Easy one-pot synthesis of new dppm-type linkers for immobilizations

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Received (in Cambridge, UK) 6th September 2004, Accepted 2nd December 2004
First published as an Advance Article on the web 25th January 2005
DOI: 10.1039/b413642j

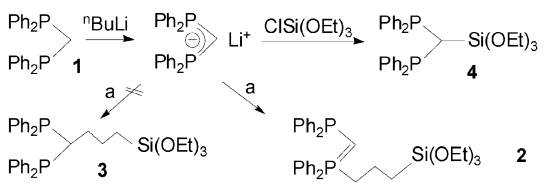
New synthetic routes to symmetric and unsymmetric dppm-type chelate linkers containing the ethoxysilane group are described and the compounds were characterized also by solid-state NMR spectroscopy and X-ray structures.

Linkers are critical in many fields of chemistry, where a soluble species has to be attached to a solid, or generally, where the surface has to be modified in a controlled manner. Thus, the interest in suitable linkers spans the broad range from combinatorial chemistry and solid-phase synthesis[1] over chromatography and silica modification[2] to immobilized catalysts.[3,4] For attaching phosphine linkers to oxidic surfaces, ethoxysilane groups are most favorable, and many dppe- and dppp-type chelate phosphine linkers have successfully been synthesized and applied for anchoring catalysts,[5a–f] after having learned about how to avoid quaternization of the phosphine moieties.[5g] Surprisingly, only one symmetrical dppm-type linker with two ethoxysilane groups has been reported which is, however, difficult to purify.[6] The lack of dppm-type linkers is most probably due to the difficulties in their synthesis, as outlined below. Bisphosphinoamine linkers, such as, *e.g.*, $(Ph_2P)_2N(CH_2)_3Si(OMe)_3$ can easily be synthesized in high yields, and they are successfully applied in coordination chemistry.[7] However, they have rather large P–N–P angles,[7,8] and they decompose on the silica surface.[8] The biggest problem when trying to introduce one ethoxysilane group to dppm (**1**) is that although it can be deprotonated readily,[9] usually electrophiles attack at the phosphine moieties, producing ylides (Scheme 1). This is *e.g.* the case when **1-Li** is reacted with $Cl(CH_2)_3Si(OEt)_3$ which, even under varied reaction conditions using different solvents, temperatures, TMEDA, crown ethers, *etc.*, leads to the ylide **2**. The desired product **3** was never present in substantial amounts, as checked by ^{31}P NMR. Also, the reaction of **1-Li** with $Si(OEt)_4$ did not result in the desired **4**. However, using the more aggressive $ClSi(OEt)_3$ as the quenching reagent, **4** could be obtained in 70% yield.

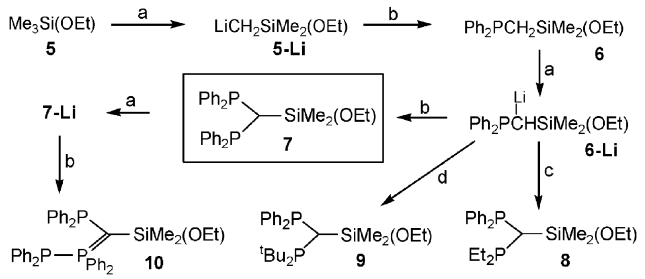
Next, we sought a versatile route that would allow us also to synthesize unsymmetrical chelates. Therefore, we made use of the regiospecific synthesis of α-lithiated alkoxysilanes, as described by Thomas *et al.*[10] The deprotonation of $Me_3Si(OEt)$ (**5**) with ^tBuLi in pentane at −78 °C leads to **5-Li** (Scheme 2). This anion can be quenched at −30 °C with Ph_2PCl to give the monodentate phosphine **6** in 77% unoptimized yield after filtration and Kugelrohr distillation. The anion **6-Li** is obtained by deprotonating **6** again in the same way with ^tBuLi, and treatment with Ph_2PCl finally gives the target molecule **7** in 82% yield after crystallization.† Using different chlorophosphines, *e.g.* Et_2PCl or $^tBu_2PCl$ in the second step also allows the easy synthesis of unsymmetrical chelate phosphines such as **8** and **9** (Scheme 2) that have great potential for later applications in asymmetric catalysis. This one-pot synthesis is all the more remarkable because, even without ethoxysilane groups, the preparation of such unsymmetric dppm derivatives has up to now been rather tedious.[11]

While the methyl group of $MeSi(OEt)_3$ could not be deprotonated in a well-defined manner, $Ph_2PCH_2Si(OEt)_3$ (**11**) could be obtained in 98% yield by the reaction of Ph_2PLi with $ClCH_2Si(OEt)_3$. Subsequent selective deprotonation of the methylene group between P and Si, and quenching with Ph_2PCl led to **4** in 87% yield.

