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Deprotonation of 1,1′-methylenebis[4-*tert*-butyl-2-(diphenylphosphino)-benzene] and its analogues: synthesis and crystal structure of {5-Bu^t-2-[4-Bu^t-2-(Ph_2P)C_6H_3(Ph)CH]C_6H_3P(Ph)K(OEt_2)}$_2$

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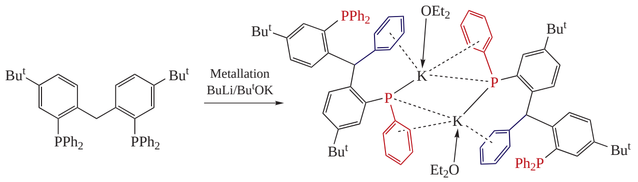
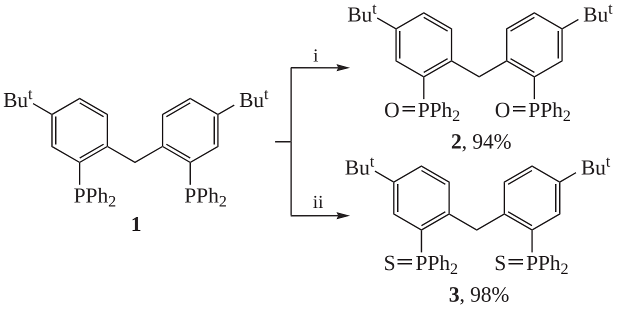
Oxidation of 1,1′-methylenebis[4-*tert*-butyl-2-(diphenylphosphino)benzene] by H_2O_2 or S_8 in toluene affords two new PCP-type pincer ligands. The methylene group deprotonation in the new ligands as well as in their precursor by *n*-BuLi or $LiCH_2SiMe_3$ failed, while the methylene group in the precursor 1,1′-methylenebis[4-*tert*-butyl-2-(diphenylphosphino)benzene] was readily metallated by Lochmann–Schlosser superbase to form the unstable potassium complex which in turn was readily transformed into new {5-Bu^t-2-[4-Bu^t-2-(Ph_2P)C_6H_3(Ph)CH]-C_6H_3P(Ph)K(OEt_2)}$_2$ complex due to phenyl group migration.



Ph group migration from P atom to the central benzhydryl carbon

Pincer ligands are extensively used in coordination chemistry due to their capability of forming robust tridentate complexes with transition metals,[1,2] which demonstrate thermal and kinetic stability as well as high catalytic activity.[3–10] The synthetic approaches, properties and catalytic applications of transition metal pincer complexes have been summarized in reviews and books published recently.[11–18] Among phosphorus-containing pincer ligands, PCP-type compounds, in which binding to the metal atom is realized through formation of a covalent M–C(sp^2) bond, are the most studied, while PCP pincer ligands with covalent bond of another M–C(sp^3) type have been less investigated to date. Symmetrical PCP-type diphenylmethane derivatives with the general formula $[4\text{-R-}2\text{-}(R'_2P)C_6H_3]_2CH_2$, where R = H or Bu^t and R′ = Me, Pr^i or Ph, have been used as neutral, mono-anionic alkyl-type $\{[4\text{-R-}2\text{-}(R'_2P)C_6H_3]_2CH\}^-$ and dianionic methylidene-type $\{[4\text{-R-}2\text{-}(R'_2P)C_6H_3]_2C\}^{2-}$ ligands for coordination of late transition metals.[19–29]

Here we report on the synthesis of new pincer ligands of the PCP type bearing P(O)Ph_2 or P(S)Ph_2 Lewis base groups in the *ortho*-positions of two phenyl rings as well as the reactivity of their P^{III}-containing precursor, 1,1′-methylenebis[4-*tert*-butyl-2-(diphenylphosphino)benzene] **1**, toward alkyl derivatives of alkali metals.



Scheme 1 *Reagents and conditions*: i, H_2O_2, toluene, room temperature, 4 h; ii, S_8, toluene, 50 °C, 4 h.

To synthesize the diphenylmethane derivatives bearing P(O)Ph_2 and P(S)Ph_2 groups, presumably suitable for coordination with ‘hard’ and ‘soft’ transition metals ions, respectively, the oxidation reactions of compound **1**[30] with 3% aqueous H_2O_2 and with S_8 were carried out in toluene resulting in formation of the expected P^V compounds 1,1′-methylenebis[4-*tert*-butyl-2-(diphenylphosphinyl)benzene] **2** and 1,1′-methylenebis[4-*tert*-butyl-2-(diphenylphosphinothioyl)benzene] **3** (Scheme 1).

