1H: δ = 7.27; ^{13}C: δ = 77.0), CD_2Cl_2 (^1H: δ = 5.32; ^{13}C: δ = 53.5) and $[D_8]$THF (^1H: δ = 3.58; ^{13}C: δ = 67.7) as internal standards, and chemical shifts (δ) in ppm with respect to 85% H_3PO_4 (^{31}P: δ = 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: With the equipment used, carbon values tend to be systematically too low in the presence of molybdenum or/and boron. Some of the analytical data given have to be interpreted with this in mind. − Melting points: Gallenkamp MFB-595 010; melting points are not corrected. − The oxetane **6** was prepared according to ref.[8g]. $[(CH_3CN)_3Mo(CO)_3]$ was obtained as described in ref.[14]. All other chemicals were commercially obtained and used without further purification.

Preparation of **1b**: A solution of lithium diphenylphosphide in THF (100 ml) was prepared by deprotonation of diphenylphosphane (8.2 g; 44 mmol) with *n*-butyllithium (17.6 ml; 44 mmol; 2.5 M in *n*-hexane) at 0°C. After stirring for 30 min, a solution of **7** (13.2 g; 40 mmol) in THF (100 ml) was added and the mixture refluxed for 2 h. The solvent was removed, water (100 ml) and diethyl ether (100 ml) were added, and the mixture was neutralized with 37% HCl. The aqueous phase was extracted with diethyl ether (2 × 100 ml) and the combined organic phases were dried and concentrated. The resulting residue was chromatographed on silica gel (20 cm, Ø = 10 cm). The fraction eluted with a mixture of petroleum ether (40/60)/diethyl ether (6:4; TLC control: R_f = 0.48) gave 15.5 g of **1b** as a colorless oil in 75% yield. − $C_{31}H_{33}OPS_2$ (516.7): calcd. C 72.07, H 6.44; found C 71.72, H 6.49. − MS(FAB); *m/z* (%): 517 (18) $[M^+ + 1]$, 425 (100) $[M^+ - C_7H_7]$. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −26.0 (s). − For ^1H- and ^{13}C-NMR data see Tables 1 and 2.

General Procedure for the Preparation of the Molybdenum Complexes **2** *and* **9**: The given tripod ligands (vide infra) were dissolved in CH_2Cl_2 (30 ml), solid $(CH_3CN)_3Mo(CO)_3$ was added (302 mg; 1 mmol) and the mixtures were stirred for 1 h at room temperature. During the reactions the $(CH_3CN)_3Mo(CO)_3$ slowly dissolved and the colors of the solutions turned from light-yellow into yellow-brown. The reaction mixtures were concentrated to 5 ml and slow stepwise addition of 50 ml of petroleum ether (40/60) gave yellow to yellow-brownish, microcrystalline solids. The crude products were washed with petroleum ether (40/60) (2 × 50 ml) and diethyl ether (2 × 50 ml) and dried in vacuo.

Follwing the above procedure using **1b** (517 mg; 1 mmol) as the tripod ligand yielded 490 mg (70%) of **2b**, m.p. 220°C (dec.). With **1a** (640 mg; 1 mmol) as the tripod ligand 740 mg (90%) of **2a** were obtained, m.p. 225°C (dec.). Starting the procedure described above with **8a** (530 mg; 1 mmol) led to 600 mg (84%) of **9a**, m.p. 210°C (dec.). Crystals suitable for an X-ray analysis were obtained for **9a** by slow diffusion of diethyl ether into a solution of 100 mg of the microcystalline product in 5 ml of a mixture of CH_2Cl_2/toluene (1:1) at room temperature after 2 d. 650 mg (90%) **9b**, m.p. 205°C (dec.) was obtained if the starting compound for the above procedure was **8b** (545 mg; 1 mmol).

2a: $C_{44}H_{39}MoO_4P_3$ (820.7): − MS (EI); *m/z* (%): 822 (4) $[M^+]$, 738 (60) $[M^+ - 3\ CO]$, 523 (100) $[M^+ - 3\ CO - C_7H_7]$. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1937 cm^{-1} (s), 1845 (s, br.). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 14.5 (s).

