Metal Complexes in Inorganic Matrixes. 18.[1] Phosphanyl-Substituted Titanium and Zirconium Alkoxides for Tethering Metal Complexes on Titania or Zirconia and the X-ray Structure Analysis of Polymeric $Zr(OPr)(O_3SMe)_3$

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The compounds $[Ph_2PCH_2CH_2COO]EO_x(OR)_{3-2x}$ (E = Ti, Zr) were obtained by two routes: by $HPPh_2$ addition to the double bond of $[CH_2{=}CHCOO]EO_{x'}(OR)_{3-2x'}$ and by reaction of $E(OR)_4$ with $Ph_2PCH_2CH_2COOH$. The second route results in less byproducts. The sulfonate derivatives $[Ph_2PCH_2CH_2SO_3]EO_x(OR)_{3-2x}$ and the hydroxamate derivatives $[Ph_2PCH_2CH_2ClO)N(H)O]EO_x(OR)_{3-2x}$ were prepared by the second route, i.e., reaction of $Na[O_3SCH_2CH_2PPh_2]$ or $K[ON(H)C(O)CH_2CH_2PPh_2]$ with $E(OR)_4$. Reaction of $(CO)_5W(OEt_2)$ with the compounds $Ph_2P{-}X{-}E(OR)_3$ gave the phosphine complexes $W(CO)_5[PPh_2{-}X{-}E(OR)_3]$ in each case. The bond between the titanium or zirconium atom and the PPh_2-substituted bidentate ligand is hydrolytically stable. The X-ray structure analysis of $Zr(OPr)(O_3SMe)_3$ showed the compound to have a chain structure with two bridging and one chelating sulfonate group per zirconium atom.

Introduction

For heterogenizing metal complex catalysts on silica or extracting metal ions from solutions, the silica surface is derivatized, mostly by reacting alkoxysilanes of the type $(RO)_3Si{-}X{-}A$ with the surface OH groups.[2,3] The group A is an organic function capable of coordinating to metal ions or metal complex fragments, and X a chemically inert spacer, for instance a $(CH_2)_n$ chain. Many silicon compounds of this type are commercially available or can be easily prepared. For the heterogenization of homogeneous catalysts, these functionalized silicas are later reacted with the metal complex, and the group A becomes part of its coordination sphere. Alternatively, the complexes $[(RO)_3Si{-}X{-}A]_nML_m$ are formed first and then reacted with the support. Many catalytically active metal complexes were heterogenized by one of these methods.[4]

The sol−gel method offers an alternative approach for the heterogenization of homogeneous catalysts using the metal complexes $[(RO)_3Si{-}X{-}A]_nML_m$ as precursors. The alkoxysilyl groups of the metal complex are incorporated into the gel network upon sol−gel processing. Contrary to the other method, the metal complex moieties are not only located at the surface of the support, but the oxide matrix is built around them. Since the porosity of the support can be tailored, the metal centers are still accessible. The advantages of this approach have been discussed elsewhere.[5]

The extension of this approach to other oxide supports without diluting the oxide by other oxide-forming elements was inhibited by the lack of suitable compounds of the type $(RO)_nE{-}X{-}A$ with E ≠ Si. The E−X bond cannot be an element−carbon bond, because such bonds are easily cleaved by water. Therefore, the functional group A has to be connected to the alkoxide moiety by another link.

We have recently reported that the modification of titanium and zirconium alkoxides with lysine results in the derivatives $(RO)_3E$(lysinate).[6] (For simplicity, only monomeric formulas are written in this article. However, in most cases dimerization or oligomerization is highly probable. For example, $(EtO)_3Ti$(glycinate) is dimeric.[6b]) They can be employed for the preparation of titanate or zirconate materials, which can bind metal ions as the alkoxysilane derivatives $(RO)_3SiCH_2CH_2CH_2NR_2$ for the preparation of functionalized silicate materials.

Since many catalytically active metal complexes contain phosphine ligands, phosphanyl-substituted metal alkoxides of the type $(RO)_nE{-}X{-}PR_2$ are needed to bind these metal complexes to TiO_2 or ZrO_2 either by tethering them to the surface of the preformed oxides or by sol−gel processing.

We previously reported preliminary results on the preparation of $(PrO)_3E(OOC{-}CH_2CH_2PPh_2)$ by reaction of $(PrO)_3E(OOC{-}CH{=}CH_2)$ with $HPPh_2$ (E = Ti, Zr) and of $(PrO)_3Zr(OOC{-}CH_2PPh_2)$ by treatment of $(PrO)_3Zr(OOC{-}CH_2Cl)$ with $LiPPh_2$. The PR_2 group is con-

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(1) (a) Part 17: Lorenz, A.; Schubert, U. *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 333. (b) Part 16: Görsmann, C.; Schubert, U.; Leyrer, J.; Lox, E. *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 625.

(2) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem.* **1986**, *98*, 237; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 236.

(3) Schubert, U.; Hüsing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010.

(4) Hartley, F. R. *Supported Metal Complexes*; D. Reidel: Dordrecht, 1985. Yermakov, Yu. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, 1981.

(5) Schubert, U. *New J. Chem.* **1994**, *18*, 1049.

(6) (a) Schubert, U.; Tewinkel, S.; Lamber, R. *Chem. Mater.* **1996**, *8*, 2047. (b) Schubert, U.; Tewinkel, S.; Müller, F. *Inorg. Chem.* **1995**, *34*, 995.

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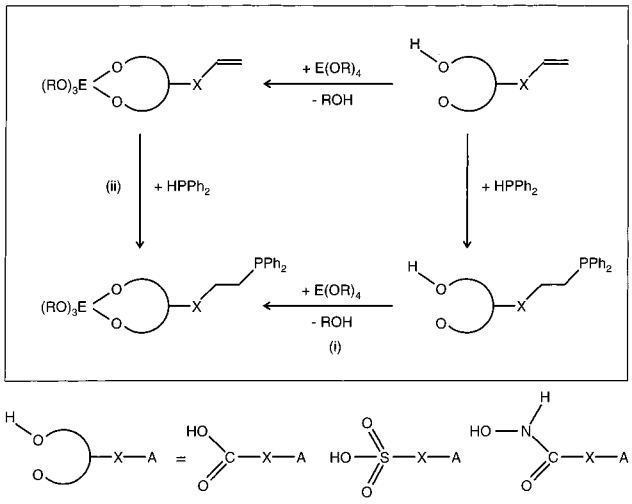
Scheme 1. General Approaches for the Preparation of $(RO)_3E-X-PPh_2$ (E = Ti, Zr)



nected with the metal alkoxide moiety via a carboxylate group in both derivatives.[7] The sulfonate derivatives $(RO)_3E[O_3SCH_2CMe_2NHC(O)CH_2CH_2PPh_2]$ were prepared either by reaction of $HO_3SCH_2CMe_2NHC(O)CH_2CH_2PPh_2$ with the tetraalkoxides or by reaction of $(RO)_3E[O_3SCH_2CMe_2NHC(O)CH{=}CH_2]$ with $HPPh_2$.[1a] In this paper we present the extension and a comprehensive summary of this work, which also includes the use of hydroxamic acid derivatives, and studies on the reactivity of the phosphanyl-substituted precursors with water and on the coordination of metal complexes to their dangling PR_2 groups.

Results and Discussion

A general outline of our approach to prepare precursors of the type $(RO)_nE-X-PPh_2$ (E = Ti, Zr) is given in Scheme 1. It involves two chemical steps: connecting $(RO)_nE$ with the carboxylate, sulfonate or hydroxamate ligand and introducing the PPh_2 group. The order of the two steps can be inverted. In route i, a PPh_2-containing acid is reacted with $E(OR)_4$ (i.e. the PPh_2 group is first introduced), while in route ii $HPPh_2$ is added to an unsaturated group already bonded to the $E(OR)_3$ moiety.

Preparation of the Carboxylate Derivatives $(RO)_3E[OOC-CH_2CH_2-PPh_2]$ (2). Carboxylic acids are often used in the sol–gel chemistry of titanium and zirconium alkoxides to moderate their reactivity. The use of functional carboxylates also offers the possibility to functionalize the oxides.[8] Unsaturated carboxylic acids, such as acrylic acid or methacrylic acid, were already used for the preparation of inorganic–organic copolymers.

In analogy to our previous results,[7] $Ti(OR)_4$ (R = Et, Pr, ^{i}Pr, Bu, ^{t}Bu) and $Zr(OnPr)_4$ were first reacted with 1 equiv of acrylic acid in refluxing toluene (eq 1). Yellow oils (a yellow waxy solid for the $Ti(OiPr)_4$ derivative) were obtained after 90 min. The IR and NMR spectra showed that no unreacted acrylic acid was left: the acrylic protons were shifted to lower field by the coordination, and the ν_{COOH} band at 1705 cm^{-1} had completely disappeared.

(7) Buhler, H.; Schubert, U. *Chem. Ber.* **1993**, *126*, 405.
(8) Schubert, U. *J. Chem. Soc., Dalton Trans.* **1996**, 3343.

$$E(OR)_4 + HOOC-CH{=}CH_2 \rightarrow ROH + (RO)_3E[OOC-CH{=}CH_2] \quad (1)$$

	E	R
1-5a	Ti	Et
1-5b	Ti	Pr
1-5c	Ti	^{i}Pr
1-5d	Ti	Bu
1-5e	Ti	^{t}Bu
1-5f	Zr	Pr

Integration of the vinylic protons against the protons of the OR groups in the ^1H NMR spectra indicated partial hydrolysis of the OR groups. There are several reasons for that: (i) The main reason is that water is produced in situ by the esterification of the acrylic acid with the cleaved alcohol. We have previously identified and structurally characterized some crystalline primary hydrolysis products in the $E(OR)_4$/(meth)acrylic acid system.[9] (ii) Conventionally dried glassware was used, but there are still Si–OH groups left at the surface, which can lead to hydrolysis reactions. (iii) Nonhydrolytic condensation reactions may also be involved.

The following compositions were obtained by integration of the NMR signals:

1a: $[CH_2{=}CHCOO]TiO_{0.45}(OEt)_{2.1}$

1b: $[CH_2{=}CHCOO]TiO_{0.5}(O^nPr)_{2.0}$

1c: $[CH_2{=}CHCOO]TiO_{0.15}(O^iPr)_{2.7}$

1d: $[CH_2{=}CHCOO]TiO_{0.1}(OBu)_{2.8}$

1e: $[CH_2{=}CHCOO]TiO_{0.05}(O^tBu)_{2.9}$

1f: $[CH_2{=}CHCOO]ZrO_{0.35}(OPr)_{2.3}$

Partial hydrolysis of the alkoxy groups is a general phenomenon throughout this work. For simplicity, we use the formulas of the unhydrolyzed alkoxides in the equations. Since the purpose of our work was not the isolation of stoichiometric compounds but instead the elaboration of reproducible procedures for the preparation of new materials, no efforts were made to avoid partial hydrolysis.