The chelate phosphine **7** crystallizes readily in large colorless single crystals of 5 mm diameter, and it could be subjected to an X-ray analysis. The crystal structure (Fig. 1) shows a P–C–P angle of 106.8(1)°. Due to steric reasons this is somewhat smaller than the ideal tetrahedral angle expected from the sp^3 configuration of the center carbon. The ethoxy group is aligned parallel to one of the phenyl groups, while the two methyl groups shield the "back side" of the molecule. The unit cell contains four molecules with eight magnetically non-equivalent ^{31}P nuclei. This is confirmed by the eight lines in the static ^{31}P CP spectra of one large single crystal that were recorded without MAS (Fig. 2). The small half-width of the lines indicates that the ^{31}P–^{31}P dipolar interactions that are not reduced by MAS here, are rather small, although the ^{31}P nuclei are not "chemically dilute" in the molecule, and rather close to each other. They even evoke an extensive set of virtual couplings with the phenyl carbon nuclei† of **7**, a sign that the intrinsic scalar $^2J_{PP}$



Scheme 1 Synthesis of compounds **2** and **4** from **1-Li**; a: $Cl(CH_2)_3Si(OEt)_3$.



Scheme 2 Synthesis of various dppm-type chelate linkers; a: ^tBuLi; b: Ph_2PCl; c: Et_2PCl; d: $^tBu_2PCl$.

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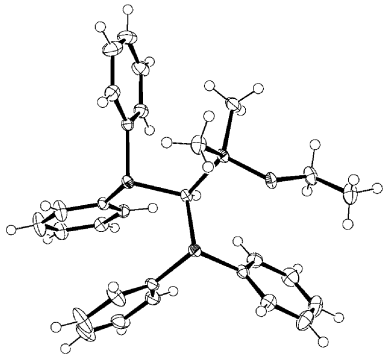

Fig. 1 Crystal structure of **7**.‡

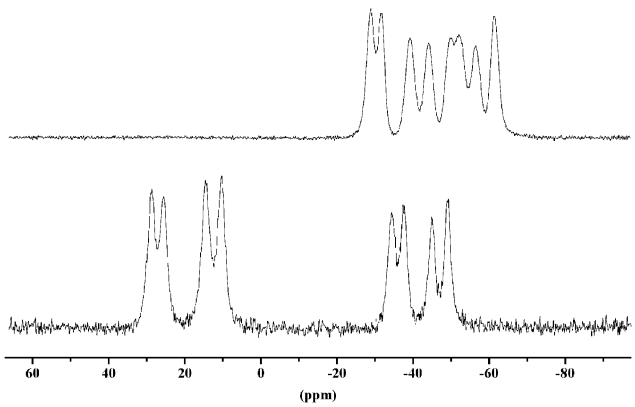

Fig. 2 ^{31}P CP spectra of two different random orientations of a single crystal of **7**. Measurement parameters see ref. 12.

value is rather large. The visible $^{2}J_{PP}$ coupling *e.g.* in **8** is 39.1 Hz. Furthermore, the lines of the single crystal on changing its orientation cover all the CSA range, as shown for two representative spectra in Fig. 2.