2b: $C_{34}H_{33}MoO_4PS_2$ (696.7): calcd. C 58.45, H 4.76, P 4.44, S 9.16; found C 57.39, H 4.99, P 4.29, S 8.87. − MS (FAB); *m/z* (%): 698 (36) $[M^+]$, 614 (44) $[M^+ - 3\ CO]$, 523 (100) $[M^+ - 3\ CO - C_7H_7]$. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1932 cm^{-1} (s), 1829 (s, br.); 1817 (vs, br.). − $^{31}P\{^1H\}$ NMR ($[D_8]$THF): δ = 20.2 (s).

9a: $C_{35}H_{35}MoO_4PS_2$ (710.7): calcd. C 59.15, H 4.96, P 4.36, S 9.03; found C 57.66, H 5.06, P 4.16, S 8.80. − MS (FAB); *m/z* (%): 712 (14) $[M^+]$, 537 (4) $[M^+ - 3\ CO - C_7H_7]$. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1932 cm^{-1} (s), 1829 (v, br.), 1815 (s, br.). − $^{31}P\{^1H\}$ NMR ($[D_8]$THF): δ = 17.2 (s). − X-ray analysis see ref.[16].

9b: $C_{36}H_{37}MoO_4PS_2$ (724.7): calcd. C 59.66, H 5.15, P 4.27, S 8.85; found C 58.94, H 4.99, P 4.21, S 8.86. − MS (FAB); *m/z* (%): 726 (18) $[M^+]$, 642 (5) $[M^+ - 3\ CO]$, 551 (20) $[M^+ - 3\ CO - C_7H_7]$. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1932 cm^{-1} (s), 1829 (s, br.), 1815 (s, br.). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 16.1 (s).

For ^1H- and ^{13}C-NMR data see Tables 1 and 2.

General Procedure for the Preparation of the Molybdenum Complexes **3** *by Alkylation of* **2a**: Compound **2a** (815 mg; 1 mmol) was dissolved in THF (50 ml) and deprotonated with KO*t*Bu (112 mg; 1 mmol). While stirring the mixture for 1 h a light-yellow precipitate of the potassium salt of **2a** formed. The alkylation reagent as specified below was added. The mixture was stirred for 2 h during which the precipitate formed in the deprotonation step slowly dissolved again. The completion of the reaction was determined by TLC control: CH_2Cl_2/petroleum ether (40/60), 3:1; **2a**: R_f = 0.35 (tailing); **3**: R_f = 0.67−0.74 (no tailing). After removal of the solvent, the resulting residue was chromatographed on silica gel (10 cm, Ø = 4 cm). The fractions eluted with a mixture of CH_2Cl_2/petroleum ether (40/60), 3:1 (TLC control: R_f = 0.67−0.74) gave pale-yellow microcrystalline solids.

Following the above procedure compounds **3** were obtained by using as alkylation reagent CH_3I (284 mg, 2 mmol) to prepare **3a**

(790 mg, 95%), triethyloxonium tetrafluoroborate (380 mg, 2 mmol) to prepare **3b** (510 mg, 60%), benzyl bromide (340 mg, 2 mmol) to prepare **3c** (820 mg, 91%), 4-chloromethylstilbene (460 mg, 2 mmol) to prepare **3d** (960 mg, 95%), and 6-bromo-*n*-hexyl *p*-toluenesulfonate (670 mg, 2 mmol) to prepare **3e** (360 mg, 37%). Crystals suitable for X-ray analyses were obtained for **3a** and for **3b** by slow diffusion of diethyl ether into a solution of 100 mg of the microcystalline products in 5 ml of CH_2Cl_2 at room temperature after 1 d.

3a: $C_{45}H_{41}MoO_4P_3$ (834.7): calcd. C 64.58, H 4.92, P 11.12; found C 63.90, H 5.24, P 10.89. − MS (EI); *m/z* (%): 836 (30) [M^+], 808 (36) [M^+ − CO], 780 (60) [M^+ − 2 CO], 752 (100) [M^+ − 3 CO]. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1932 cm^{-1} (s), 1835 (s, br.). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 16.0 (s). − X-ray analysis see ref.[16].

3b: $C_{46}H_{43}MoO_4P_3$ (848.7): calcd. C 64.93, H 5.10, P 10.93; found C 64.87, H 5.26, P 10.76. − MS (EI); *m/z* (%): 850 (20) [M^+], 821 (30) [M^+ − CH_2CH_3], 793 (58) [M^+ − CO − CH_2CH_3], 766 (100) [M^+ − 3 CO]. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1929 cm^{-1} (s), 1833 (s, br.). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 15.9 (s). − X-ray analysis see ref.[16].