Another inherent problem for the identification of the new compounds was that elemental analysis was difficult to perform due to the moisture sensitivity of the compounds. Furthermore, too low carbon values were consistently obtained, mainly for the titanium compounds, due to the formation of carbides. Since the carbon values are thus rendered meaningless, we will not quote them and will mainly base the analytical characterization on the values of P, S, and N (if present).

For the second step of the synthesis of the PPh_2-substituted alkoxides, the derivatives **1a–f** were freshly prepared and dissolved in benzene. After addition of 1.1 molar equivalents of $HPPh_2$, and AIBN as a radical starter, the solutions were heated to 70 °C for several hours. The alkoxides **2a–f** were obtained as beige

(9) Schubert, U.; Arpac, E.; Glaubitt, W.; Helmerich, A.; Chau, C. *Chem. Mater.* **1992**, *4*, 291. Kickelbick, G.; Schubert, U. *Chem. Ber.* **1997**, *130*, 473. Kickelbick, G.; Wiede, P.; Schubert, U. *Inorg. Chem.*, submitted. Kickelbick, G.; Schubert, U. *Chem. Ber.*, submitted.

powders in 40−55% yield (eq 2), sparingly soluble in benzene, acetone, $HCCl_3$, or DMSO.

$$(RO)_3E[OOC-CH{=}CH_2] + HPPh_2 \rightarrow \underset{\mathbf{1a-f}}{} (RO)_3E[OOC-CH_2CH_2-PPh_2] \underset{\mathbf{2a-f}}{} \quad (2)$$

The composition of **2a**−**f** by integration of the NMR signals is as follows. All compounds contain adsorbed alcohol.

2a: $[Ph_2PCH_2CH_2COO]TiO_{1.05}(OEt)_{0.9}\cdot 0.2EtOH$

2b: $[Ph_2PCH_2CH_2COO]TiO_{0.65}(OPr)_{1.7}\cdot 0.5PrOH$

2c: $[Ph_2PCH_2CH_2COO]TiO_{1.0}(O^iPr)_{1.0}\cdot 0.3^iPrOH$

2d: $[Ph_2PCH_2CH_2COO]TiO_{0.85}(OBu)_{1.3}\cdot 0.3BuOH$

2e: $[Ph_2PCH_2CH_2COO]TiO_{1.2}(O^tBu)_{0.6}\cdot 0.1^tBuOH$

2f: $[Ph_2PCH_2CH_2COO]ZrO_{0.95}(OPr)_{1.1}\cdot 0.4PrOH$

The derivatives **2a**−**f** show a signal around −15 ppm in the ^{31}P NMR spectra, typical of tertiary phosphines. There are also signals around +31 ppm indicating the formation of phosphine oxides, which could not be separated during workup. There were no signals for unreacted $HPPh_2$ or vinyl groups in the NMR spectra in any case.

Photochemical reaction of $HPPh_2$ with **1a**−**f** did not improve the yields or suppress the condensation reaction. In the contrary, even more side reactions were observed, probably due to partial polymerization of the acrylate groups.

We therefore probed the inverse order of bond formation, i.e., preparation of $HOOC-CH_2CH_2PPh_2$ and its subsequent reaction with $E(OR)_4$. 3-Diphenylphosphinopropionic acid was obtained according to Issleib[10] by reaction of ethyl-3-chloropropionate with sodium diphenyl phosphide in THF.

Reaction of $HOOC-CH_2CH_2PPh_2$ with $E(OR)_4$ previously led to unsoluble products difficult to identify and was therefore not followed up.[7] This was probably due to the use of ethanol as the solvent, which results in esterification of the carboxylic acid, and thus the production of water and hydrolysis of the alkoxy groups. Therefore, $HOOC-CH_2CH_2PPh_2$ and an equimolar amount of $E(OR)_4$ were reacted at ambient temperature in benzene or toluene instead. The compounds **2′a**−**f** were obtained as viscous yellow oils in 70−98% yield. They were soluble in petroleum ether except compound **2′e**, which became solid on washing with this solvent.

$$HOOC-CH_2CH_2PPh_2 + E(OR)_4 \rightarrow \underset{\mathbf{2'a-f}}{(RO)_3E[OOC-CH_2CH_2PPh_2]} + ROH \quad (3)$$

(the notation **2′** is used to distinguish the products from those obtained in eq 2)

No ν_{COOH} band of $HOOC-CH_2CH_2PPh_2$ at 1710 cm^{-1} was left in the IR spectra after the reaction. Instead a weak band at 1560−1580 cm^{-1} appeared, assigned to ν_{COO} of $OOC-CH_2CH_2PPh_2$. The ^{31}P NMR spectra were less indicative, because both the compounds **2′a**−**f** and the uncoordinated acid have a signal around −14.8 ppm. Contrary to the other method of preparation (eq 2), there was no signal for phosphine oxides. The signals of the CH_2 groups in the ^1H NMR spectra are shifted by 0.1−0.3 to lower field ppm relative to $HOOC-CH_2CH_2PPh_2$.

The composition of **2′a**−**f** by integration of the NMR signals was as follows. They all contain adsorbed alcohol.

2′a: $[Ph_2PCH_2CH_2COO]TiO_{0.45}(OEt)_{2.1}\cdot 0.1EtOH$

2′b: $[Ph_2PCH_2CH_2COO]TiO_{0.1}(OPr)_{2.8}\cdot 0.1PrOH$

2′c: $[Ph_2PCH_2CH_2COO]TiO_{0.3}(O^iPr)_{2.4}\cdot 0.2^iPrOH$

2′d: $[Ph_2PCH_2CH_2COO]TiO_{0.35}(OBu)_{2.3}\cdot 0.2BuOH$

2′e: $[Ph_2PCH_2CH_2COO]TiO_{0.2}(O^tBu)_{2.6}\cdot 0.1^tBuOH$

2′f: $[Ph_2PCH_2CH_2COO]ZrO_{0.6}(OPr)_{1.8}\cdot 0.1PrOH$

Preparation of the compounds **2** by the second method (eq 3) has several advantages compared to the addition of $HPPh_2$ to **1** (eqs 1 and 2): (i) there was less cleavage of the alkoxide groups, i.e., less condensed products were obtained; (ii) no phosphine oxide byproducts were formed; (iii) the reaction conditions were milder.

Sulfonate Derivatives $(RO)_3E[O_3S-CH_2CMe_2-NHC(O)CH_2CH_2CH_2PPh_2]$ (3). We have previously shown that PPh_2-substituted sulfonate derivatives of the alkoxides can be prepared by the same routes (Scheme 1) as the phosphinopropionate derivatives **2**, starting from the commercially available 2-acrylamido-2-methyl-1-propanesulfonic acid.[1a] Reaction of preformed $Li[O_3S-CH_2CMe_2NHC(O)CH_2CH_2PPh_2]$ with $E(OR)_4$ (eq 4) also gave better results compared to the $HPPh_2$ addition to the double bond of $(RO)_3E[O_3S-CH_2CMe_2NHC(O)-CH{=}CH_2]$, although extensive cleavage of the alkoxide groups was observed.

$$Li[O_3SR] + E(OR)_4 \rightarrow \underset{\mathbf{3a-f}}{(RO)_3E[O_3SR]} + \ldots \quad (4)$$

$$(R = Ph_2PCH_2CH_2C(O)NHCMe_2CH_2)$$

The composition of **3a**−**f** (by integration of the NMR signals) was

3a: $[RSO_3]TiO_{1.45}(OEt)_{0.1}\cdot 1.6EtOH$

3b: $[RSO_3]TiO_{1.15}(OPr)_{0.9}\cdot 1.5PrOH$

3c: $[RSO_3]TiO_{1.45}(O^iPr)_{0.1}\cdot 0.8^iPrOH$

3d: $[RSO_3]TiO_{1.2}(OBu)_{0.6}\cdot 1.6BuOH$

3e: $[RSO_3]TiO_{1.4}(O^tBu)_{0.2}\cdot 0.4^tBuOH$

3f: $[RSO_3]ZrO_{1.15}(OPr)_{0.7}\cdot 1.3PrOH$

These compounds are included here for comparison and to discuss their reactions with water and their ability to coordinate metals (vide infra).

(10) Issleib, K.; Thomas, G. *Chem. Ber.* **1960**, *93*, 803.

Table 1. Crystallographic Data for $[Zr(OPr)(O_3SMe)_3]_\infty$

formula	$C_6H_{16}O_{10}S_3Zr$
formula weight	435.6
crystal system	triclinic
space group	*P*-1
a (pm)	847.1(2)
b (pm)	861.8(2)
c (pm)	1118.9(4)
α (deg)	84.00(2)
β (deg)	83.30(2)
τ (deg)	69.35(2)
V (pm^3)	757.3×10^6
Z	2
D (calc) (g cm^{-3})	1.91
μ (Mo Kα) (mm^{-1})	1.180
temp (K)	203
crystal size (mm)	$0.18 \times 0.18 \times 0.16$
diffractometer	Siemens SMART
radiation	Mo Kα (71.073 pm)
monochromator	graphite
2*θ*-range (deg)	1.84−30.50
reflections collected	6527
independent reflections	4523
GOF	1.13
R [$I > 2\sigma(I)$]	0.033
R_w	0.082
largest diff., e·$Å^{-3}$	0.884

The ability of sulfonate groups to link PPh_2-containing organic groups and $E(OR)_3$ fragments was also probed with $Ph_2PCH_2CH_2-SO_3H$. $Na[O_3S-CH_2CH_2PPh_2]$ was prepared from $Na[O_3S-CH_2CH_2Br]$ and $NaPPh_2$ as the corresponding carboxylic acid.[10] The IR spectrum of the product showed characteristic ν_{SO} bands at 1420 and 1050 cm^{-1}, and the ^{31}P NMR spectrum a signal at −16.6 ppm.

