

Notiz / Note

Metal Complexes in Inorganic Matrices, 10^[1]Preparation of Phosphanyl–Spacer-Substituted Metal Alkoxides
(RO)₃E–X–PPh₂ (E = Ti, Zr; X = Spacer)

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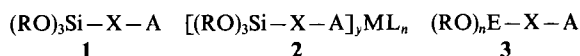
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Heterogenization of metal complexes

The reaction of HPPH₂ with (PrO)₃E(O₂CCH=CH₂) (E = Ti, Zr), formed in situ by the reaction of E(OPr)₄ with acrylic acid, gives the phosphanylpropionate derivatives (PrO)₃E(O₂CCH₂CH₂PPh₂). The phosphanylacetate derivative

(PrO)₃Zr(O₂CCH₂PPh₂) was obtained by treatment of (PrO)₃Zr(O₂CCH₂Cl) with LiPPh₂. (BuO)₃Ti(π-C₅H₄[CH₂]₂PPh₂) was prepared by the reaction of Li(C₅H₄[CH₂]₂PPh₂) with (BuO)₃-TiCl.

Hydrolyzable silanes of the type (RO)₃Si–X–A (**1**) having a functional organic group A bound to the silicon atom via a hydrolytically stable spacer X have found widespread industrial applications^[2]. One of the many possible functions of A is that of binding metal ions or metal complex fragments ML_n. There is an extensive chemistry of Si(OR)₃-substituted complexes of the general formula [(RO)₃Si–X–A]_nML_n (**2**), mostly with X = [CH₂]_n, with respect to binding catalytically active metal complex moieties to silica^[3], either by reaction of these compounds with the surface OH groups of silica gels or by employing them in the sol-gel method^[1,2,4].



For some catalytic reactions other supports than silica may be more interesting, for instance to make use of synergistic effects between the metal complex and its support. To link metal complex moieties or metal ions to other supports, for instance alumina, titania or zirconia, organically modified alkoxides of the type (RO)_nE–X–A (**3**) (E = Al, Ti, Zr, etc.) are required. However, such compounds are not readily available. Due to their hydrolytic lability, E–C bonds cannot be used to link the functional group A to the E(OR)₃ moiety. Therefore, other spacers X, such as carboxylate, β-diketonate or related groups, must be chosen (see ref.^[5] for an example). It is well-known that on reaction of Al, Ti or Zr alkoxides with carboxylic acids some of the alkoxy groups are replaced by carboxylate ligands. The carboxylate-modified alkoxides can be used as precursors in the sol-gel process, during which the alkoxy groups and not the carboxylate ligand are primarily hydrolyzed^[6].

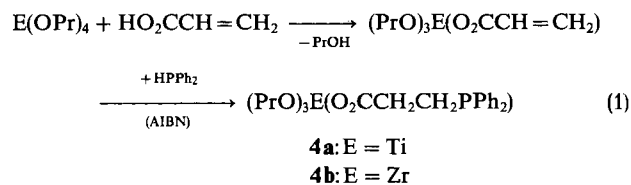
In this paper we report on the preparation of compounds of the type (RO)₃E–X–A (E = Ti, Zr) in which the group A is a PPh₂ moiety.

Results and Discussion

When Ti(OEt)₄ in ethanol was treated with an equimolar amount of (diphenylphosphanyl)succinic acid or 3-(diphenylphosphanyl)-

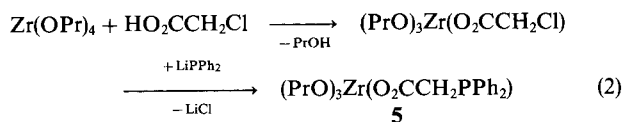
propionic acid, only insoluble precipitates were obtained. We therefore tried to prepare derivatives of the type (RO)₃E(O₂C[CH₂]_nPPh₂) (E = Ti, Zr) by stepwise routes. [In this article only monomeric formulae are given for simplicity, although compounds (RO)₃E(O₂CR') are probably dimeric or oligomeric.]