The attempt to synthesize a chelate with three phosphine moieties by deprotonating **7**, and subsequently treating it with Ph_2PCl led to the ylide **10**. Interestingly, no *trans*-ylide forms, most probably because of the steric hindrance of the Ph_2PCl attack from the back side due to the bulky $SiMe_2(OEt)$ group. Furthermore, no rearrangement to the triphosphine could be detected, as described for ylides without ethoxysilane groups.[13] Compound **10** crystallized readily and gave the X-ray structure displayed in Fig. 3, with two crystallographically independent molecules. The main difference between both molecules was found to be the inclination

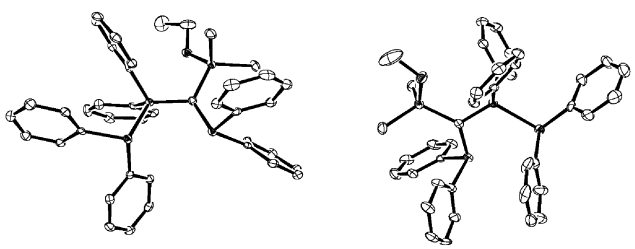

Fig. 3 Crystal structures of **10**, two crystallographically independent molecules.‡

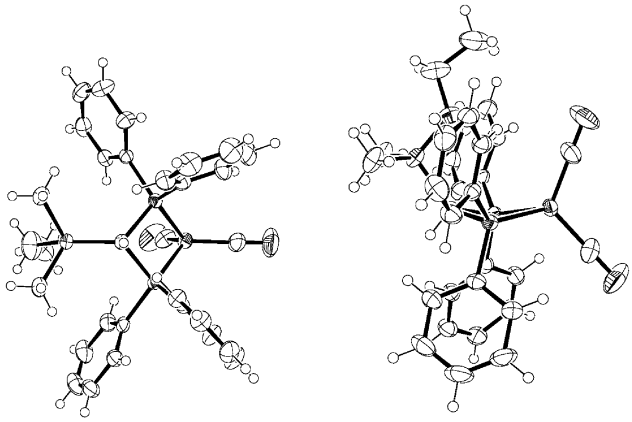

Fig. 4 Two views of the crystal structure of **11**.‡

angles of corresponding phenyl rings, while the torsion angles P–P–C–P were almost identical.

In order to test the potential of **7** as a coordinating ligand, we synthesized its dicarbonylnickel complex **11** in 98% raw yield§ according to the procedure described previously.[5e,f] The most interesting NMR feature is again the presence of virtual couplings in the ^{13}C spectrum.§ As the X-ray structure analysis of a crystal of the dicarbonylnickel complex shows in Fig. 4, **11** represents a not-quite planar four-membered metallacycle with a folding angle of 24.5° with respect to the P,P diagonal. The P–C–P angle in **11** is reduced to 93.4° due to the coordination. Both C–P–Ni angles of the metallacycle are similar with 93.3/93.4°, while P–Ni–P is merely 74.9°, thus deviating very much from the theoretical angle required for tetrahedral coordination. The phenyl groups are aligned in such a way as to accommodate the $Ni(CO)_2$ fragment (Fig. 4).

In this contribution we have outlined short and versatile synthetic routes that give easy access not only to symmetric, but also to unsymmetric chelate linkers with ethoxysilane groups. As a first step towards the many possible applications, we showed in one representative case that the ligand can coordinate to a transition metal in a well-defined manner. We will study the immobilization and the catalytic properties of such metal complexes next.

We thank the Deutsche Forschungsgemeinschaft (DFG, SFB 623) for financial support.

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Notes and references

† Colorless crystals, mp 60 °C (from n-pentane); δ(^{1}H) (300 MHz, C_6D_6) 7.63 (t, $^3J_{HH}$ 3.5 Hz, H_o), 7.04–6.99 (m, H_m, H_p), 3.31 (q, $^3J_{HH}$ 7.0 Hz, OCH_2), 3.04 (s, C*H*), 0.92 (t, $^3J_{HH}$ 7.0 Hz, CH_2CH_3), −0.04 (s, $SiCH_3$); δ(^{13}C) (75.5 MHz, acetone-d_6) 139.3 (virtual t, J_{PC} 3.8 Hz, C_i), 138.5 (virt. t, J_{PC} 5.9 Hz, C_i'), 135.1 (virt. t, J_{PC} 11.7 Hz, C_o), 134.5 (virt. t, J_{PC} 11.7 Hz, C_o'), 129.3 (s, C_p), 128.9 (s, C_p'), 128.6 (virt. t, J_{PC} 3.8 Hz, C_m), 128.3 (virt. t, J_{PC} 3.8 Hz, C_m'), 58.4 (s, CH_2), 20.1 (t, $^1J_{PC}$ 21.0 Hz, *C*H), 18.3 (s, CH_2CH_3), −0.14 (s, $SiCH_3$); δ(^{31}P) (121.5 MHz, C_6D_6) −12.64; δ(^{29}Si) (99.4 MHz. C_6D_6) 12.59 (t, J_{PSi} 10.7 Hz); elemental analysis: C 71.29, H 6.60, P 12.56% (calcd. C 71.58, H 6.63, P 12.74%); MS (EI) *m*/*z* (%) 486 (73) [M^+], 383 (40) [$M^+ - SiMe_2OEt$], 301 (46) [$M^+ - PPh_2$], 262 (100) PPh_3, 103 (55) [$M^+ - Ph_2PPPh_2$].