A suspension of $Na[O_3S-CH_2CH_2PPh_2]$ in THF was reacted with an equimolar amount of $Ti(OR)_4$ (R = Et, Pr, ^{i}Pr) or $Zr(OPr)_4$ at 60 °C for 6 h (eq 5).

$$Na[O_3S-CH_2CH_2PPh_2] + E(OR)_4 \rightarrow (RO)_3E[O_3S-CH_2CH_2PPh_2] + ROH \quad (5)$$

4a−c,f

Yellow solids were isolated in 52−90% yield. The ν_{SO} bands of the product were not shifted relative to the starting sodium salt, and the ^1H NMR signals of the CH_2 groups were only slightly shifted to higher field. The ^{31}P NMR spectra showed new signals for the products around −16.6 ppm. The most prominent feature of the ^1H NMR spectra was the low or missing intensity of the OR groups; i.e., the samples **4b,c** were completely hydrolyzed, while **4a,f** contained only a minor amount of alkoxy groups. Integration of the NMR signals gave the following compositions:

4a: $[Ph_2PCH_2CH_2CH_2SO_3]TiO_{1.45}(OEt)_{0.1}\cdot 0.7EtOH$

4b: $[Ph_2PCH_2CH_2CH_2CH_2SO_3]TiO_{1.5}\cdot 0.5PrOH$

4c: $[Ph_2PCH_2CH_2SO_3]TiO_{1.5}\cdot 0.5{}^iPrOH$

4f: $[Ph_2PCH_2CH_2SO_3]ZrO_{1.4}(OPr)_{0.2}\cdot 0.4PrOH$

While the use of carboxylate ligands for the modification of metal alkoxides is well established and an understanding of the structural chemistry of such derivatives and their primary hydrolysis products is developing, the use of sulfonate ligands is new. We therefore crystallized a sulfonate-substituted alkoxide with a simpler sulfonate ligand as a model compound, to get information on the bonding of these ligands to metal alkoxide moieties.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10$) for $[Zr(OPr)(O_3SMe)_3]_\infty$

	x	*y*	*z*	*U*(eq)
Zr(1)	7515(1)	237(1)	3499(1)	11(1)
O(10)	7667(3)	2285(3)	2098(2)	23(1)
O(11)	5713(3)	988(2)	2035(2)	19(1)
O(12)	6632(3)	2275(3)	129(2)	31(1)
S(13)	6244(1)	2363(1)	1403(1)	18(1)
C(14)	4589(4)	4236(4)	1697(3)	29(1)
O(20)	5470(2)	2239(2)	4400(2)	19(1)
O(21)	5559(3)	3149(3)	6359(2)	27(1)
O(22)	4148(2)	1208(2)	6172(2)	18(1)
S(23)	4591(1)	2646(1)	5614(1)	14(1)
C(24)	2709(4)	4293(3)	5374(3)	25(1)
O(30)	9326(2)	1214(2)	4032(2)	17(1)
O(31)	12044(2)	877(2)	4679(2)	17(1)
O(32)	10693(3)	3231(3)	3333(2)	28(1)
S(33)	10936(1)	1521(1)	3676(1)	15(1)
C(34)	11971(4)	319(4)	2466(3)	26(1)
O(40)	9158(2)	−1478(2)	2670(2)	19(1)
C(41)	10203(4)	−2779(4)	1937(3)	32(1)
C(42)	9444(6)	−2660(6)	756(4)	50(1)
C(43)	7830(7)	−3046(8)	892(6)	68(2)

Table 3. Bond Lengths (pm) and Angles (deg) for $[Zr(OPr)(O_3SMe)_3]_\infty$

Zr(1)−O(40)	187.5(2)	S(13)−C(14)	175.6(3)
Zr(1)−O(30)	215.7(2)	O(20)−S(23)	148.4(2)
Zr(1)−O(22)	216.6(2)	O(21)−S(23)	142.9(2)
Zr(1)−O(31)*	217.5(2)	O(22)−S(23)	147.6(2)
Zr(1)−O(20)	220.1(2)	S(23)−C(24)	174.7(3)
Zr(1)−O(11)	225.7(2)	O(30)−S(33)	148.1(2)
Zr(1)−O(10)	226.4(2)	O(31)−S(33)	148.2(2)
O(10)−S(13)	148.8(2)	O(32)−S(33)	143.0(2)
O(11)−S(13)	149.4(2)	S(33)−C(34)	174.7(3)
O(12)−S(13)	142.8(2)	O(40)−C(41)	142.7(4)

O(40)−Zr(1)−O(30)	94.15(8)	O(31)*−Zr(1)−O(20)	84.41(8)
O(31)*−Zr(1)−O(11)	145.79(7)	O(40)−Zr(1)−O(22)	90.88(8)
O(31)*−Zr(1)−O(10)	147.57(8)	O(40)−Zr(1)−O(31)*	97.77(9)
O(22)−Zr(1)−O(31)*	76.38(8)	O(40)−Zr(1)−O(20)	176.41(9)
O(22)−Zr(1)−O(20)	86.86(8)	O(40)−Zr(1)−O(11)	94.85(9)
O(22)−Zr(1)−O(11)	71.74(7)	O(40)−Zr(1)−O(10)	95.04(9)
O(22)−Zr(1)−O(10)	133.17(8)	O(30)−Zr(1)−O(22)	153.00(8)
O(20)−Zr(1)−O(11)	81.80(8)	O(30)−Zr(1)−O(31)*	76.65(7)
O(20)−Zr(1)−O(10)	84.51(8)	O(30)−Zr(1)−O(20)	89.11(8)
O(20)−Zr(1)−S(13)	80.90(6)	O(30)−Zr(1)−O(11)	133.96(7)
O(11)−Zr(1)−O(10)	61.48(7)	O(30)−Zr(1)−O(10)	72.79(8)
S(13)−O(10)−Zr(1)	98.4(1)	S(33)−O(31)−Zr(1)*	151.1(1)
S(13)−O(11)−Zr(1)	98.5(1)	O(10)−S(13)−O(11)	101.6(1)
S(23)−O(20)−Zr(1)	140.5(1)	O(22)−S(23)−O(20)	108.8(1)
S(23)−O(22)−Zr(1)	152.4(1)	O(30)−S(33)−O(31)	108.5(1)
S(33)−O(30)−Zr(1)	145.5(1)	C(41)−O(40)−Zr(1)	171.3(2)

Crystals of $Zr(OPr)(O_3SMe)_3$ were obtained by reacting $Zr(OPr)_4$ with a 5-fold excess of $MeSO_3H$. The X-ray structure analysis (Tables 1−3, Figure 1) revealed that this is a polymeric compound with both chelating and bridging $MeSO_3$ groups. Each zirconium atom is coordinated by seven oxygen atoms from a terminal propoxy group, and one chelating and four bridging sulfonate groups. The coordination polyhedron is a nearly ideal pentagonal bipyramid, with the propoxy group and the oxygen atom of one bridging sulfonate group in the axial positions. The cis,cis-bridging of neighboring zirconium atoms by two sulfonate ligands each results in the formation of zig-zag chains of linked polyhedra, related to each other by a crystallographic center of inversion. The main structural difference between the commonly used carboxylate ligands and the sulfonate ligands in $Zr(OPr)(O_3SMe)_3$ is the greater variability of the latter. Five-membered rings are formed when a carboxylate or

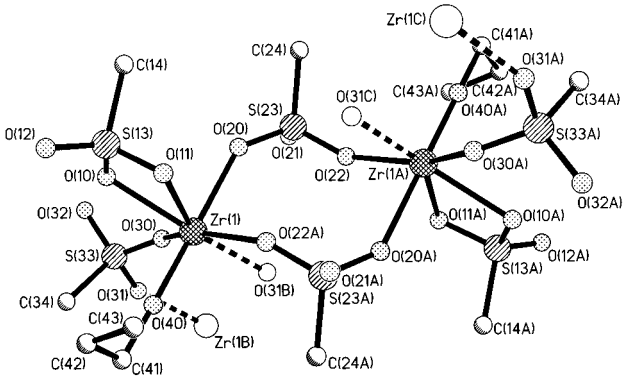
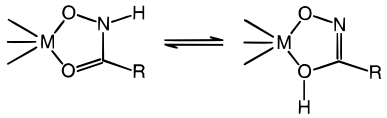


Figure 1. Molecular structure of $[Zr(OPr)(O3SMe)_3]_\infty$.

Scheme 2. Coordination of Hydroxamate Ligands



sulfonate ligand bridges two Zr atoms. Almost planar rings were found in the structures of carboxylate-bridged oxo/alkoxy zirconium clusters.[9] In $Zr(OPr)(O_3SMe)_3$ these "rings" are strongly twisted, i.e., the Zr···Zr distance is very long. This is mainly due to the large Zr−O−S angles and the large dihedral angles Zr−O−O−Zr. In generalizing these results, one would expect more condensed cluster structures with carboxylate ligands and a smaller structure-directing influence of sulfonate ligands.

Preparation of the Hydroxamate Derivatives $(RO)_3E[ON(H)C(O)-CH_2CH_2PPh_2]$ (5). Hydroxamic acids RC(O)N(H)OH are prepared by reaction of carboxylic esters with H_2NOH. Hydroxamates are strongly chelating ligands due to the formation of thermodynamically stable five-membered metallacycles (Scheme 2). Hydroxamic acids can also be used for the modification of metal alkoxides and provide a particularly stable link between the organic group R and the metal alkoxide moiety.[11]

In principle, the hydroxamate derivatives **4** could be prepared by the same two routes as the carboxylate and sulfonate derivatives **2** and **3** (Scheme 1). However, H_2NOH adds to the double bond of the acrylic ester instead of forming the unsaturated hydroxamic acid.[12] Furthermore, the addition of $HPPh_2$ to the double bond of alkoxide derivatives with unsaturated carboxylate or sulfonate ligands was less suitable compared to the reaction of the PPh_2-substituted acids with $E(OR)_4$. We therefore only investigated the second possibility for the hydroxamate derivatives.

The potassium salt $K[ON(H)C(O)-CH_2CH_2PPh_2]$ was prepared from $EtOC(O)-CH_2CH_2PPh_2$ and $[H_3NOH]Cl$ in methanolic KOH according to ref 13. The elemental analysis of the obtained yellow solid was consistent with the composition $K[ON(H)C(O)-CH_2CH_2PPh_2]\cdot 0.4KCl$. No attempts were made to separate the KCl, because it should not interfere with the following reactions. The solid showed characteristic ν_{CO} bands at 1580 and 1435 cm^{-1} in the IR spectrum. Two multiplets shifted to higher field relative to $EtOC(O)-CH_2CH_2PPh_2$ were observed at 2.21 and 1.87 ppm in the ^1H NMR spectrum. The latter multiplet was assigned to CH_2 next to the hydroxamate group. The ^{31}P NMR spectrum showed the product signal at −14.7 ppm and some weak signals for decomposition products and phosphine oxides.

$K[ON(H)C(O)-CH_2CH_2PPh_2]\cdot 0.4KCl$ was reacted with equimolar amounts of $Ti(OEt)_4$, $Ti(OiPr)_4$, or $Zr(OPr)_4$ in benzene at 40 °C (eq 6). Yellow powders were obtained after separation of KCl, removal of the solvent, and washing with petroleum ether.

$$K[ON(H)C(O)-CH_2CH_2PPh_2]\cdot 0.4KCl + E(OR)_4 \rightarrow (RO)_3E[ON(H)C(O)-CH_2CH_2PPh_2] + 0.4KCl + ROH \quad (6)$$

5a,c,f

The product had intense ν_{CO} bands at 1580 and 1435 cm^{-1}, not shifted relative to the starting potassium salt. The ^{31}P NMR spectra showed new signals for the products at −15.6 ppm (**5a**), −15.7 ppm (**5c**), and −15.8 ppm (**5f**). However, the signal of the potassium salt at −14.7 ppm was also observed in considerable intensity (30−50%), indicating incomplete reaction. The samples also contained signals of phosphine oxides (10−30%), partially already present in the starting compound.