We have recently shown that Ti(OEt)₄ or Zr(OPr)₄ react with an equimolar amount of methacrylic acid to give (RO)₃E(O₂CC(Me)=CH₂)^[7]. The compounds (PrO)₃E(O₂CCH=CH₂) were analogously prepared by the reaction of E(OPr)₄ with acrylic acid in toluene (Eq. 1). Although the acrylate derivatives were not isolated, the IR and ¹H-NMR spectra clearly indicated their formation. The addition of HPPH₂ to the acrylic double bond in the presence of a radical initiator [Azobisisobutyronitrile (AIBN)] proceeded smoothly at elevated temperatures. The resulting 3-(diphenylphosphanyl)propionate derivatives **4** were isolated as colorless solids. Due to the formation of small amounts of phosphonium compounds (probably by the reaction of **4** with unreacted acrylic acid), which could not be separated, the new metal alkoxide derivatives **4a**, **b** were only spectroscopically characterized. However, the spectroscopic data, particularly the disappearance of the PH and CH=CH₂ signals in the ¹H-NMR spectra and the appearance of new signals characteristic of a O₂CCH₂CH₂P grouping, were fully consistent with the composition of **4**.



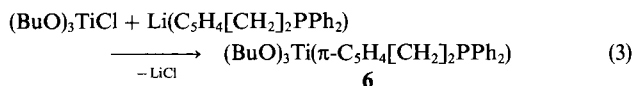
In another approach Issleib's method of preparing (phosphanylalkyl)carboxylic acids by the reaction of HO₂CCHRY (Y = halide) with PPh₂^[8] was successfully applied to a chloroacetate-substituted zirconium alkoxide. The latter was prepared in situ by the reaction of Zr(OPr)₄ with chloroacetic acid (Eq. 2). The liberated propanol was removed by azeotropic distillation. The reaction of the formed

(PrO)₃Zr(O₂CCH₂Cl) with LiPPh₂ gave the (diphenylphosphanyl)-acetate derivative **5** in good yield.



We were unable to prepare the corresponding titanium derivative due to decomposition reactions, which could not be avoided even by variation of the reaction conditions.

Compounds of the type (π -C₅H₄R)Ti(OR')₃ are known for a variety of substituents at the cyclopentadienyl (Cp) ring. The Ti–Cp bond is stable under mild hydrolytic conditions. Therefore, a π -C₅H₄[CH₂]_n moiety may also serve as the group X in compounds of the type (RO)₃E–X–PR₂ to link E(OR)₃ moieties and phosphanyl groups. Li(C₅H₄[CH₂]₂PPh₂) was prepared from spiro-[4.2]hepta-1,3-diene and LiPPh₂^[9]. Its reaction with (BuO)₃TiCl gave the phosphanyl-containing titanium alkoxide **6** in very high yield (Eq. 3). The analogous zirconium compound, (PrO)₃Zr(π -C₅H₄[CH₂]₂PPh₂), prepared in the same way proved to be more difficult to purify.



The ³¹P-NMR resonance signals of the new compounds **4**–**6** are in the typical range of tertiary phosphanes, indicating that there is no significant interaction between the phosphorus and the titanium or zirconium atom. Preliminary experiments indeed show that **4**–**6** can be used as novel phosphane ligands in transition-metal complexes.

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Experimental

All operations were performed under dry and O₂-free N₂ by using dried and N₂-saturated solvents. – IR: Perkin-Elmer 283. – ¹H NMR: Bruker AC200 and Jeol FX-90Q. – ³¹P NMR: Jeol FX-90Q (36.23 MHz) rel. to ext. 85% H₃PO₄. – ¹³C NMR: Bruker AC 200 (50.3 MHz). – Melting points: Differential thermal analysis; DuPont Thermal Analyzer 990.

