Notiz / Note

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Preparation of Phosphanyl – Spacer-Substituted Metal Alkoxides $(RO)_3E-X-PPh_2$ (E = Ti, Zr; X = Spacer)

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The reaction of $HPPh_2$ with $(PrO)_3E(O_2CCH{=}CH_2)$ (E = Ti, Zr), formed in situ by the reaction of $E(OPr)_4$ with acrylic acid, gives the phosphanylpropionate derivatives $(PrO)_3E(O_2CCH_2CH_2PPh_2)$. The phosphanylacetate derivative $(PrO)_3Zr(O_2CCH_2PPh_2)$ was obtained by treatment of $(PrO)_3Zr(O_2CCH_2Cl)$ with $LiPPh_2$. $(BuO)_3Ti(\pi\text{-}C_5H_4[CH_2]_2PPh_2)$ was prepared by the reaction of $Li(C_5H_4[CH_2]_2PPh_2)$ with $(BuO)_3TiCl$.

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 $[(RO)_3Si-X-A]_yML_n$ (**2**), mostly with X = $[CH_2]_n$, 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].

$$\underset{\mathbf{1}}{(RO)_3Si-X-A} \quad \underset{\mathbf{2}}{[(RO)_3Si-X-A]_yML_n} \quad \underset{\mathbf{3}}{(RO)_nE-X-A}$$

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 PPh_2 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 $(RO)_3E(O_2C[CH_2]_nPPh_2)$ (E = Ti, Zr) by stepwise routes. [In this article only monomeric formulae are given for simplicity, although compounds $(RO)_3E(O_2CR')$ 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 $(RO)_3E[O_2CC(Me){=}CH_2]$[7]. The compounds $(PrO)_3E(O_2CCH{=}CH_2)$ 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 $HPPh_2$ 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 $CH{=}CH_2$ signals in the ^1H-NMR spectra and the appearance of new signals characteristic of a $O_2CCH_2CH_2P$ grouping, were fully consistent with the composition of **4**.

$$E(OPr)_4 + HO_2CCH{=}CH_2 \xrightarrow[-PrOH]{} (PrO)_3E(O_2CCH{=}CH_2)$$

$$\xrightarrow[(AIBN)]{+HPPh_2} (PrO)_3E(O_2CCH_2CH_2PPh_2) \qquad (1)$$

4a: E = Ti
4b: E = Zr

In another approach Issleib's method of preparing (phosphanylalkyl)carboxylic acids by the reaction of HO_2CCHRY (Y = halide) with PPh_2^- [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

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$(PrO)_3Zr(O_2CCH_2Cl)$ with $LiPPh_2$ gave the (diphenylphosphanyl)-acetate derivative **5** in good yield.

$$\mathrm{Zr(OPr)_4 + HO_2CCH_2Cl \xrightarrow[-\,PrOH]{} (PrO)_3Zr(O_2CCH_2Cl)}$$
$$\mathrm{\xrightarrow[-\,LiCl]{+\,LiPPh_2} \underset{\mathbf{5}}{(PrO)_3Zr(O_2CCH_2PPh_2)}} \qquad (2)$$

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 $(\pi\text{-}C_5H_4R)Ti(OR')_3$ are known for a variety of substituents at the cyclopentadienyl (Cp) ring. The Ti–Cp bond is stable under mild hydrolytic conditions. Therefore, a $\pi\text{-}C_5H_4[CH_2]_n$ moiety may also serve as the group X in compounds of the type $(RO)_3E-X-PR_2$ to link $E(OR)_3$ moieties and phosphanyl groups. $Li(C_5H_4[CH_2]_2PPh_2)$ was prepared from spiro[4.2]hepta-1,3-diene and $LiPPh_2$[9]. Its reaction with $(BuO)_3TiCl$ gave the phosphanyl-containing titanium alkoxide **6** in very high yield (Eq. 3). The analogous zirconium compound, $(PrO)_3Zr(\pi\text{-}C_5H_4[CH_2]_2PPh_2)$, prepared in the same way proved to be more difficult to purify.

$$\mathrm{(BuO)_3TiCl + Li(C_5H_4[CH_2]_2PPh_2)}$$
$$\mathrm{\xrightarrow[-\,LiCl]{} \underset{\mathbf{6}}{(BuO)_3Ti(\pi\text{-}C_5H_4[CH_2]_2PPh_2)}} \qquad (3)$$

The ^{31}P-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 O_2-free N_2 by using dried and N_2-saturated solvents. – IR: Perkin-Elmer 283. – ^1H NMR: Bruker AC200 and Jeol FX-90Q. – ^{31}P NMR: Jeol FX-90Q (36.23 MHz) rel. to ext. 85% H_3PO_4. – ^{13}C NMR: Bruker AC 200 (50.3 MHz). – Melting points: Differential thermal analysis; DuPont Thermal Analyzer 990.