The determination of the composition of **5a,c,f** by NMR spectroscopy was not possible because of the presence of the other compounds and because the product signals were not significantly shifted.

Hydrolytic Stability of the E−X Link. The use of the derivatives $(RO)_3E-X-PPh_2$ for the incorporation of the PPh_2 groups in sol−gel materials requires sufficient hydrolytic stability of the E−X link. This was tested with selected examples of the compounds **2**−**5**.

Four equivalents of water were added to a THF solution of the freshly prepared *carboxylate* derivative **2′c**, having the initial composition $[Ph_2PCH_2CH_2COO]TiO_{0.3}(OiPr)_{2.4}\cdot 0.2^iPrOH$ (ROH was not used as the solvent to avoid side reactions with the alcohol). The solvent was removed after 20 h, and the yellow residue was analyzed by elemental analysis and spectroscopy. The IR spectrum was unchanged. Neither the IR nor the NMR spectra showed signals for uncoordinated $Ph_2PCH_2CH_2COOH$ or the corresponding ester. The composition of the hydrolysis product of **2′c** by integration of the NMR signals was $[Ph_2PCH_2CH_2COO]TiO_{1.35}(O^iPr)_{0.3}\cdot 0.4^iPrOH$. Under the relatively mild conditions of this experiment, the Ti−carboxylate link was fully retained, while a large part of the alkoxide groups were hydrolyzed.

The yellow 2-propanol solution of the sulfonate derivative **3c**, having the initial composition $[RSO_3]TiO_{1.45}(O^iPr)_{0.1}\cdot 0.8^iPrOH$, was equally treated with a 6-fold excess of water at ambient temperature for 32 h. The IR spectrum of the pale yellow solid was unchanged. No signals of alkoxy groups were observed in the ^1H NMR spectrum, i.e., the $E(OR)_3$ group was completely hydrolyzed. The composition of the hydrolysis product by integration of the NMR signals was $[Ph_2PCH_2-$

(11) Barglik-Chory, C. Dissertation, Universität Würzburg, 1995. Barglik-Chory, C.; Schubert, U.; Neumann, G. German Patent Appl. DE 195 24 859.7, 1995.

(12) Zeeh, B.; Metzger, H. In *Methoden der Organischen Chemie (Houben-Weyl)*; Müller, E., Ed.; Thieme: Stuttgart 1991; Vol. X/1, p 1097.

(13) Blatt, A. H. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 67.

$CH_2C(O)NHCMe_2CH_2SO_3]TiO_{1.5}\cdot 0.3^iPrOH\cdot 0.9H_2O$. This composition was confirmed by elemental analysis.

Cleavage of all alkoxy groups, but retention of the sulfonate ligand, was also observed in a hydrolysis experiment with a THF solution of the unsaturated derivative $[H_2C{=}CHC(O)NHC(CH_3)_2CH_2SO_3]TiO_{0.65}(OBu)_{1.7}\cdot 1.1BuOH$, using a 15-fold excess of water.

Treatment of the derivative **4b**, which was already completely hydrolyzed during its preparation, with a 4-fold excess of water in THF for 16 h at room temperature did not result in any noticeable change of the spectra. These results consistently demonstrate the high hydrolytic stability of the Ti−sulfonate link.

A yellow precipitate was obtained after 15 min, when a 4-fold excess of water was added to the yellow benzene solution of the hydroxamate derivative **5a**. The ^{1}H NMR spectrum of the precipitate (in DMSO) showed no ethoxy group signals. As mentioned above, the signals of the hydroxamate ligand are not significantly affected by the coordination and therefore cannot be used as indicators for the other groups bonded to the titanium atom. The ^{31}P NMR signal was shifted from −15.6 ppm in **5a** to −14.7 ppm in the hydrolysis product. Although this is the same chemical shift as for $K[ON(H)C(O)-CH_2CH_2PPh_2]$, we can exclude the presence of both the potassium salt and the hydroxamic acid, because both are soluble in benzene. The unsoluble hydrolysis product therefore should be $[Ph_2PCH_2CH_2-C(O)N(H)NO]TiO_{1.5}$.

When the benzene solution of the hydrolysis experiment was concentrated after filtration of the precipitate of $[Ph_2PCH_2CH_2-C(O)N(H)NO]TiO_{1.5}$, another yellow solid was obtained, which was identified as $K[ON(H)C(O)-CH_2CH_2PPh_2]$ by all the spectroscopic data. It should be kept in mind that the sample of **5a** contained unreacted $K[ON(H)C(O)-CH_2CH_2PPh_2]$. The isolated yields of $[Ph_2PCH_2CH_2-C(O)N(H)NO]TiO_{1.5}$ and $K[ON(H)C(O)-CH_2CH_2PPh_2]$ after hydrolysis were approximately in the same ratio as the alkoxide derivative and the potassium salt in the starting compound. Therefore, it is safe to conclude that the hydroxamate ligand is also fully retained upon hydrolysis.

Coordination of Metal Complexes to the PPh_2 Group. The $W(CO)_5$ fragment was chosen to probe the availability of the PPh_2 group in compounds **2**−**5** for the coordination of metal complexes. This fragment is particularly good example, because the ν_{CO} bands in the infrared spectra of $W(CO)_5L$ and the $^1J_{W-P}$ coupling constants are highly indicative of the nature of the ligand L. Complexes of the type $W(CO)_5(PR_3)$ are easily obtained by reaction of the solvent complex $W(CO)_5(OEt_2)$ with phosphines.

Selected examples of **2**−**5** (**2′c**, **2′f**, **3c**, **3f**, **4b**, **4f**, **5a**, and **5f**) were reacted with an equimolar amount of $W(CO)_5(OEt_2)$ in diethyl ether for 16 h (eq 7). The signals of the starting compounds disappeared in each case, and characteristic product signals were observed. The IR spectra of the products showed the typical ν_{CO} pattern of $W(CO)_5L$ complexes, the bands distinctly shifted to higher wavenumbers relative to $W(CO)_5(OEt_2)$ (see Experimental Section). The ^{31}P NMR chemical shifts were in the range of 8.0−10.7 ppm (depending on the $Ph_2P-X-E(OR)_3$ ligand) and the $^1J_{W-P}$ coupling constants (116−118 Hz) typical for $W(CO)_5(PR_3)$ complexes.

$$W(CO)_5(OEt_2) + Ph_2P-X-E(OR)_3 \rightarrow W(CO)_5[PPh_2-X-E(OR)_3] + OEt_2 \quad (7)$$

A problem associated with the formation of the metal complexes $W(CO)_5[PPh_2\text{-}X-E(OR)_3]$ was the formation of phosphine oxides (identified by their characteristic ^{31}P NMR chemical shifts), and phosphorus-containing decomposition products and byproducts, which were not identified. The portion of these products increased in the order **2** (no phosphine oxides) < **4**, **5** < **3** (up to 50%).

A special phenomenon was observed for the sulfonate derivatives **3** and **4**. The ^{31}P NMR spectra of the reaction products of **3c** and **3f** with $W(CO)_5(OEt_2)$ showed the weak signal of a byproduct at +9.2 ppm ($^1J_{W-P}$ = 114.7 Hz) besides that of the main product at +10.2 ppm ($^1J_{W-P}$ = 118.4 Hz). Both chemical shifts and coupling constants are in the range observed for $W(CO)_5(PR_3)$ complexes. The latter signal was assigned to $W(CO)_5$(**3**) because the coupling constant is nearly identical with comparable $W(CO)_5(PR_3)$ complexes. The same phenomenon was observed for the reaction products of **4b** and **4f** with $W(CO)_5(OEt_2)$ (main product δ = +8.0 ppm, $^1J_{W-P}$ = 118.4 Hz; byproduct δ = +7.8 ppm, $^1J_{W-P}$ = 114.7 Hz). We currently have no explanation for the second signal. It may be a due to some intramolecular interaction.

The hydrolytic stability of the complexes $(CO)_5W[PPh_2-X-E(OR)_3]$ was tested for $(CO)_5W$(**2′c**), $(CO)_5W$(**3f**), $(CO)_5W$(**4b**), and $(CO)_5W$(**5a**). Benzene or THF solutions of these compounds were treated with a great excess of water for several hours. Spectroscopic investigation of the resulting solids gave no indication that either the W−P bond or the E−X bond was cleaved. While some of the alkoxy groups were retained in the hydrolysis experiment of $(CO)_5W$(**2′c**), no alkoxy groups were left in the other compounds.

In the mentioned experiments, the complexes $W(CO)_5[PPh_2\text{-}X-E(OR)_3]$ were prepared by reaction of $W(CO)_5(OEt_2)$ with $Ph_2P-X-E(OR)_3$ (eq 7). An alternative approach would be the reaction of $W(CO)_5(PPh_2-X-H)$ or $[W(CO)_5(PPh_2-X)]^-$ with $E(OR)_4$. Such complexes were prepared by reaction of $W(CO)_5(OEt_2)$ with $Ph_2PCH_2CH_2COOH$, $Li[O_3S-CH_2CMe_2NHC(O)CH_2CH_2PPh_2]$, $Na[O_3S-CH_2CH_2PPh_2]$, or $K[ON(H)C(O)-CH_2CH_2PPh_2]\cdot 0.4KCl$, respectively. However, most of the reactions were accompanied by extensive decomposition and side reactions. The spectra of the product mixtures obtained upon subsequent reaction with $Ti(OR)_4$ showed that the complexes $W(CO)_5[PPh_2-X-E(OR)_3]$ were also formed by this route. However, in every case the yields were much lower, and the portion of the byproducts was larger. Therefore, the complexes are better prepared by the approach shown in eq 7.

Conclusions

We have prepared several compounds of the general type $Ph_2P-X-E(OR)_3$ (E = Ti, Zr), in which a PPh_2-substituted bidentate organic ligand is bonded to a titanium or zirconium alkoxide moiety. The bidentate group may be a carboxylate group, as in $[Ph_2PCH_2CH_2-COO]EO_x(OR)_{3-2x}$, a sulfonate group, as in $[Ph_2PCH_2-CH_2-SO_3]EO_x(OR)_{3-2x}$ or $[Ph_2PCH_2CH_2C(O)NHC(CH_3)_2-CH_2-SO_3]EO_x(OR)_{3-2x}$, or a hydroxamate group, as in $[Ph_2PCH_2CH_2-C(O)N(H)O]EO_x(OR)_{3-2x}$. In each case,

partial hydrolysis was observed during preparation, probably due to the water-producing ester formation as a side reaction. The obtained mixed oxy−alkoxy derivatives can nevertheless be used as sol−gel precursors, because all of them are soluble in organic solvents.