Preparation of (PrO)₃E(O₂C[CH₂]₂PPh₂) (4a: E = Ti; 4b: E = Zr): A solution of 5 mmol of E(OPr)₄ and 5 mmol (0.36 g) of acrylic acid in 20 ml of toluene is refluxed for 1 h. To characterize the compounds (PrO)₃E(O₂CCH=CH₂), the toluene/propanol mixture is removed in vacuo to give colorless oils. – ¹H NMR (CDCl₃, 30°C; for both E = Ti and Zr): δ = 6.5 (m, 3H, CH=CH₂), 4.4 (m, 6H, OCH₂), 1.8 (m, 6H, CH₂CH₃), 1.2 (m, 9H, CH₂CH₃). – For the preparation of **1**, 5 mmol (0.93 g) of HPPPh₂ and ca. 100 mg of AIBN is added to the toluene solution of (PrO)₃E(O₂CCH=CH₂), which is then heated to 60°C for 2 h. The reaction is monitored by IR spectroscopy [disappearance of ν (PH)]. The solution is concentrated to 5 ml. Upon addition of 10 ml of pentane compounds **1** precipitate as colorless solids.

4a: Yield 0.9 g (37%). – ¹H NMR (CDCl₃, 30°C): δ = 7.7–7.0 (m, 10H, Ph), 4.3 (m, 6H, OCH₂), 3.5 (m, 2H, PCH₂), 2.3 (m, 2H, O₂CCH₂), 1.4 (m, 6H, CH₂CH₃), 0.7 (m, 9H, CH₂CH₃). – ³¹P{¹H} NMR (CDCl₃, 30°C): δ = –15.6.

5b: Yield 1.1 g (42%). – ¹H NMR (CDCl₃, 30°C): δ = 7.8–7.1 (m, 10H, Ph), 4.2 (m, 6H, OCH₂), 3.6 (m, 2H, PCH₂), 2.5 (m, 2H,

O₂CCH₂), 1.5 (m, 6H, CH₂CH₃), 0.8 (m, 9H, CH₂CH₃). – ³¹P{¹H} NMR (CDCl₃, 30°C): δ = –15.3.

Preparation of (PrO)₃Zr(O₂CCH₂PPh₂) (5): 3 mmol (0.98 g) of Zr(OPr)₄ is allowed to react with 3 mmol (0.28 g) of chloroacetic acid in 20 ml of toluene at 25°C for 1 h. The produced propanol is removed by azeotropic distillation. The residue, consisting of (PrO)₃Zr(O₂CCH₂Cl), is dissolved in 15 ml of THF/ether (1:1), then 3 mmol (0.58 g) of LiPPh₂ in 10 ml of THF is added dropwise to the solution. After stirring at room temp. for 1 h, the precipitated LiCl is filtered off. After concentration of the filtrate to 5 ml and addition of 10 ml of pentane, **5** precipitates as a colorless solid. Yield 0.73 g (62%); m.p. 54°C (dec.). – ¹H NMR (CDCl₃, 30°C): δ = 7.2 (m, 10H, Ph), 3.9 (m, 6H, OCH₂), 1.5 (m, 8H, PCH₂ and CH₂CH₃), 0.8 (m, 9H, CH₂CH₃). – ³¹P{¹H} NMR (CDCl₃, 30°C): δ = –14.9. – For elemental analysis **5** is converted into its phosphonium salt: An excess of MeI is added dropwise to a toluene solution of **5**. The mixture is then stirred at room temp. for 2 h. The colorless precipitate is filtered off, washed with 2 ml of pentane and dried in vacuo.