3c, $C_{51}H_{45}MoO_4P_3$ (910.7): calcd. C 67.26, H 4.98, P 10.20; found C 66.78, H 5.18, P 10.06. − MS (FAB); *m/z* (%): 912 (46) [M^+], 884 (30) [M^+ − CO], 856 (34) [M^+ − 2 CO], 828 (35) [M^+ − 3 CO]. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1929 cm^{-1} (s), 1829 (s, br.). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 15.8 (s).

3d: $C_{59}H_{51}MoO_4P_3$ (1012.9): calcd. C 69.96, H 5.54; found C 69.40, H 5.54. − MS (FAB); *m/z* (%): 1014 (80) [M^+], 986 (36) [M^+ − CO], 958 (64) [M^+ − 2 CO], 930 (54) [M^+ − 3 CO]. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1937 cm^{-1} (s), 1844 (s, br.). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 15.7 (s).

3e: $C_{50}H_{50}BrMoO_4P_3$ (983.7): calcd. C 61.05, H 5.12; found C 62.18, H 5.51. − MS (FAB); *m/z* (%): 984 (80) [M^+], 956 (50) [M^+ − CO], 928 (68) [M^+ − 2 CO], 900 (100) [M^+ − 3 CO]. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1937 cm^{-1} (s), 1844 (s, br.).

For ^1H- and ^{13}C-NMR data see Tables 3 and 4.

Preparation of **4**: NEt_3 (600 mg, 6 mmol) and methanesulfonyl chloride (570 mg, 5 mmol) were added to a solution of **2a** (819 mg, 1 mmol) in CH_2Cl_2 (50 ml). After stirring the light-yellow mixture for 30 min, water was added (50 ml). After separation of the phases, the aqueous phase was extracted with CH_2Cl_2 (2 × 50 ml) and the residue of the dried ($MgSO_4$) and concentrated organic phases was chromatographed on silica gel (10 cm, Ø = 4 cm). Concentrating the fractions eluted with a mixture of CH_2Cl_2/petroleum ether (40/60) (3:1; TLC control: R_f = 0.50) gave **4** as a pale-yellow microcrystalline product (810 mg, 90%). − $C_{45}H_{41}BrMoO_6P_3S$ (898.7): calcd. C 60.14, H 4.60; found C 58.71, H 4.73. − MS (EI); *m/z* (%): 899 (20) [M^+ − 1], 872 (26) [M^+ − CO], 844 (60) [M^+ − 2 CO], 816 (100) [M^+ − 3 CO]. − IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1927 cm^{-1} (s), 1844 (s), 1826 (s). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 14.0 (s). − For ^1H- and ^{13}C-NMR data see Tables 3 and 4.

Preparation of **3b** *Starting from* **4**: To a solution of lithium ethoxide in THF (50 ml), prepared by deprotonation of ethanol (138 mg, 3 mmol) with 1.2 ml of *n*-butyllithium (2.5 M in *n*-hexane) at 0°C, **4** (450 mg, 0.5 mmol) was added. After stirring the yellow mixture for 4 h at 50°C, the solvent was removed and the residue chromatographed on silica gel (10 cm, Ø = 4 cm). Concentrating the fractions eluted with a mixture of CH_2Cl_2/petroleum ether (40/60) (3:1; TLC control: R_f = 0.73) gave **3b** as a pale-yellow microcrystalline product (148 mg, 35%). − Analytical data: vide supra.

Liberating **5b** *from* **3b**: Compound **3b** (829 mg, 1 mmol) was dissolved in CH_2Cl_2 (200 ml), pyridine *N*-oxide was added (1.90 g, 20 mmol) and the reaction mixture was irradiated in a "Duran 50" ("Pyrex") apparatus with a mercury lamp (TQ 150 Hanau) at −5°C for 1 h. After removal of the solvent the brownish residue was chromatographed on silica gel. The fractions eluted with a mixture of petroleum ether (40/60)/diethyl ether (9:1; TCL control: R_f = 0.40) gave 401 mg (60%) of **5b** as a colorless, viscous oil. − Analytical data: vide supra.