According to the X-ray analysis† (Figure 1, Table S1, see Online Supplementary Materials), the ArCH$_2$Ar fragment in compound **2** is not planar: the dihedral angle between both phenyl rings and the C$_{ipso}$–C(1)–C$_{ipso}$ plane is 62.43(5)°. Diphenylphosphinyl groups are located on the opposite sides with respect to this plane. The P=O and P–C$_{Ar}$ bond lengths are similar to those found in triphenylphosphine (P=O 1.491–1.494 Å, P–C 1.797–1.808 Å)[31] and 1,1′-carbonylbis[2-(diphenylphosphinyl)-3,4,5,6-tetrafluorobenzene] [P=O 1.479(2) and 1.482(2) Å, P–C 1.796(2) and 1.846(2) Å].[32]

In the ^{1}H NMR spectra of products **2** and **3**, the central methylene protons appear as slightly broadened singlets at 4.28 and 4.27 ppm, respectively, while the corresponding methylene

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† *Crystal data for* **2**. $C_{45}H_{46}O_2P_2$, C_7H_8 (M = 772.89), the crystals are orthorhombic, space group *Pbcn*, a = 24.3597(7), b = 18.3745(5) and c = 9.5748(3) Å, V = 4285.7(2) Å^3, Z = 4, d_{calc} = 1.198 g cm^{-3}, μ(MoKα) = = 0.142 mm^{-1}, F_{000} = 1648. Total of 53142 reflections were measured and 5522 independent reflections (R_{int} = 0.0496) were used in a further refinement. The refinement converged to wR_2 = 0.1033 and GOF = 1.063 for all independent reflections [R_1 = 0.0573 was calculated against F for 5522 observed reflections with $I > 2\sigma(I)$].

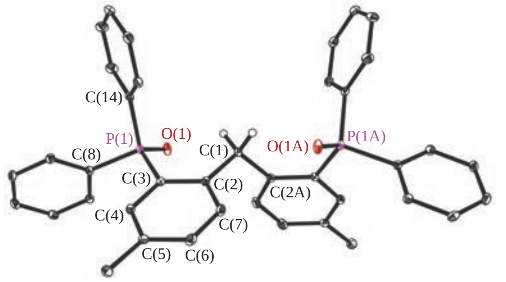


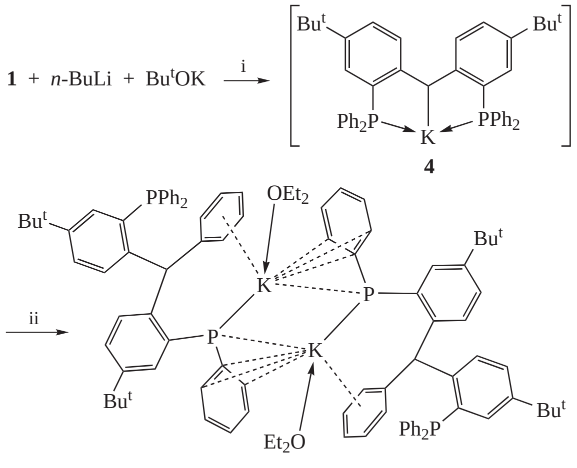
Figure 1 Molecular structure of compound **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except for methylene group) and Me groups of Bu^t moieties are omitted for clarity.

carbons in the $^{13}C\{^1H\}$ NMR spectra give rise to triplets at 37.1 ($^3J_{CP}$ 4.8 Hz) and 37.4 ppm ($^3J_{CP}$ 6.0 Hz) for compounds **2** and **3**, respectively. Oxidation of P^{III} compound **1** to the P^V counterparts results in a strong shift of the signals in the $^{31}P\{^1H\}$ NMR spectra to the low-field region: compounds **2** and **3** display singlets at 37.1 and 42.9 ppm, respectively, while in the spectrum of ligand **1** a singlet at –13.5 ppm is present. Similar differences in the chemical shifts were observed for a series of Ph_3P (δ_P –4.7 ppm),[33] $Ph_3P{=}O$ (δ_P 29.3 ppm) and $Ph_3P{=}S$ (δ_P 43.2 ppm) compounds.[34]

