Synthesis and X-ray structure of [(THF)K($C_5H_4CH_2CH_2PPh_2$)]$_\infty$: a structurally characterized heavier alkali metal phosphane complex

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Reaction of spiro[2.4]hepta-4,6-diene with $KPPh_2$ in THF gives K($C_5H_4CH_2CH_2PPh_2$) 1, which crystallizes from THF and shows coordination of a neutral phosphane functionality to potassium.

Stable complexes with phosphorus to alkali metal bonds are obtained with anionic phosphane type ligands like phosphanides {*e.g.* [KPHMes*]$_\infty$,[1] [K_3(THF){PH(Mes)}$_3$]$_\infty$,[2] [K(THF)P($SiMe_3$)$_2$][3]}. In these complexes phosphorus is of the σ^2, λ^3-type. So far there is no example for coordination of a neutral phosphane (σ^3, λ^3) to a heavier alkali metal center (K, Rb, Cs)[4] with one remarkable exception: In [{(Bu^tP)$_2$H}K•pmdeta]$_2$ (pmdeta = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine), a 'secondary coordinative interaction' of the neutral phosphorus to potassium is defined, containing a long K–P interaction of 3.658 (3) Å. This phosphorus is directly attached to a neighbouring phosphanide P-atom,[5] formally introducing the negative charge on the ligand. This resembles the situation in phosphanomethanides, where a carbanion enhances the donor capacity of the adjacent neutral phosphorus atom to an extent, that a variety of phosphane complexes including very electropositive metals (alkali, alkaline earth, lanthanide metals) have successfully been synthesized.[6]

In contrast, in alkyl substituted cyclopentadienyl ligands with an additional phosphane functionality in the side chain ('anionic phosphane ligands') the negative charge is well separated from the phosphane donor functionality. Nevertheless these anionic ligands likewise bind to electropositive metal centers. Remarkable results have been obtained in the field of lanthanide chemistry.[7]

The additional phosphane functionality, in contrast to 'simple' cyclopentadienyl derivatives, provides a labile and hence reversible coordination to metal centers, thus combining coordinative 'protection' with enhanced reactivity and therefore is of great interest for catalytic reactions, particularly when combined with transition or lanthanide metal centers. Lithium derivatives[7,8a] have been used to transfer the anionic phosphanoalkyl cyclopentadienide moiety to these metals,[7] but derivatives of the heavier alkali metals often have advantages in salt separation from the reaction mixtures.

We report here the synthesis and the solid state structure of [(THF)K($C_5H_4CH_2CH_2PPh_2$)]$_\infty$**1**, the first molecular example exhibiting a coordinative interaction of a neutral phosphane donor with a heavier organo alkali metal center.

Phosphanoethyl substituted cyclopentadienides {M[$C_5H_4(CH_2)_2PR_2$], M = Li, Na,} are best prepared by reaction of the corresponding phosphanide with spiro[2.4]hepta-4,6-diene.[8] Anionic lithium and sodium compounds with R = Ph, Pr^i, Bu^t,[8] Me[7] are known, but not structurally characterized. The complex K[$C_5H_4(CH_2)_2PPh_2$]† was synthesized by reaction of spiro[2.4]hepta-4,6-diene with $KPPh_2$ in THF (Scheme 1).

Scheme 1

In the $^{31}P\{^1H\}$ NMR spectrum (dioxane-d^8) only one singlet at δ −13.27 is detected. The signal remains unchanged upon varying the temperature. This result indicates that the compound is not involved in dynamic processes but there is no indication of the actual species present in solution. In particular, the kind of ligation around potassium and the degree of association remains unknown.

The crystal structure‡ of [(THF)K($C_5H_4CH_2CH_2PPh_2$)]$_\infty$ consists of polymeric zigzag chains [Fig. 1(a)] as, for example, in CpK,[9] CpK•Et_2O,[10] Cp*K•2Py[11] and ($C_5H_4SiMe_3$)K.[12]

The potassium atom is surrounded by two cyclopentadienyl rings in an η^5 fashion. The K–Cp$_{center}$ distances are 2.821(2) (intramolecular) and 2.792(2) Å (K-Cp$_{center}$ distance to the next molecule) [Fig. 1(b)], *i.e.* the 'intermolecular' distance is shorter than the 'intramolecular' one. Therefore, the ligand $CpCH_2CH_2PPh_2^-$ can be regarded a bridging rather than a chelating ligand.