Preparation of $(PrO)_3E(O_2C[CH_2]_2PPh_2)$ (**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 $(PrO)_3E(O_2CCH=CH_2)$, the toluene/propanol mixture is removed in vacuo to give colorless oils. – ^1H NMR ($CDCl_3$, 30°C; for both E = Ti and Zr): δ = 6.5 (m, 3H, $CH=CH_2$), 4.4 (m, 6H, OCH_2), 1.8 (m, 6H, CH_2CH_3), 1.2 (m, 9H, CH_2CH_3). – For the preparation of **1**, 5 mmol (0.93 g) of $HPPh_2$ and ca. 100 mg of AIBN is added to the toluene solution of $(PrO)_3E(O_2CCH=CH_2)$, 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 ($CDCl_3$, 30°C): δ = 7.7–7.0 (m, 10H, Ph), 4.3 (m, 6H, OCH_2), 3.5 (m, 2H, PCH_2), 2.3 (m, 2H, O_2CCH_2), 1.4 (m, 6H, CH_2CH_3), 0.7 (m, 9H, CH_2CH_3). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 30°C): δ = –15.6.

5b: Yield 1.1 g (42%). – ^1H NMR ($CDCl_3$, 30°C): δ = 7.8–7.1 (m, 10H, Ph), 4.2 (m, 6H, OCH_2), 3.6 (m, 2H, PCH_2), 2.5 (m, 2H, O_2CCH_2), 1.5 (m, 6H, CH_2CH_3), 0.8 (m, 9H, CH_2CH_3). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 30°C): δ = –15.3.

Preparation of $(PrO)_3Zr(O_2CCH_2PPh_2)$ (**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 $(PrO)_3Zr(O_2CCH_2Cl)$, is dissolved in 15 ml of THF/ether (1:1), then 3 mmol (0.58 g) of $LiPPh_2$ 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 ($CDCl_3$, 30°C): δ = 7.2 (m, 10H, Ph), 3.9 (m, 6H, OCH_2), 1.5 (m, 8H, PCH_2 and CH_2CH_3), 0.8 (m, 9H, CH_2CH_3). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 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.

$C_{24}H_{33}IO_5PZr$ (508.5) Calcd. C 44.10 H 5.55
Found C 44.07 H 5.26

Preparation of $(BuO)_3Ti(\pi\text{-}C_5H_4[CH_2]_2PPh_2)$ (**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 $Li(C_5H_4[CH_2]_2PPh_2)$[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 **3** as a yellowish oil. – ^1H NMR (C_6D_6, 30°C): δ = 7.5 (m, 10H, Ph), 6.0 (m, 4H, C_5H_4), 4.2 [t, 6H, OCH_2, ^3J(HCCH) = 6 Hz], 2.72 and 2.40 (m, 4H, $C_5H_4CH_2CH_2$), 1.3 (m, 12H, $OCH_2[CH_2]_2$), 0.9 [t, 9H, CH_2CH_3]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 30°C): δ = –15.9. – ^{13}C NMR ($CDCl_3$, 30°C): δ = 138.0, 132.8, 132.1, 131.6, 130.6, 128.4 (C_6H_5); 112.0 (C_5H_4, C-*i*); 76.2 (C_5H_4); 62.1 (OCH_2); 35.9 (OCH_2CH_2); 28.5 [PCH_2CH_2, ^2J(PCC) = 12 Hz], 25.4 [PCH_2, ^1J(PC) = 20 Hz], 18.9 ($OCH_2CH_2CH_2$), 13.9 (CH_3). – For elemental analysis **6** is converted into its phosphonium salt as described for **5**; m.p. 72°C (dec.).

$C_{33}H_{48}IO_3PTi$ (686.5) Calcd. C 55.99 H 7.05
Found C 55.44 H 5.86

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