The bonding mode of carboxylate ligand to titanium or zirconium alkoxides or their primary hydrolysis products is well established for other carboxylate groups (see ref 9 for related examples). The X-ray structure of $[Zr(OPr)(O_3SMe)_3]_\infty$ as a model compound reported in this paper shows that sulfonate ligands can similarly act as bridging and chelating ligands to zirconium alkoxide moieties. The hydroxamate group is probably chelating, given the known preference of such ligands to form five-membered metallacycles. This was found in Ti_3O_3(benzohydroxamate)$_6$, obtained by reaction of $Ti(OR)_4$ with benzohydroxamic acid.[8]

The PPh_2 group in all compounds $Ph_2P-X-EO_x(OR)_{3-2x}$ is available for the coordination to metal complex moieties, as shown for the $W(CO)_5$ derivatives as an example. Reaction of both $Ph_2P-X-EO_x(OR)_{3-2x}$ and $(CO)_5W[PPh_2-X-EO_x(OR)_{3-2x}]$ with water resulted in no significant cleavage of the bond between the titanium or zirconium atom and the bidentate ligand. The long-term stability and the stability under more forceful conditions still has to be tested. The PPh_2-substituted titanium and zirconium alkoxide derivatives can thus be used to tether metal complexes to titania or zirconia supports (either by surface modification or by sol−gel processing) in the same way as $Ph_2P(CH_2)_n$-$Si(OR)_3$ is used for tethering to silica.

Experimental Section

All operations were performed in an atmosphere of dry and oxygen-free argon, using dried solvents. All starting compounds were used as received and stored under argon. Acrylic acid was destilled in vacuo before use. Glassware was dried by heating in vacuo.

A mercury high-pressure Heraeus lamp TQ 150 (emission maximum at 366 nm) in a quartz vessel was used for the UV irradiations.

Infrared spectra were obtained on Perkin-Elmer spectrometers model 1310 and 1320 (CaF_2 cuvettes, or NaCl plates for Nujol mulls and films). ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker AMX 400 (^1H, 400.1 MHz; ^{31}P, 162.0 MHz) and a Bruker AC 250 (^1H, 250 MHz; ^{31}P, 101 MHz) spectrometer. Melting point determinations and DSC analyses were performed on a Shimadzu DSC-50.

The "theoretical" values of the elemental analysis were calculated from the compositions determined by integration of the ^1H NMR signals.

Reaction of Acrylic Acid with Metal Alkoxides. Ten millimoles of the metal alkoxide (2.09 mL of $Ti(OEt)_4$, 2.73 mL of $Ti(OPr)_4$, 2.93 mL of $Ti(O^iPr)_4$, 3.40 mL of $Ti(OBu)_4$, 3.82 mL of $Ti(O^tBu)_4$, 4.48 mL of $Zr(OPr)_4$ [70% in *n*-propanol]) was added dropwise to a solution of acrylic acid (10 mmol, 0.68 mL) in 40 mL of toluene. The clear yellow solution was refluxed for 2 h. After removal of all volatiles in vacuo, yellow oils (**1c**: solid) were obtained.

1a: Yield 2.09 g (95%). ^1H NMR ($CDCl_3$, δ, ppm) 1.32 (OCH_2CH_3, 6.3 H), 4.49 (OCH_2, 3.3 H), 5.87 (d, $=CH_2$, 1 H), 6.20 (dd, =CH, 1 H), 6.44 (d, $=CH_2$, 1 H). IR (toluene, cm^{-1}) 1730 (w, COO), 1670 (w), 1640 (s, C=C), 1560 (s, br, COO), 1540 (sh, COO), 1435 (s, COO), 1370 (s), 1310 (w, COO), 1265 (w), 1185 (vw), 1130 (s, br), 1060 (m, br).

1b: Yield 2.28 g (93%). ^1H NMR ($CDCl_3$, δ, ppm) 0.99, 1.74 (CH_2CH_3 and CH_2CH_3, 10.1 H), 4.54 (t, OCH_2, 3.9 H), 5.31 (d, $=CH_2$, 1H), 6.12 (dd, $=CH_2$, 1 H), 6.43 (d, =CH, 1 H). IR (toluene, cm^{-1}) 1725 (w, COO), 1670 (w), 1640 (s, C=C), 1580 (s, COO), 1490 (sh, COO), 1430 (s, COO), 1395 (vw), 1370 (s), 1310 (sh, COO), 1295 (w), 1273 (s), 1225 (w), 1120 (s, br), 1065.

1c: Yield 2.55 g (91%). ^1H NMR (C_6D_6, δ, ppm) 1.45 (d, $CH(CH_3)_2$, 16.2 H), 5.10 (m, OCH, 2.7 H), 5.45 (d, $=CH_2$, 1 H), 6.25 (dd, =CH, 1H), 6.56 (d, $=CH_2$, 1 H). IR (benzene, cm^{-1}) 1735 (w, COO), 1632 (s, C=C), 1560 (s, COO), 1540 (s, br, COO), 1430 (s, COO), 1363 (s), 1310 (w, COO), 1265 (w), 1155 (s), 1120 (m, br), 1055 (w).

1d: Yield 2.94 g (90%). ^1H NMR (C_6D_6, δ, ppm) 1.02 (m, CH_2CH_3, 8.4 H), 1.58 (m, CCH_2, 5.6 H), 1.80 (m, CCH_2, 5.5 H), 4.67 (t, OCH_2, 5.5 H), 5.44 (d, $=CH_2$, 1 H), 6.19 (dd, =CH, 1 H), 6.48 (d, $=CH_2$, 1 H). IR (benzene, cm^{-1}) 1730 (w, COO), 1640 (s, C=C), 1560 (s, br, COO), 1545 (sh), 1400 (s,COO), 1375 (s), 1300 (w, COO), 1275 (s), 1265 (sh, w), 1175 (m, br), 1120 (m, br), 1100 (m, br).

1e: Yield 3.26 g (98%). ^1H NMR (C_6D_6, δ, ppm) 1.42 (s, CCH_3, 26.2 H), 5.45 (d, $=CH_2$, 1 H); 6.37 (dd, =CH, 1 H), 6.44 (d, $=CH_2$, 1 H). IR (benzene, cm^{-1}) 1660 (m, sh), 1640 (s, C=C), 1580 (s, COO), 1520 (s, br, COO), 1450 (sh, COO), 1440 (s, COO), 1375 (sh), 1360 (s), 1310 (m, COO), 1270 (m), 1230 (w), 1170 (w, br).

1f: Yield 2.91 g (96%). ^1H NMR (C_6D_6, δ, ppm) 1.13 (CCH_3, 6.92 H), 1.72 (m, CH_2CH_3, 4.6 H), 4.39 (t, OCH_2, 4.5 H), 5.49 (d, $=CH_2$, 1 H), 6.28 (dd, =CH, 1 H), 6.52 (d, $=CH_2$, 1 H). IR (benzene, cm^{-1}) 1730 (w, COO), 1640 (s, C=C), 1580 (s, COO), 1540 (sh, COO), 1450 (sh, COO), 1435 (s, COO), 1375 (sh), 1360 (s), 1300 (w, COO), 1270 (m), 1225 (w), 1170 (w, br).

Addition of $HPPh_2$ to $(RO)_3E[OOC-CH=CH_2]$ (1). Eleven millimoles (1.91 mL) of $HPPh_2$ and about 150 mg of AIBN (as the radical starter) were added to the solution of 10 mmol of the acrylate-substituted metal alkoxide (**1a**−**f**) in 40 mL of benzene. The solution was heated to 70 °C for 6−7 h. The reaction was controlled by IR spectroscopy. After a few minutes, the clear solutions turned turbid. After removal of all volatiles in vacuo yellow oils were obtained, which solidified by washing with petroleum ether. The beige to pale yellow solids were dried in vacuo at 50 °C.

2a: Yield 1.67 g (45%). ^1H NMR ($CDCl_3$, δ, ppm) 0.86 (t, $HOCH_2CH_3$, 0.6 H), 1.23 (m, $TiOCH_2CH_3$, 2.8 H), 2.33 (m, PCH_2CH_2, 4 H), 3.69 (quintet, $HOCH_2CH_3$, 0.4 H), 4.38 (m, $TiOCH_2CH_3$ and OH, 2 H), 7.35 (m, Ph, 10 H). ^{31}P NMR ($CDCl_3$, δ, ppm) −15.5, +31.5 (traces of phosphine oxide). IR (toluene, cm^{-1}) 1720 (w, COO), 1580 (sh, COO), 1560 (s, COO), 1425 (s, COO), 1410 (sh, COO), 1315 (m, COO), 1265 (m), 1220 (w), 1180 (m), 1160 (w), 1120 (m), 1100 (m, br), 1060 (m).

2b: Yield 1.78 g (40%). ^1H NMR ($CDCl_3$, δ, ppm) 0.91 (m, CH_3, 6.6 H), 1.56 (m, CCH_2, 4.5 H), 2.36 (m, PCH_2CH_2, 4 H), 3.57 (m, HO, 0.9 H), 4.18 (m, OCH_2, 3.9 H), 7.38 (m, Ph, 10 H). ^{31}P NMR ($CDCl_3$, δ, ppm) −15.5, +31.5 (phosphine oxide). IR (toluene, cm^{-1}) 1725 (w, br, COO), 1415 (s, br, COO), 1365 (s), 1310 (w, COO), 1265 (w), 1225 (s), 1120 (sh, w), 1090 (m, br). Anal. Calcd: P, 6.94. Found: P, 6.88.

2c: Yield 2.19 g (55%). ^1H NMR ($CDCl_3$, δ, ppm) 1.19 (d, $HOCH(CH_3)_2$, 1.8 H), 1.23 (d, $TiOCH(CH_3)_2$, 6.1 H), 2.33 (m, PCH_2CH_2, 4 H), 3.99 (m, HO, 0.3 H), 4.98 (m, OCH, 1.3 H), 7.30 (m, Ph, 10 H). ^{31}P NMR ($CDCl_3$, δ, ppm) −15.4, +30.4 (phosphine oxide). IR (toluene, cm^{-1}) 1715 (w, COO), 1570 (sh), 1560 (m, COO), 1540 (s, COO), 1410 (s, COO), 1360 (s), 1300 (w, COO), 1218 (s), 1160 (m), 1120 (m, br), 1085 (w, br).

2d: Yield 2.13 g (49%). ^1H NMR ($CDCl_3$, δ, ppm) 1.03 (m, CH_3, 4.8 H), 1.45 (m, $CH_2CH_2CH_3$, 6.4 H), 2.44 (m, PCH_2CH_2, 4 H), 4.14 (m, HO, 0.6 H), 4.39 (m, OCH_2, 3.1 H), 7.31 (m, Ph, 10 H). ^{31}P NMR ($CDCl_3$, δ, ppm) −15.3, +31.4 (phosphine oxide). IR (toluene, cm^{-1}) 1730 (w, COO), 1560 (s, br, COO), 1425 (sh, COO), 1410 (s, COO), 1365 (m), 1310 (w, COO), 1285 (sh, w), 1270 (s), 1120 (s), 1090 (m, br).