In the IR spectra of compounds **2** and **3**, intense absorption bands at 1190 and 645 cm^{-1} (Figure S7, see Online Supplementary Materials) related to the stretching vibrations of the P=O and P=S bonds are present. The observed values are very close to those published for $Ph_3P{=}O$ (1190 cm^{-1}) and $Ph_3P{=}S$ (630 cm^{-1}).[35]

It was reported that the methanide moieties of the ligands based on diphenylmethane scaffold, namely diphenylmethane itself,[36,37] $(RMe_2Si)CHPh_2$ (R = Me, Bu^t or Ph)[38] and $(2\text{-}Me_2N\text{-}5\text{-}MeC_6H_3)_2CH_2$,[39] readily undergo metallation by *n*-butyllithium or methyllithium in hexane, diethyl ether or THF. To attempt the synthesis of lithium diphenylmethanides from compounds **1**–**3**, their interaction with *n*-butyllithium and trimethylsilylmethyllithium was investigated. Monitoring of the mixtures in C_6D_6 by ^1H NMR spectroscopy revealed no reaction after heating at 60 °C for 12 h. Moreover, no metallation occurred as well in diethyl ether solution or in the presence of TMEDA.

On the other hand, ligand **1** was found to be metallated by Lochmann–Schlosser superbase. The addition of *n*-butyllithium to the mixture of equimolar amounts of compound **1** and potassium *tert*-butoxide in diethyl ether resulted in the formation of red amorphous precipitate with presumable structure of {bis[4-*tert*-butyl-2-(diphenylphosphino)phenyl]methyl}potassium **4** (Scheme 2). Compound **4** was insoluble in toluene or benzene, so it was impossible to record its NMR spectra in aromatic solvents. Mild hydrolysis of complex **4** with air moisture in C_6D_6 solution led to the formation of the starting ligand **1**, this could be an indirect confirmation of its diphenylmethanide structure. Compound **4** proved to be unstable in diethyl ether and THF solutions. Heating of complex **4** in diethyl ether at 35 °C for 24 h resulted in the migration of phenyl ring from one of the diphenylphosphino groups to the central methanide carbon. This rearrangement afforded the potassium phosphine-phosphido complex $\{5\text{-}Bu^t\text{-}2\text{-}[4\text{-}Bu^t\text{-}2\text{-}(Ph_2P)C_6H_3(Ph)CH]C_6H_3\text{–}P(Ph)K(OEt_2)\}_2$ **5** (Scheme 2). The P–C bond cleavage with elimination of R groups from PR_2 moieties giving a phosphido anionic donor was recently reported for cerium PNP-type pincer complexes.[40] Complex **5** was isolated as yellow-orange crystals in 60% yield. In THF-d_8 solution the transformation of compound **4** into **5** was completed in a few minutes. The mild hydrolysis of complex **5** afforded phosphine $5\text{-}Bu^t\text{-}2\text{-}[4\text{-}Bu^t\text{-}2\text{-}(Ph_2P)C_6H_3(Ph)\text{–}CH]C_6H_3P(Ph)H$ **6** (see Online Supplementary Materials).



4

5, 60%

Scheme 2 *Reagents and conditions*: i, Et_2O, 20 °C, 1 h; ii, Et_2O, 35 °C, 24 h.

The X-ray analysis revealed that the formation of compound **5** resulted from the cleavage of one covalent C–P bond followed by the formation of covalent C–C and K–P bonds. Complex **5** adopts a dimeric structure (Figure 2, Table S1), in which two potassium ions are bridged by two phosphido atoms of two new monoanionic phosphine-phosphido ligands. The K_2P_2 moiety is planar with significantly different distances: K(1)–P(1) 3.387(2) Å

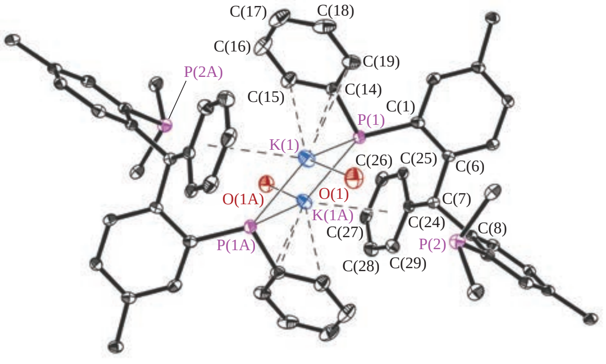


Figure 2 Molecular structure of compound **5**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and carbon atoms of diethyl ether, CH moieties of phenyl substituents, non-coordinated Ph groups of diphenylphosphino moieties and Me groups of Bu^t moieties are omitted for clarity.