C₂₄H₃₃I_{0.5}PZr (508.5) Calcd. C 44.10 H 5.55
Found C 44.07 H 5.26

Preparation of (BuO)₃Ti(π -C₅H₄[CH₂]₂PPh₂) (6): A solution of 43 mmol (13.0 g) of (BuO)₃TiCl^[10] in 25 ml of pentane is added to 43 mmol (12.1 g) of Li(C₅H₄[CH₂]₂PPh₂)^[9] in 25 ml of pentane. After 2 h at room temperature, LiCl is filtered off. Removal of the solvent in vacuo gives 21 g (90%) of **6** as a yellowish oil. – ¹H NMR (C₆D₆, 30°C): δ = 7.5 (m, 10H, Ph), 6.0 (m, 4H, C₅H₄), 4.2 [t, 6H, OCH₂, ³J(HCCH) = 6 Hz], 2.72 and 2.40 (m, 4H, C₅H₄CH₂CH₂), 1.3 (m, 12H, OCH₂[CH₂]₂), 0.9 [t, 9H, CH₂CH₃]. – ³¹P{¹H} NMR (CDCl₃, 30°C): δ = –15.9. – ¹³C NMR (CDCl₃, 30°C): δ = 138.0, 132.8, 132.1, 131.6, 130.6, 128.4 (C₆H₅); 112.0 (C₅H₄, C-*i*); 76.2 (C₅H₄); 62.1 (OCH₂); 35.9 (OCH₂CH₂); 28.5 [PCH₂CH₂, ²J(PCC) = 12 Hz], 25.4 [PCH₂, ¹J(PC) = 20 Hz], 18.9 (OCH₂CH₂CH₂), 13.9 (CH₃). – For elemental analysis **6** is converted into its phosphonium salt as described for **5**; m.p. 72°C (dec.).

C₃₃H₄₈I_{0.5}PTi (686.5) Calcd. C 55.99 H 7.05
Found C 55.44 H 5.86

- [1] Part 9: U. Schubert, B. Breitscheidel, H. Buhler, C. Egger, W. Urbaniak, *Mater. Res. Soc. Symp. Proc.* **1992**, 271, 621.
- [2] U. Deschler, P. Kleinschmit, P. Panster, *Angew. Chem.* **1986**, 98, 237; *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 236.
- [3] F. R. Hartley, *Supported Metal Complexes*, D. Reidel Publ. Comp., Dordrecht, **1985**; Yu. I. Yermakov, B. N. Kuznetsov, V. A. Zakharov, *Catalyses by Supported Complexes*, Elsevier Sci. Publ. Comp., Amsterdam, **1981**; C. U. Pitman, Jr., in *Comprehensive Organometallic Chemistry* (Ed.: G. Wilkinson), vol. 8, Pergamon Press, New York, **1982**, p. 253.
- [4] U. Schubert, K. Rose, H. Schmidt, *J. Non-Cryst. Solids* **1988**, 105, 165; U. Schubert, C. Egger, K. Rose, C. Alt, *J. Mol. Catal.* **1989**, 55, 330; M. Capka, U. Schubert, B. Heinrich, J. Hyortkjaer, *Coll. Czech. Chem. Comm.*, in press; M. Capka, M. Czakoova, W. Urbaniak, U. Schubert, *J. Mol. Catal.* **1992**, 74, 335.
- [5] U. Schubert, H. Buhler, B. Hirle, *Chem. Ber.* **1992**, 125, 999.
- [6] C. Sanchez, J. Livage, M. Henry, F. Babonneau, *J. Non-Cryst. Solids* **1988**, 100, 65; C. Sanchez, J. Livage, *New J. Chem.* **1990**, 14, 513.
- [7] U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich, C. Chau, *Chem. Mater.* **1992**, 4, 291.
- [8] K. Issleib, G. Thomas, *Chem. Ber.* **1960**, 93, 803.
- [9] T. Kauffmann, J. Ennen, H. Lhotak, A. Rensing, F. Steinseifer, A. Woltermann, *Angew. Chem.* **1980**, 92, 321; *Angew. Chem. Int. Ed. Engl.* **1980**, 19, 328.
- [10] H. Holloway, *Chem. Ind. (London)* **1962**, 214.

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