2e: Yield 1.93 g (51%). ^1H NMR ($CDCl_3$, δ, ppm) 1.29 (s, $OC(CH_3)_3$, 6.3 H), 2.38 (m, $Ph_2CH_2CH_2$, 4 H), 4.10 (s, HO, 0.1 H), 7.35 (m, Ph, 10 H). ^{31}P NMR ($CDCl_3$, δ, ppm) −15.1, +32.9 (phosphine oxide). IR (toluene, cm^{-1}) 1725 (w, COO), 1570 (s, COO), 1420 (s, COO), 1300 (w, COO),1230 (m), 1170 (m), 1120 (w), 1090 (w).

2f: Yield 2.39 g (53%). ^{1}H NMR ($CDCl_3$, δ, ppm) 1.14 (m, CH_3, 4.6 H), 1.72 (m, CCH_2, 3.0 H), 2.43 (m, PCH_2CH_2, 4 H), 3.57 (m, HO, 0.8 H), 4.22 (m, OCH_2, 2.6 H), 7.36 (m, Ph, 10 H). ^{31}P NMR ($CDCl_3$, δ, ppm) −15.2, +30.5 (phosphine oxide). IR (toluene, cm^{-1}) 1720 (vw, COO), 1560 (s, COO), 1425 (s, COO), 1415 (sh, COO), 1310 (vw, COO), 1265 (m), 1220 (m), 1180 (m), 1120 (m), 1090 (w).

Reaction of $Ph_2PCH_2CH_2COOH$ with Metal Alkoxides. Ten millimoles of the metal alkoxide (2.09 mL of $Ti(OEt)_4$, 2.73 mL of $Ti(OPr)_4$, 2.93 mL of $Ti(O^iPr)_4$, 3.40 mL of $Ti(OBu)_4$, 3.82 mL of $Ti(O^tBu)_4$, 4.48 mL of $Zr(OPr)_4$ (70% in *n*-propanol)) was slowly added to a solution of 10 mmol (2.58 g) of Ph_2PCH_2-CH_2COOH[10] in 60 mL of benzene. The yellow color of the solution immediately became more intense. After 1 h at room temperature, the solvent was removed in vacuo at 50 °C to yield yellow oils.

2′a: Yield 4.03 g (98%). ^{1}H NMR (C_6D_6, δ, ppm) 1.40 (m, CH_3, 6.6 H), 2.54 (m, PCH_2CH_2, 4 H), 3.95 (quintet, HO, 0.2 H), 4.69 (m, OCH_2, 4.3 H), 7.47 m (Ph, 10 H). ^{31}P NMR (C_6D_6, δ, ppm) −14.8. IR (benzene, cm^{-1}) 1740 (w, COO), 1570 (s, br, COO), 1435 (s, COO), 1410 (sh, COO), 1380 (w), 1355 (w), 1330 (sh), 1310 (w, COO), 1265 (m), 1239 (sh), 1130 (s, br), 1100 (sh), 1070 (m), 1040 (sh).

2′b: Yield 3.98 g (95%). ^{1}H NMR (C_6D_6, δ, ppm) 1.06 (t, CH_3, 8.8 H), 1.79 (m, CCH_2, 5.8 H), 2.57 (m, PCH_2CH_2, 4 H), 3.92 (m, HO, 0.2 H), 4.64 (m, OCH_2, 5.7 H), 7.48 (m, Ph, 10 H). ^{31}P NMR (C_6D_6, δ, ppm) −14.9. IR (benzene, cm^{-1}) 1740 (w, COO), 1570 (s, COO), 1550 (sh, COO), 1430 (s, COO), 1410 (sh, COO), 1375 (w), 1355 (vw), 1310 (m), 1270 (sh), 1260 (m), 1230 (sh), 1200 (sh), 1120 (m), 1075 (m), 1030 (sh).

2′c: Yield 4.17 g (90%). ^{1}H NMR (C_6D_6, δ, ppm) 1.07, 1.36 (d, $CH(CH_3)$, 15.6 H), 2.42 (m, PCH_2CH_2, 4 H), 4.59 (m, HO, 0.2 H), 5.05 (m, CH, 2.6 H), 7.45 (m, Ph, 10 H). ^{31}P NMR (C_6D_6, δ, ppm) −14.9. IR (benzene, cm^{-1}) 1730 (w, COO), 1580 (s, COO), 1560 (m, COO), 1540 (sh, COO), 1470 (m, COO), 1410 (s, COO), 1360 (m), 1320 (m), 1300 (w), 1215 (m), 1160 (sh), 1115 (s, br), 1000 (m, br).

2′d: Yield 4.84 g (98%). ^{1}H NMR (C_6D_6, δ, ppm) 0.85, 1.02 (t, CH_3, 7.5 H), 1.56 (m, $CH_2CH_2CH_3$, 10.1 H), 2.62 (m, PCH_2CH_2, 4 H), 4.02 (q, HO, 0.4 H), 4.49, 4.69 (m, $HOCH_2$, 4.8 H), 7.49 (m, Ph, 10 H). ^{31}P NMR (C_6D_6, δ, ppm) −14.8. IR (benzene, cm^{-1}) 1740 (w, COO), 1595 (s, COO), 1565 (s, COO), 1540 (sh, COO), 1420 (sh, COO), 1410 (s, br, COO), 1305 (m, COO), 1260 (vw), 1220 (m, br), 1180 (w, sh), 1125 (s, br), 1090 (m, br), 1030 (sh).

2′e: Yield 4.46 g (88%). 1.59 g (20%) of a pale yellow powder were obtained by stirring with petroleum ether. ^{1}H NMR (C_6D_6, δ, ppm) 1.38 (s, $HOC(CH_3)_3$, 1 H), 1.42 (s, $TiOC(CH_3)_3$, 23.4 H), 2.52 (m, PCH_2CH_2, 4 H), 3.93 (s, HO, 0.1 H), 7.43 (m, Ph, 10 H). ^{31}P NMR (C_6D_6, δ, ppm) −14.7. IR (petroleum ether, cm^{-1}) 1730 (w, COO), 1570 (s, COO), 1435 (s, COO), 1410 (sh, COO), 1360 (m), 1305 (w, COO), 1270 (w), 1230 (m), 1180 (m, br), 1130 (w, sh), 1100 (w), 1070 (vw), 1000 (vw).

2′f: Yield 2.29 g (70%). ^{1}H NMR (DMSO-d_6, δ, ppm) 0.84 (m, CH_3, 5.7 H), 1.48 (m, CCH_2, 3.8 H), 2.30 (m, PCH_2CH_2, 4 H), 3.31 (q, HO, 0.2 H), 3.91 (t, $ZrOCH_2$, 3.6 H), 4.35 (t, $HOCH_2$, 0.1 H), 7.36 (m, Ph, 1 H). ^{31}P NMR (DMSO-d_6 δ, ppm) −14.7. IR (petroleum ether, cm^{-1}) 1740 (w, COO), 1570 (s, br, COO), 1430 (s, COO), 1410 (sh, COO), 1310 (m, COO), 1275 (w), 1120 (w), 1150 (sh), 1140 (m), 1080 (w), 1045 (w), 1000 (w).

Preparation of $Na[O_3S-CH_2CH_2PPh_2]$. Ph_2PCl [0.10 mol (17.95 mL)] in 100 mL of THF and 0.50 mol (11.49 g) of Na were refluxed until the color of the solution changed from yellow to red. The solution was kept at room temperature for an additional 10 h and then the excess of sodium was separated. The $NaPPh_2$ solution was cooled to 0 °C and added to a suspension of 0.10 mol (21.10 g) of $BrCH_2CH_2SO_3H$ in 100 mL of THF within 1 h. The solution slowly got colorless. The solution was stirred for 2 h at room temperature, filtered, and concentrated in vacuo. The resulting pale yellow solid was washed with petroleum ether and diethyl ether and dried in vacuo. Yield 20.38 g (64%). ^{1}H NMR (DMSO-d_6, δ, ppm) 2.36 (m, CH_2, 4 H), 7.36 (m, Ph, 10 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −16.6. IR (Nujol, cm^{-1}) 1605 (m, aryl), 1580 (m, aryl), 1420 (sh, s, SO_3^-), 1300 (m), 1270 (s), 1210 (sh, m), 1180 (vs, br), 1140 (m), 1090 (sh, m), 1050 (s, S═O), 1030 (sh, m, S═O). Anal. Calcd for $C_{14}H_{14}NaO_3PS\cdot0.23NaBr$: C, 49.46; H, 4.15; P, 9.11; S, 9.43. Found: C, 49.27; H, 4.13; P, 9.07; S, 9.39.

Reaction of $Na[O_3S-CH_2CH_2PPh_2]$ with Metal Alkoxides. The metal oxide (0.01 mol) (2.09 mL of $Ti(OEt)_4$, 2.73 mL of $Ti(OPr)_4$, 2.93 mL of $(Ti(O^iPr)_4$, 4.48 mL of $Zr(OPr)_4$ (70% in *n*-propanol)) was added dropwise to a suspension of 0.01 mol (3.16 g) of $Na[O_3S-CH_2CH_2PPh_2]$ in 60 mL of THF. The solution was stirred at 60 °C for 6 h, filtered, and concentrated in vacuo. The resulting pale yellow solids were washed with petroleum ether.

*IR (Nujol, cm^{-1}) for **4a−c,f***: 1605 (m, aryl), 1580 (m, aryl), 1420 (sh, s, SO_3), 1300 (m), 1270 (s), 1210 (sh, m), 1180 (vs, br), 1140 (m), 1090 (sh, m), 1050 (s, S═O), 1030 (sh, m, S═O).

4a: Yield 2.65 g (61%). ^{1}H NMR (DMSO-d_6, δ, ppm) 1.04 (t, CH_3, 2.3 H), 2.33 (m, PCH_2CH_2, 4 H), 3.42 (quintet, $HOCH_2$-CH_3, 1.4 H), 4.33 (t, $HOCH_2CH_3$, 0.7 H), 4.75 (m, $TiOCH_2$, 0.1 H), 7.36 (m, Ph, 10 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −16.6. Anal. Calcd: P, 7.81; S, 7.97. Found: P, 7.79; S, 8.08.

4b: Yield 2.04 g (52%). ^{1}H NMR (DMSO-d_6, δ, ppm) 0.82 (t, $HOCH_2CH_2CH_3$, 1.5 H), 1.40 (sext, $HOCH_2CH_2CH_3$, 1.0 H), 2.33 m (PCH_2CH_2, 4 H), 3.32 (q, $HOCH_2CH_2CH_3$, 1.0 H), 4.37 (t, $HOCH_2CH_2CH_3$, 0.5 H), 7.36 (m, Ph, 10 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −16.6. Anal. Calcd: P, 7.84; S, 8.11. Found: P, 7.74; S, 7.98.