Preparation of **7**: Compound **6** (13.0 g; 50 mmol) was dissolved in THF (100 ml) and the solution cooled to 0°C. A solution of lithium benzylthiolate (100 mmol in 300 ml of THF), obtained by deprotonation of 12.4 g (100 mmol) of benzylthiole with 40 ml of *n*-butyllithium (2.5 M in *n*-hexane) at 0°C, was slowly added and the mixture stirred for 4 h at room temperature to give a voluminous white precipitate of lithium mesylate and lithium bromide. The solvent was removed in vacuo, water (200 ml) and diethyl ether (200 ml) were added and the mixture was neutralized with 37% HCl. The aqueous phase was extracted with diethyl ether (2 × 150 ml) and the combined organic phases were dried and concentrated. Destillation of the residue (b.p. 205−210°C/1 mbar) yielded 14.9 g (90%) of **7** as a viscous, colorless oil. − $C_{19}H_{22}OS_2$ (330.5): calcd. C 69.07, H 6.72, S 19.37; found C 68.81, H 6.50, S 18.68. − MS (FAB); *m/z* (%): 331 (72) [M^+ + 1], 239 (100) [M^+ − C_7H_7]. − For ^1H- and ^{13}C-NMR data see Tables 1 and 2.

Preparation of **8a** *and* **8b**: For the synthesis of **8a** a solution of **1b** (5.17 g; 10 mmol) in THF (100 ml) was deprotonated with KO*t*Bu (1.12 g; 10 mmol). The mixture was cooled to −15°C, then CH_3I (1,42 g; 10 mmol) was slowly added (temperature was held below −10°C) and a white precipitate of potassium iodide instantaneously formed. The progress of the reaction was determined by TLC [petroleum ether (40/60)/diethyl ether, 6:4; **1b**: R_f = 0.48; **8a**: R_f = 0.80].

To synthesize **8b** a slightly modified procedure was applied: A solution of **1b** (2.58 g, 5 mmol) in 50 ml of THF was deprotonated with KO*t*Bu (560 mg, 5 mmol). The mixture was cooled to 0°C, iodethane (780 mg, 5 mmol) was slowly added and a white precipitate of potassium iodide slowly formed. After 10 min, the progress of the reaction was determined by TLC control [petroleum ether (40/60)/diethyl ether, 6:4; **1b**: R_f = 0.48; **8b**: R_f = 0.81]. After the first "deprotonation-alkylation" sequence, the reaction was incomplete. For obtaining higher yields it was necessary to repeat this sequence five times. The isolation procedures for **8a** and **8b** were similar:

After completion of the reaction, water was added (1 ml) and the mixture was allowed to warm to 20°C. The solvent was removed, water (100 ml) and diethyl ether (100 ml) were added und the mixture was neutralized with 37% HCl. The aqueous phase was extracted with diethyl ether (2 × 100 ml) and the combined organic phases were dried and concentrated. The resulting residue was chromatographed on silica gel (15 cm, Ø = 6 cm).

8a: The fraction eluted with a mixture of petroleum ether (40/60)/diethyl ether (6:4; TLC control: R_f = 0.8) gave 3.45 g of **8a** as a colorless oil in 65% yield. − $C_{32}H_{35}OPS_2$ (530.7): calcd. C 72.42, H 6.65, P 5.84; found C 71.95, H 7.03, P 5.46. − MS (FAB); *m/z* (%): 531 (34) [M^+ + 1], 439 (100) [M^+ − C_7H_7]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −26.4 (s).

8b: The fraction eluted with a mixture of petroleum ether (40/60)/diethyl ether (9:1; TLC control: R_f = 0.4) gave 1.91 g of **8b** as a colorless oil in a 70% yield. − $C_{33}H_{37}OPS_2$ (544.8): calcd. C 72.75, H 6.85, P 5.59, S 11.77; found C 72.77, H 7.13, P 5.58, S 11.75. − MS (FAB); *m/z* (%): 545 (18) [M^+ + 1], 453 (100) [M^+ − C_7H_7]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −26.8 (s). −For ^1H- and ^{13}C-NMR data see Tables 1 and 2.