These values can be compared with the K–Cp$_{center}$ distance in the coordination polymers of KCp [mean 2.816(3) Å][9] and

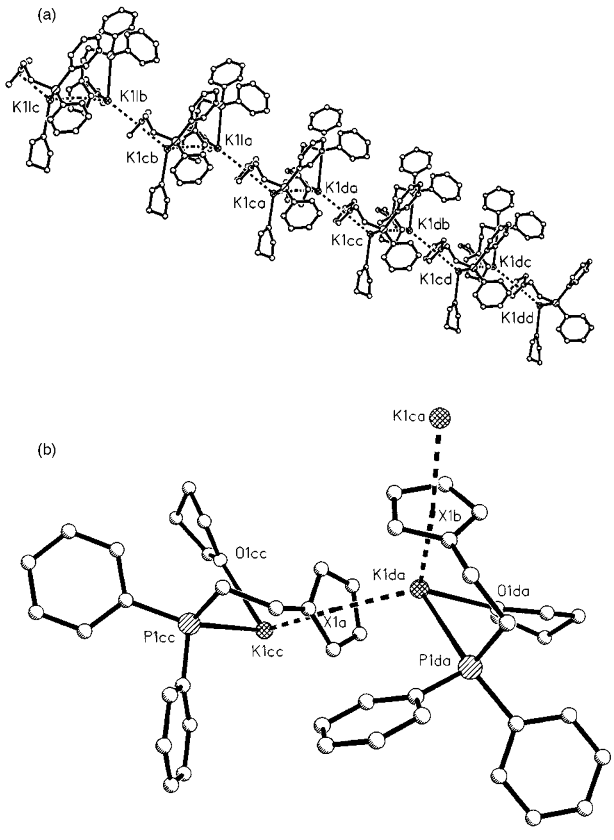

Fig. 1 Structure of [(THF)K($C_5H_4CH_2CH_2PPh_2$)]$_\infty$ **1** (a) Polymer chain; (b) detail of the structure. Selected bond lengths (Å) and angles (°):K1da–P1da 3.320(2), K1da–O1da 2.708(2), K1da–X1a 2.792(2), K1da–X1b 2.821(2); P1d–K1da–O1da 88.75(4), P1d–K1da–X1a 123.90(5), O1da–K1da–X1a 109.32(4), O1da–K1da–X1b 126.7(6), K1da–X1a–K1cc 173.10(4); X: centroids of the Cp-rings.

KCp*•2Py (mean 2.79 Å).[11] An unique feature of the solid state structure is the additional P–K bond due to an intramolecular coordination of the alkyl phosphano functionality. The P–K distance of 3.320(2) Å is only slightly longer than in the phosphanide compounds $[\mathrm{Bu^t{}_2SiFK(THF)_2PC_6H_2Me_3}]_2$[13] [3.230(1)], $[\mathrm{K_3(THF)_2\{PH(Mes)\}_3}]_\infty$[2] [3.368(1), 3.397(1), 3.453(1), 3.306(2) Å], $[\{(\mathrm{Bu^tP})_2\mathrm{H}\}\mathrm{K{\bullet}pmdeta}]_2$[5] [3.251(2) Å], $[\mathrm{KPH(2,4,6\text{-}Bu^t{}_3C_6H_2)}]_\infty$[2] [shortest distance 3.271(2), longest distance 3.357(2) Å] and $[\mathrm{K(THF)P(SiMe_3)_2}]_\infty$[3] [3.317(7) Å], but considerably shorter (0.332 Å) than the only other K–P distance involving a neutral phosphane donor as mentioned earlier[5].