‡ Crystal data: for **7**: $C_{29}H_{32}OP_2Si$, M = 486.58, monoclinic, space group $P2_1/n$, a = 11.282(3), b = 12.582(3), c = 18.736(4) Å, β = 90.513(5)°, V = 2659.4(10) Å^3, T = 100 K, Z = 4, μ = 0.228 mm^{-1}, T_{min} = 0.94, T_{max} = 0.98, 26813 reflections measured, 6585 unique (R_{int} = 0.051), 5419 observed [$I > 2\sigma(I)$], R_1 = 0.056, wR_2 = 0.111 [$I > 2\sigma(I)$]. CCDC 249320. For **10**: $C_{41}H_{41}OP_3Si$, M = 670.74, triclinic, space group $P\bar{1}$, a = 10.662(1), b = 11.165(1), c = 31.824(3) Å, α = 81.616(2)°, β = 81.460(2)°, γ = 73.455(2)°, V = 3569.7(6) Å^3, T = 100 K, Z = 4, μ = 0.232 mm^{-1}, T_{min} = 0.94, T_{max} = 0.98, 28088 reflections measured, 12028 unique (R_{int} = 0.054), 9256 observed [$I > 2\sigma(I)$], R_1 = 0.059, wR_2 = 0.110 [$I > 2\sigma(I)$]. CCDC 249321. For **11**: $C_{31}H_{32}NiO_3P_2Si$, M = 601.31, orthorhombic, space group $Pca2_1$, a = 18.9502(3), b = 10.9104(2), c = 14.8819(2) Å, V = 3076.90(9) Å^3, T = 200(2) K, Z = 4, μ = 0.803 mm^{-1}, T_{min} = 0.79, T_{max} = 0.88, 30254 reflections measured, 7017 unique (R_{int} = 0.050), 5547 observed [$I > 2\sigma(I)$], R_1 = 0.031, wR_2 = 0.063 [$I > 2\sigma(I)$].CCDC 256229. See http://www.rsc.org/suppdata/cc/b4/b413642j/ for crystallographic data in .cif or other electronic format.

§ Colorless powder; δ(^{1}H) (300 MHz, C_6D_6) 8.10 (virt. q, J_{PH} 5.4 Hz, H_o), 7.94 (virt. q, J_{PH} 5.4 Hz, H_o'); 7.17–6.99 (m, H_m, H_p), 4.53 (t, $^2J_{PH}$ 9.7 Hz, C*H*), 3.16 (q, $^3J_{HH}$ 6.9 Hz, OC*H*$_2$), 1.07 (t, $^3J_{HH}$ 7.0 Hz, CH$_2$C*H*$_3$), −0.44 (s, SiC*H*$_3$); δ(^{13}C) (75.5 MHz, acetone-d_6) 204.0 (*C*O), 200.8 (*C*O′), 138.3 (virt. t, J_{PC} 17.2 Hz, C_i, C_i'), 135.3 (virt. t, J_{PC} 8.5 Hz, C_o), 132.6 (virt. t, J_{PC} 7.9 Hz, C_o'), 131.0 (s, C_p), 130.1 (s, C_p'), 129.2 (virt. t, J_{PC} 4.8 Hz, C_m), 128.8 (virt. t, J_{PC} 5.1 Hz, C_m'), 58.2 (s, *C*H$_2$), 44.5 (t, $^1J_{PC}$ 7.6 Hz, *C*H), 18.3 (s, CH$_2$*C*H$_3$), −0.7 (s, Si*C*H$_3$); δ(^{31}P) (121.5 MHz, C_6D_6) 20.32; δ (^{29}Si) (59.6 MHz, C_6D_6) 8.95 (t, J_{PSi} 9.0 Hz).

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