4c: Yield 2.62 g (67%). ^{1}H NMR (DMSO-d_6, δ, ppm) 1.02 (d, $HOCH(CH_3)_2$, 6.1 H), 2.33 m (PCH_2CH_2, 4 H), 3.76 (m, $HOCH(CH_3)_2$, 0.5 H), 4.38 (d, $HOCH(CH_3)_2$, 0.5 H), 7.36 (m, Ph, 10 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −16.6. Anal. Calcd: P, 7.84; S, 8.11. Found: P, 7.88; S, 8.12.

4f: Yield 3.98 g (90%). ^{1}H NMR (DMSO-d_6, δ, ppm) 0.82 (t, CH_3, 1.8 H), 1.40 (m, CH_2CH_3, 1.0 H), 2.33 m (PCH_2CH_2, 4 H), 3.32 (q, $HOCH_2$, 0.8 H), 3.82 (m, $ZrOCH_2$, 0.4 H), 4.37 (t, HO, 0.4 H), 7.36 (m, Ph, 10 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −16.7.

Preparation of $[Zr(OPr)(O_3SMe)_3]_\infty$. One milliliter (3.2 mmol) of $Zr(OPr)_4$ (70% in *n*-propanol)) was mixed with 1 mL (15.9 mmol) of methane sulfonic acid. The mixture was refluxed for 2 h and then kept at room temperature for 24 h. The light brown precipitate (0.87 g) was separated. It mainly consisted of an amorphous phase (about 90 vol %) and a crystalline phase. Suitable crystals were separated by hand.

Structure Determination of $[Zr(OPr)(O_3SMe)_3]_\infty$ (Table 1). A crystal was sealed in a glass capillary and mounted on a Siemens SMART diffractometer with a CCD camera. A hemisphere of data was collected at 203 K, by a combination of three sets of exposures. Each set had a different ϕ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction was applied. The structure was solved by direct methods (SHELS86). The positions of the hydrogen atoms were calculated according to an idealized geometry. Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL93) with anisotropic thermal parameters for all non-hydrogen atoms. The parameters of the hydrogen atoms were refined with a riding model.

Preparation of $K[ON(H)C(O)-CH_2CH_2PPh_2]$. The solution of 0.1 mol (5.61 g) of KOH in 30 mL of MeOH was warmed to 40 °C and added dropwise to a cooled solution of 0.07 mol (4.65 g) of $NH_2OH\cdot HCl$ in 30 mL of MeOH. After 10 min stirring at room temperature, the solution was filtered and 0.07 mol (19.05 g) of $Ph_2PCH_2CH_2COOEt$ was added. The solution was stirred for 10 min and filtered. The residue was washed with a small amount of methanol. The combined filtrates were concentrated in vacuo, and the resulting viscous oil was washed with petroleum ether until a nearly colorless solid was obtained. The solid is washed with three portions of diethyl ether and dried in vacuo. Yield 11.85 g (57%). ^{1}H NMR (DMSO-d_6, δ, ppm) 1.87 (m, PCH_2CH_2, 2 H), 2.21 (m, PCH_2CH_2, 2 H), 7.32 (m, Ph and NH, 10.5 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −14.7 (product, 90%), −18.9 (decomposition product, <5%), +32.3 (phosphine oxide, 5%). IR (benzene, cm^{-1}) 3300 (br, NH), 1580 (br, vs, C═O), 1435 (s, C═O), 1390 (br, s), 1300 (m), 1260 (w), 1130 (br, m), 1120 (vw), 1090 (vw). Anal. Calcd for $C_{15}H_{14}KNO_2P\cdot0.4KCl$: C, 52.80; H, 4.43; N, 4.10; P, 9.07. Found: C, 52.97; H, 4.72; N, 3.80; P, 8.95.

Reaction of K[ON(H)C(O)−$CH_2CH_2PPh_2$]·0.4KCl with Metal Alkoxides. The metal alkoxide (4.00 mmol) (0.84 mL of $Ti(OEt)_4$, 1.17 mL of $Ti(O^iPr)_4$, 1.79 mL of $Zr(OPr)_4$ (70% in *n*-PrOH)) was added dropwise to a solution of 4.00 mmol (1.36 g) of K[ON(H)C(O)$CH_2CH_2PPh_2$]·0.4KCl in 40 mL of benzene. The solution was heated to 50 °C for 2 h, filtered and concentrated in vacuo. The resulting viscous oils were washed with petroleum ether until pale yellow solids were obtained, which were dried in vacuo.

5a: Yield 1.37 g. ^{1}H NMR (DMSO-d_6, δ, ppm) 1.05 (m, CH_3, 7.7 H), 1.84 (m, PCH_2, 2 H), 2.21 (m, PCH_2CH_2, 2 H), 3.43 (quintet, HO, 1 H), 4.10 (q, $TiOCH_2$, 4.1 H), 4.53 (t, $HOCH_2$, 0.5 H), 7.32, 7.46, 7.81 (m, Ph and NH, 10.5 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −15.6 (product, 45%), −14.7 (starting compound, 35%), +31.5, +32.8 (phosphine oxides, 10%). IR (benzene, cm^{-1}) 3350 (br, NH), 3060 (vw, NH), 1580 (br, vs, C═O), 1565 (sh, C═O), 1440 (sh, s, C═O), 1300 (br, m), 1270 (vw), 1160 (br, m), 1120 (sh, m), 1110 (m), 1060 (s), 1030 (w).

5c: Yield 1.54 g. ^{1}H NMR (DMSO-d_6, δ, ppm) 1.02, 1.09 (d, CH_3, 6.7 H), 1.86, 2.21 (m, PCH_2CH_2, 4 H), 3.75 (m, HO, 0.3 H), 4.56 (m, CH, 1.1 H), 7.34, 7.51, 7.76 (m, Ph and NH, 10.5 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −15.7 (product, 55%), −14.7 (starting compound, 30%), +31.5, +32.5 (phosphine oxides, 15%). IR (benzene, cm^{-1}) 3300 (br, NH), 3060 (m, NH), 1575 (br, vs, C═O), 1435 (s, C═O), 1300 (br, s), 1260 (sh), 1180 (sh, m), 1165 (s), 1125 (br, s), 1110 (sh), 1070 (w), 1030 (w).

5f: Yield 1.34 g. ^{1}H NMR (DMSO-d_6, δ, ppm) 0.83 (m, CH_3, 6.1 H), 1.35 (m, CCH_2, 4.1 H), 1.84 (m, PCH_2CH_2, 2 H), 2.17 (m, PCH_2CH_2, 2 H), 3.36 (m, $HOCH_2$, 2.8 H), 3.85 (m, $ZrOCH_2$, 1.2 H), 4.48 (m, HO, 1.4 H), 7.32, 7.45, 7.71 (m, Ph and NH, 10.5 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −15.8 (product, 40%), −14.6 (starting compound, 50%), +31.4, +32.3 (phosphine oxides, 10%). IR (benzene, cm^{-1}) 3350 (br, NH), 3060 (m, NH), 1580 (br, vs, C═O), 1435 (s, C═O), 1300 (br, m), 1265 (sh, m), 1175 (br, m), 1120 (w), 1110 (w), 1075 (m), 1030 (vw).

Hydrolysis of [$Ph_2PCH_2CH_2COO$]$TiO_{0.3}(O^iPr)_{2.4}$·0.2^{i}PrOH (2′c). Water (20.0 mmol) (0.36 mL) in 10 mL of THF was added to a solution of freshly prepared 5 mmol sample of **2′c** in 100 mL of THF. After 20 h at room temperature the solvent was removed in vacuo. Yield 1.78 g (92%), orange-colored solid. ^{1}H (DMSO-d_6, δ, ppm) 1.03 (d, $HOCH(CH_3)_2$, 2.4 H), 1.13 (d, $TiOCH(CH_3)_2$, 1.8 H), 2.27 (m, PCH_2CH_2, 4 H), 3.34 (H_2O, O.6 H), 3.76 (m, OCH, 0.4 H), 4.36 (d, HO, 0.4 H), 4.80 (sept, TiOCH, 0.3 H), 7.36 (Ph, 10 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −15.8, +30.7 (phosphine oxide). IR (Nujol, cm^{-1}) 3400 (br, OH), 1730 (w, br, COO), 1580 (sh, COO), 1560 (sh, COO), 1540 (s, COO), 1440 (s, COO), 1310 (w, COO), 1260 (w), 1235 (vw), 1160 (w), 1125 (m), 1110 (w), 1070 (vw), 1030 (vw), 1000 (w). Anal. Calcd: P, 8.28. Found: P, 8.13.

Hydrolysis of [$Ph_2PCH_2CH_2$−C(O)NH$C(CH_3)_2CH_2SO_3$]-$TiO_{1.45}(O^iPr)_{0.1}$·0.8^{i}PrOH (3c). Water (6.0 mmol) (0.11 mL) was added dropwise to a solution of 1.0 mmol (517 mg) of **3c** in 100 mL of 2-propanol. The solution was stirred for 32 h at room temperature, and then the solvent was removed in vacuo. The resulting pale yellow solid was several times washed with petroleum ether. ^{1}H NMR (DMSO-d_6, δ, ppm) 1.02 (d, $HOCH(CH_3)_2$, 1.8 H), 1.36 (s, $C(CH_3)_2$, 6 H), 2.00 (m, PCH_2, 2 H), 2.22 (m, PCH_2CH_2, 2 H), 2.64 (s, CH_2SO_3, 2 H), 3.35 (s, H_2O, 1.8 H), 3.76 (m, HOCH, 0.3 H), 4.33 (d, HO, 0.3 H), 7.35 (m, Ph, 10 H), 8.14 (s, NH, 1 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −15.3. Anal. Calcd: N, 2.81; P, 6.21; S, 6.42. Found: N, 2.78; P, 6.19; S, 6.21.

Hydrolysis of [CH_2═CHC(O)NH$C(CH_3)_2CH_2$−SO_3]$TiO_{0.65}$-$(OBu)_{1.7}$·1.1 BuOH. Water (45.0 mmol) (0.81 mL) was added dropwise to a solution of 3.00 mmol (1.41 g) of CH_2═CHC(O)NH$C(CH_3)_2CH_2$−$SO_3TiO_{0.65}(OBu)_{1.7}$·1.1BuOH in 150 mL of THF. The solution was stirred for 28 h at room temperature, and then the solvent was removed in vacuo. Pale orange solid, yield 1.10 g (87%). ^{1}H NMR (DMSO, δ, ppm) 0.86 (t, $HOCH_2CH_2CH_2CH_3$, 1.8 H), 1.30 (m, $CH_2CH_2CH_3$, 2.4 H), 1.42 (s, $C(CH_3)$2, 6 H), 2.74 (s, CH_2SO3, 2 H), 3.36 (q, $HOCH_2$, 1.2 H), 4.01 (m, HO, 1.2 H) 5.49 (dd, $=CH_2$, 1 H), 5.98 (m, $=CH_2$ and =CH, 2 H), 8.35 (s, NH, 1 H). IR (Nujol, cm^{-1}) 3300 (br, m, NH), 3080 (w, NH), 1660 (s, C═O), 1630 (w, C═C), 1585 (br, s, C═O), 1550 (sh), 1410 (vw), 1280 (sh,m), 1250 (br, s), 1140 (br, s, C−O), 1070 (m, S═O), 1040 (m, S═O), 1000 (vw). Anal. Calcd: N, 4.24; S, 9.72. Found: N, 4.14; S, 9.54.