General Procedure for the Preparation of Ethers **5** *by Direct Alkylation of* **1a**: Compound **1b** (640 mg; 1 mmol) was dissolved in THF (20 ml) and cooled to −5°C by means of an ice/salt bath. 1.5 equivalents of KO*t*Bu were added to the colorless solution, which immediately turned yellow. The mixture was stirred for 5 min and the given alkyl iodides or toluenesulfonic esters (vide infra) were added. In case of the alkyl iodides the mixture immediately became turbid white, in case of the toluenesulfonic esters the mixture was slowly brought to room temperature and the mixture became turbid yellow-brown. The completion of the reaction was determined by TLC control. Water (0.5 ml) was added and the solvent was removed in vacuo. The residue was dissolved in dichloromethane and filtered through silica gel. The solvent was removed and the residue was chromatographed on silica gel (15−25 cm, ∅ = 4 cm).

Following the above procedure compounds **5** were obtained by using as alkylation reagents iodomethane (982 mg, 6.91 mmol) to prepare **5a** (470 mg, 72%), iodoethane (200 mg, 1.33 mmol) to prepare **5b** (461 mg, 69%), *n*-decyl *p*-toluenesulfonate (667 mg, 2.14 mmol) to prepare **5c** (253 mg, 33%), *n*-docosanyl *p*-toluenesulfonate (510 mg, 1.06 mmol) to prepare **5d** (425 mg, 44%), undecenyl *p*-toluenesulfonate (475 mg, 1.46 mmol) to prepare **5e** (300 mg, 38%), 6-chloro-*n*-hexyl *p*-toluenesulfonate (347 mg, 1.2 mmol) to prepare **5f** (394 mg, 52%), triethyleneglycol monomethyl ether *p*-toluenesulfonic ester (400 mg, 1.25 mmol) to prepare **5g** (415 mg, 53%).

5a: $C_{42}H_{41}OP_3$ (654.1): calcd. C 77.04, H 6.32; found C 76.79, H 6.37. − MS (EI); *m/z* (%): 654 (11) [M^+], 577 (100) [M^+ − Ph], 469 (16) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −28.4 (s).

5b: $C_{43}H_{43}OP_3$ (668.7): calcd. C 77.22, H 6.49; found C 75.51, H 6.63. − MS (EI); *m/z* (%): 668 (10) [M^+], 591 (100) [M^+ − PPh_2], 485 (38) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −28.3 (s).

5c: $C_{51}H_{59}OP_3$ (780.5): calcd. C 78.48, H 7.56; found C 78.10, H 7.83. − MS (EI); *m/z* (%): 780 (9) [M^+], 703 (100) [M^+ − PPh_2], 595 (11) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −28.6 (s).

5d: $C_{63}H_{83}OP_3$ (949.3): calcd. C 79.71, H 8.81; found C 79.34, H 10.01. − MS (EI); *m/z* (%): 949 (17) [M^+], 872 (100) [M^+ − PPh_2], 764 (20) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −25.3 (s).

5e: $C_{52}H_{59}OP_3$ (792.5): calcd. C 78.75, H 7.50; found C 78.88, H 7.75. − MS (EI); *m/z* (%): 792 (20) [M^+], 715 (100) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −28.2 (s).

5f: $C_{47}H_{50}ClOP_3$ (759.3): calcd. C 74.35, H 6.58; found C 73.77, H 7.10. − MS (EI); *m/z* (%): 758 (10) [M^+], 681 (100) [M^+ − PPh_2], 573 (10) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −25.1 (s).

5g: $C_{48}H_{53}OP_3$ (786.9): calcd. C 73.27, H 6.79; found C 73.10, H 6.83. − MS(EI); *m/z* (%): 786 (9) [M^+], 709 (100) [M^+ − PPh_2], 601 (11) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −28.6 (s).

For ^{1}H- and ^{13}C-NMR data see Tables 3 and 4.

Preparation of **5i**: A solution of **5f** (759 mg, 1 mmol) in DMSO (3 ml) was slowly added to a stirred mixture of 1 g of KCN in 5 ml of DMSO at 90°C. After the addition, the mixture was heated to 140°C for 5 h. The solvent was removed and the residue was chromatographed on silica gel. The fractions eluted by a mixture of petroleum ether (40/60)/diethyl ether (3:1) at R_f = 0.30 were collected to give 300 mg (40%) of **5i** as a colorless oil after evaporation of the solvent. − $C_{48}H_{50}NOP_3$ (749.8): calcd. C 76.89, H 6.72, N 1.87; found C 76.40, H 6.75, N 1.61. − MS (FAB); *m/z* (%): 750 (33) [M^+], 672 (100) [M^+ − PPh_2], 564 (16) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −28.3 (s). − For ^{1}H- and ^{13}C-NMR data see Tables 3 and 4.