Crystal data for **5**. $C_{98}H_{110}K_2O_2P_4$ (M = 1521.93), the crystals are monoclinic, space group $P2_1/c$, a = 13.4828(4), b = 17.1014(5) and c = 18.2785(5) Å, V = 4214.2(2) Å^3, Z = 2, d_{calc} = 1.199 g cm^{-3}, μ(MoKα) = 0.237 mm^{-1}, F_{000} = 1624. Total of 63135 reflections were measured and 8290 independent reflections (R_{int} = 0.1471) were used in a further refinement. The refinement converged to wR_2 = 0.1903 and GOF = 1.021 for all independent reflections [R_1 = 0.1209 was calculated against F for 8290 observed reflections with $I > 2\sigma(I)$].

The X-ray data for compounds **2** and **5** were collected on Bruker D8 QUEST and Agilent Xcalibur diffractometers, respectively (MoKα-radiation, ω-scans technique, λ = 0.71073 Å, T = 100 K) using APEX3 and CrysAlis Pro software packages. The structures were solved by dual-space methods and refined by full-matrix least squares on F^2 for all data using SHELX. SADABS and CrysAlis Pro software packages were used to perform area-detector scaling and absorption correction. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. Methylene hydrogen atoms in ligand **2** were also found from Fourier syntheses of electron density and refined isotropically. Other hydrogen atoms in compounds **2** and **5** were placed in calculated positions and were refined in the ‘riding’ model with $U(H)_{iso} = 1.2U_{eq}$ of their parent atoms [$U(H)_{iso} = 1.5U_{eq}$ for methyl groups].

CCDC 1883061 and 1883062 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

and K(1A)–P(1) 3.175(2) Å. However, these potassium–phosphorus bond lengths fall into the range of the values [3.206(2)–3.495(2) Å] typical of potassium diaryl phosphido complexes $(Ph_2PK)_n$, $\{K(PPh_2)[MeN(CH_2CH_2NMe_2)_2]\}_n$ and $[K(PPh_2)_2$-(18-crown-6)$_2]$.[41–43] Besides, the short contacts were detected between potassium ion and *ipso*-carbon atom [3.056(4) Å] as well as two *ortho*-carbon atoms [3.230(4) and 3.475(4) Å] of one phenyl group in phenylphosphido moiety, revealing η^3-coordination. Moreover, η^6-coordination of the phenyl ring bound to the trisubstituted methane carbon atom to potassium ion was observed [K(1)–C_{Ph} 3.203(4)–3.534(4) Å and K(1)–centroid$_{Ph}$ 3.067(8) Å]. Coordination of aromatic π-system to potassium ion is common for potassium phosphides.[41,42] Surprisingly, despite the presence of the non-coordinated diphenylphosphino group in the structure of complex **5**, the η^6-coordination with the phenyl ring turned out to be preferable for potassium ion.

Phosphorus atoms of diphenylphosphino group and phenylphosphido moiety in compound **5** are non-equivalent in the $^{31}P\{^1H\}$ NMR spectrum in THF-d_8, appearing as two doublets at –17.0 and –16.0 ppm, respectively with $^6J_{PP}$ 17.0 Hz. *tert*-Butyl protons in the ^1H NMR spectrum of complex **5** are also non-equivalent and give rise to two singlets at 1.13 and 1.21 ppm. The proton at the trisubstituted methane carbon atom appears as a multiplet at 7.06 ppm overlapping with the protons of aromatic rings, while the corresponding carbon atom gives a triplet at 52.1 ppm with $^3J_{CP}$ 23.2 Hz in the ^{13}C NMR spectrum.

Compounds **2** and **3** did not afford the isolable products under the conditions employed for the deprotonation of compound **1**.

In summary, new pincer ligands **2** and **3** were synthesized by oxidation of P^{III} atoms in compound **1** with H_2O_2 and S_8, respectively. Diphenylmethane derivatives **1**–**3** were found to be inert toward alkyllithium reagents like *n*-butyllithium or trimethylsilylmethyllithium, but compound **1** readily reacted with Lochmann–Schlosser superbase with formation of diphenylmethanido complex **4**. The latter appeared to be unstable in diethyl ether or THF and underwent migration of one phenyl group from phosphorus atom to the central methanido carbon giving dimeric potassium complex **5** containing new monoanionic phosphinophosphide ligands.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.05.031.

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