Hydrolysis of [$Ph_2PCH_2CH_2$−C(O)NHO]$Ti(OEt)_3$ (5a). Water (2.78 mmol) (0.05 mL) was added dropwise to a solution of 300 mg of **5a** in 30 mL of benzene. After 15 min a pale yellow solid precipitated, which was separated, washed with petroleum ether, and dried in vacuo (solid **1**, 162 mg). On concentration of the filtrate in vacuo 118 mg of a yellow solid was obtained (solid **2**).

*Solid **1***: ^{1}H NMR (DMSO-d_6, δ, ppm) 1.80 (PCH_2, 2 H), 2.21 (m, PCH_2CH_2, 2 H), 3.41 (s, br, H2O, 6.2 H), 7.34, 7.50, 7.75 (m, Ph and NH, 10.5 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −14.7 (product, 70%), +31.4, +32.5, +33.6 (phosphine oxides, 30%).

*Solid **2***: ^{1}H NMR (DMSO-d_6, δ, ppm) 1.84 (PCH_2, 2 H), 2.21 (m, PCH_2CH_2, 2 H), 3.38 (s, br, H_2O, 4.4 H), 7.36, 7.51, 7.73 (m, Ph and NH, 10.5 H). ^{31}P NMR (DMSO-d_6, δ, ppm) −14.7 ($Ph_2PCH_2CH_2C(O)NHOK$, 80%), +31.4, +33.6 (phosphine oxides, 20%).

Coordination of $W(CO)_5$ to Ph_2P−X−$EO_x(OR)_{3-2x}$. A solution of 1.0−1.3 mmol of $W(CO)_6$ in 150−250 mL of diethyl ether was irradiated for 3 h at room temperature. The reaction was controlled by IR spectroscopy. A suspension of an equimolar amount of **2′c**, **2′f**, **3c**, **3f**, **4b**, **4f**, **5a**, or **5f** in 30 mL of diethyl ether or the neat compound was added at −20 °C to the solution of $(CO)_5W(OEt_2)$. The mixture was warmed to room temperature and stirred for 16 h. After removal of all volatiles in vacuo, pale yellow solids were obtained.

*Reaction of **2′c**: $(CO)_5W[Ph_2PCH_2CH_2COOTiO_{0.95}(O^iPr)_{1.1}]$·1.8^{i}PrOH*. Yield 903 mg (85%) ^{1}H NMR (DMSO-d_6, δ, ppm) 1.02, (d, $HOCH(CH_3)_2$, 10.8 H), 1.09 (d, $TiOCH(CH_3)_2$, 6.6 H), 2.19 (m, PCH_2, 2 H), 2.93 (m, PCH_2CH_2, 2 H), 3.75 (m, $HOCH(CH_3)_2$, 1.8 H), 4.35 (d, $HOCH(CH_3)_2$, 1.8 H), 4.77 (m, $TiOCH(CH_3)_2$, 1.1 H), 7.52 (m, Ph, 10 H). ^{31}P NMR (DMSO-d_6, δ, ppm) +10.7 ($^1J_{W-P}$ 118.4 Hz). IR (Et_2O, cm^{-1}) ν(CO) 2070 (s), 1975 (s), 1940 (vs), 1885 (sh). Anal. Calcd: P, 3.79. Found: P, 3.77.

*Reaction of **2′f**: $(CO)_5W[Ph_2PCH_2CH_2COOZrO_{0.8}(O^nPr)_{1.4}]$·2.3PrOH*. Yield 885 mg (75%). ^{1}H NMR (DMSO-d_6, δ, ppm) 0.85 (m, CH_3, 11.1 H), 1.33 (m, CH_2CH_3, 7.4 H), 2.21 (m, PCH_2, 2 H), 2.91 (m, PCH_2CH_2, 2 H), 3.36 (m, $HOCH_2$, 4.6 H), 3.89 (m, $ZrOCH_2$, 2.3 H), 4.31 (br, HO, 2.3 H), 7.53 (m, Ph, 10 H). ^{31}P NMR (DMSO-d_6, δ, ppm) +10.7 ($^1J_{W-P}$ 118.3 Hz). IR (Et_2O, cm^{-1}) ν(CO) 2070 (s), 1975 (s), 1965 (sh), 1940 (vs). Anal. Calcd: P, 3.41. Found: P, 3.56.

*Reaction of **3c***: ^{1}H NMR (DMSO-d_6, δ, ppm) 1.02 (d, $TiOCH(CH_3)_2$), 1.11 (d, $HOCH(CH_3)_2$), 1.34 (s, $C(CH_3)_2$), 2.21 (m, PCH_2CH_2 and $P(O)CH_2CH_2$), 2.65 (m, PCH_2 and CH_2SO_3), 3.30 (m, $P(O)CH_2CH_2$), 3.75 (m, HOCH), 4.34 (m, HO), 4.77 (m, TiOCH), 7.51, 7.78 (m, Ph), 8.14 (s, NH). ^{31}P NMR (DMSO-d_6, δ, ppm) +10.2 ($^1J_{W-P}$ 118.4 Hz, 45%), +9.2 ($^1J_{W-P}$ 114.7 Hz, 5%), +30.5, +31.5, +33.0, +34.1, +40.8 (phosphine oxides and decomposition products, 50%) ppm. IR (THF, cm^{-1}) ν(CO) = 2070 (vs), 2010 (s), 1980 (vs).

*Reaction of **3f***: ^{1}H NMR (DMSO-d_6, δ, ppm) 0.82 (t, CH_3), 1.36, 1.40 (s and m, $C(CH_3)_2$ and CH_2CH_3), 2.23 (m, PCH_2CH_2 and $P(O)CH_2CH_2$), 2.62 (m, PCH_2 and CH_2SO_3), 3.29 (m, Ph_2P-$(O)CH_2$ and $HOCH_2$), 3.82 (t, $ZrOCH_2$), 4.36 (s, HO), 7.51, 7.78 (m, Ph), 8.13 (s, NH). ^{31}P NMR (DMSO-d_6, δ, ppm) +10.2 ($^1J_{W-P}$ 118.4 Hz, 45%), +9.2 ($^1J_{W-P}$ 114.7 Hz, 5%), +30.5, +31.7, +32.9, +34.0, +40.8 (phosphine oxides and decomposition products, 50%). IR (THF, cm^{-1}) ν(CO) = 2070 (vs), 2010 (s), 1980 (vs).

*Reaction of **4b**: $(CO)_5W[PPh_2CH_2CH_2SO_3TiO_{1.5}]$*. ^{1}H NMR (DMSO-$d_6$, δ, ppm) 0.82 (t, $HOCH_2CH_2CH_3$), 1.40 (m, $HOCH_2$-CH_2CH_3), 2.05, 2.26 (CH_2CH_2, decomposition products), 2.57, 2.82 (m, PCH_2CH_2 and $P(O)CH_2CH_2$), 3.35 (m, $HOCH_2$), 4.36 (t, HO), 7.23, 7.39, 7.51, 7.75 (m, Ph). ^{31}P NMR (DMSO-d_6, δ, ppm) +8.0 ($^1J_{W-P}$ 118.4 Hz, 50%), +7.8 ($^1J_{W-P}$ 114.7 Hz, 30%), +14.20 (5%), +30.7 (phosphine oxide, 10%), +31.53 (phosphine oxide, 5%). IR (Nujol, cm^{-1}) ν(CO) = 2060 (s), 2000 (s), 1970 (vs).

*Reaction of **4f**: $(CO)_5W[PPh_2CH_2CH_2SO_3ZrO_{1.5}]$*. ^{1}H NMR (DMSO-$d_6$, δ, ppm) 0.84 (t, $HOCH_2CH_2CH_3$), 1.38 (m, $HOCH_2$-CH_2CH_3), 2.06, 2.27 (CH_2CH_2, decomposition products), 2.54, 2.82 (m, PCH_2CH_2 and $P(O)CH_2CH_2$), 3.35 (m, $HOCH_2$), 4.36 (t, HO), 7.25, 7.51, 7.76 (m, Ph). ^{31}P NMR (DMSO-d_6, δ, ppm)

+8.0 ($^1J_{W-P}$ 118.4 Hz, 20%), +7.8 ($^1J_{W-P}$ 114.7 Hz, 35%), +14.2 (5%), +30.8 (phosphine oxide, 35%), +31.6 (phosphine oxide, 5%). IR (Nujol, cm^{-1}) ν(CO) = 2060 (s), 2000 (vs), 1970 (vs).

Reaction of ***5a****:* ^{1}H NMR (DMSO-d_6, δ, ppm) 0.85 (m, $HOCH_2CH_3$), 1.04 (t, $TiOCH_2CH_3$), 1.79 (m, PCH_2CH_2), 2.19 (PCH_2CH_2), 2.75 (m, $WPPh_2CH_2CH_2$), 3.40 (m, $HOCH_2$), 4.13 (m, $TiOCH_2$), 4.53 (s, br, HO), 7.49, 7.68 (m, Ph and NH). ^{31}P NMR (DMSO-d_6, δ, ppm) +9.0 ($^1J_{W-P}$ 115.9 Hz, 50%), +10.1 (15%), +21.4 (decomposition product, 10%), +31.4, +32.3 (phosphine oxides, 25%). IR (Nujol, cm^{-1}) ν(CO) 2070 (vs), 2010 (s), 1985 (vs).

Reaction of ***5a****:* ^{1}H NMR (DMSO-d_6, δ, ppm) 0.85 (t, CH_3), 1.34 (m, CH_2CH_3), 1.79 (m, PCH_2CH_2), 2.19 (PCH_2CH_2), 2.75 (m, $WPPh_2CH_2$), 3.34 (m, $HOCH_2$), 3.85 (m, $ZrOCH_2$), 4.34 (t, HO), 7.49, 7.68 (m, br, Ph and NH). ^{31}P NMR (DMSO-d_6, δ, ppm) +8.9 ($^1J_{W-P}$ 115.9 Hz, 35%), 10.1 (10%), +21.4 (decomposition product, 20%), +31.4, +32.3 (phosphine oxide, 35%). IR (Nujol, cm^{-1}) 2065 (vs), 2010 (m), 1980 (vs).

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Supporting Information Available: An ORTEP plot with the labeling scheme, full crystal characterization, listings of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

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