Preparation of **5j**: A solution of **5i** (430 mg , 0.6 mmol) in a 1:1 mixture of ethanol/water (25 ml) and KOH (580 mg, 10.4 mmol) was heated under reflux for 4 h. After cooling, the reaction mixture was acidified with 37% hydrochloric acid. The water phase was extracted with dichloromethane (3 ×), the organic phase was dried with $MgSO_4$, the solvent was removed in vacuo and the residue was chromatographed on silica gel. The fractions eluted with diethyl ether at R_f = 0.40 were collected to give 220 mg (48%) of **5j** as a colorless oil after evaporation of the solvent. − $C_{48}H_{51}O_3P_3$ (768.8): calcd. C 74.99, H 6.69; found C 74.42, H 6.82. − MS (FAB); *m/z* (%): 768 (35) [M^+], 691 (100) [M^+ − PPh_2], 582 (21) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −28.2 (s). − IR (Nujol): $\tilde{\nu}$(COO) = 1708 cm^{-1} (m). − For ^{1}H- and ^{13}C-NMR data see Tables 3 and 4.

Preparation of **5k**: A solution of **5j** (50 mg, 0.07 mmol) in THF (5 ml) was added to a stirred suspension of $LiAlH_4$ (30 mg, 0.8 mmol) in THF (5 ml). The mixture was heated under reflux for 2 h and after cooling to 20°C hydrolized with water. The products of hydrolysis were washed with dichloromethane, the combined organic phases were dried ($MgSO_4$) and the solvents were removed in vacuo. The residue, a colorless oil, was investigated by mass spectrometry and NMR spectroscopy. − $C_{48}H_{53}O_2P_3$ (755). − MS (FAB); *m/z* (%): 755 (27) [M^+], 678 (100) [M^+ − PPh_2], 571 (18) [M^+ − PPh_2]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −28.1 (s). − For ^{1}H-and ^{13}C-NMR data see Tables 3 and 4.

Preparation of **10**: Compound **5a** (654 mg, 1 mmol) was dissolved in acetonitrile (20 ml) and 476 mg (1 mmol) of $[Fe(CH_3CN)_6](BF_4)_2$, dissolved in 10 ml of acetonitrile, was added. The mixture immediately turned red and was stirred at room temperature for 1 h. The solvent was removed and the residue was washed with diethyl ether (3 ×). After drying in vacuo, 930 mg (92%) of **10** was obtained as a red powder. Crystals suitable for X-ray analysis were obtained by diffusion of diethyl ether into a solution of **10** in CH_2Cl_2 within 1 d at room temperature. − $C_{48}H_{50}B_2F_8FeN_3OP_3$ (1007.4): calcd. C 57.23, H 5.00, N 4.17; found C 54.04, H 6.83, N 4.18. − MS (FAB); *m/z* (%): 729 (100) [M^+ − 3 MeCN − B_2F_7], 655 (73) [free ligand], 576 (52) [free ligand-Ph]. − ^{1}H NMR ($CDCl_3$): δ = 2.03 (br. s, 2 H, OCH_2), 2.41 (br. s, 9 H, CH_3CN), 2.58 (br. s, 6 H, CH_2P), 3.61 (br. s, 3 H, CH_3O), 7.25-7.37 (br. m, 30 H, *H* arom.). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 4.9 (s, CH_3CN); 129.3, 130.8, 132.4, 142 (m, *C* arom.). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = +31.7 (s). − IR (KBr): $\tilde{\nu}$(CN) = 2343 cm^{-1} (w), 2287 (m).

☆ Dedicated to Prof. Dr. *Achim Müller*, Universität Bielefeld, on the occasion of his 60th birthday.

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[16] Compounds **3a**, **3b**, **9a**, **10** were characterized by single-crystal X-ray analyses. The constitution as given above was corroborated in each case. Distances and angles are in the range characteristic of $(tripod)Mo(CO)_3$ [8l][8k][8l] or $[(tripod)Fe(MeCN)_3]^{2+}$ [8l][8m][8n][8o][8p] compounds throughout. 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-407890 for **3a**, -407891 for **3b**, -407892 for **9a**, -407889 for **10**.

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