In **1** the K–$\mathrm{Cp_{center}}$–K angle is 173.1(4)° and the $\mathrm{Cp_{center}}$–K–$\mathrm{Cp_{center}}$ angle amounts to 126.7°. To complete the coordination sphere one molecule of THF is coordinated to potassium. The K–O distance of 2.708(2) Å lies in the expected range for a K–O interaction {2.781(2) in $[\mathrm{K(THF)P(SiMe_3)_2}]_\infty$}.[3]

The first organopotassium compound with an additional potassium–phosphorus bond presented here establishes the first example of a potassium to phosphorus bond exhibiting a 'normal' bond length and involving a neutral phosphane donor and is the first structurally characterized alkali metal cyclopentadienide with a phosphanoalkyl side chain. All other known molecules with potassium phosphorus bonds contain phosphanide ligands. Particularly noteworthy is the fact that the potassium–phosphorus bond is formed even on precipitation from THF solution, *i.e.* this bonding can successfully compete with a potassium–THF interaction. As in many other K–Cp compounds a polymeric zigzag chain of alternating cyclopentadienyl groups and potassium atoms is adopted in the solid state structure of **1**.

Notes and references

† To a solution of 0.041 mol (9.1 g) $\mathrm{KPPh_2}$ in 150 ml of THF 0.041 mol (3.59 g) spiro[2.4]hepta-4,6-diene in 20 ml of THF were added by means of a pipette. After stirring the reaction mixture for 12 h at room temperature the solvent was removed and the product was washed three times with pentane. After drying the residue, 8.9 g (68%) of a colorless solid were obtained. Decomp. 181 °C; correct elemental analysis.

^{1}H NMR (dioxane-d^8, room temp., 400 MHz) δ 1.76 (m, 4H, $\mathrm{C}H_2\mathrm{CH_2O}$), 2.21 (m, 2H, $\mathrm{CpCH_2C}H_2\mathrm{PPh_2}$), 3.52 (m, 2H, $\mathrm{CpC}H_2\mathrm{CH_2PPh_2}$), 3.62 (m, 4H, $\mathrm{CH_2C}H_2\mathrm{O}$), 5.29 (s, 4H, $\mathrm{C_5}H_4\mathrm{CH_2CH_2}$), 7.19–7.44 (10H, phenyl);^{13}C{^{1}H} NMR (dioxane-d^8, room temp., 100.4 MHz) δ 26.16 (s, $C\mathrm{H_2CH_2O}$), 26.93 (d, $^2J_{\mathrm{CP}}$ 15.6 Hz, $C\mathrm{H_2CH_2PPh_2}$), 31.83 (d, $^1J_{\mathrm{CP}}$ 10.1 Hz, $C\mathrm{H_2P}$), 67.57 (s, $\mathrm{CH_2}C\mathrm{H_2O}$), 104.11 (s, $\mathrm{CH_2C}C\mathrm{H}$), 121.1 (d,$^3J_{\mathrm{CP}}$ 11.0 Hz, *ipso*-C), 128.92 (d, $^3J_{\mathrm{CP}}$ 6.4 Hz, C3, phenyl), 129.01 (s, C4, phenyl), 133.64 (d, $^2J_{\mathrm{CP}}$ 18.4 Hz, C2, phenyl), 140.57 (d, $^1J_{\mathrm{CP}}$ 13.8 Hz, *ipso*-C, phenyl); ^{31}P{^{1}H} NMR (dioxane-d^8, room temp., 161.7 MHz) δ −13.27 (s).

‡ Colorless crystals of $[\mathrm{(THF)K(C_5H_4CH_2CH_2PPh_2)}]_\infty$ precipitate on concentrating a solution of $\mathrm{K[C_5H_4(CH_2)_2PPh_2]}$ in THF. *Crystal data* for $\mathrm{C_{23}H_{26}KOP}$: M = 388.51, monoclinic, space group $P2_1/c$, a = 10.432(1), b = 19.929(1), c = 10.026(1) Å, β = 90.56(1)°, U = 2084.3(3) Å^3, T = 199 K, Z = 4, μ = 0.340 mm^{-1} 4763 reflections measured, 4528 independent. The final $wR(F^2)$ was 0.085 (all data). The structure was solved by direct methods and refined by full-matrix least squares on F^2(SHELXL-93).[14] CCDC 182/1349. See http//www.rsc.org/suppdata/cc/1999/1695/ for crystallographic files in .cif format.

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