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Lithium−Palladium Complex Supported by Phosphonatophosphine and Chloride Ligands

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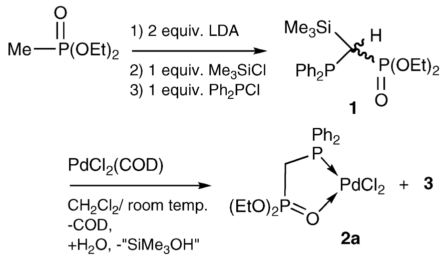
The reaction of the phosphonatophosphine ligand $Ph_2PCH(SiMe_3)P(O)(OEt)_2$ with $[PdCl_2(COD)]$ in the presence of LiCl afforded the neutral, mixed-metal complex $[LiPd_2Cl_5\{\mu\text{-}Ph_2PCH_2P(O)(OEt)_2\}_2]$ in which the Li^+ cation is tetrahedrally coordinated by the P═O bonds and two Pd-bound Cl atoms.

The highly electropositive nature of the alkali metals accounts for the polar nature of their bonds to other elements. A considerable number of structures have been reported for lithium complexes and aggregates whose diversity results from the range of alkali-metal−ligand interactions available.[1] Lithium derivatives play a considerable role in organometallic and organic synthesis, and mixed complexes or aggregates, such as the lithium cuprates, possess a reactivity very different from that of the corresponding homometallic systems.[2] It is also known that some reactions work better in the presence of added salts, e.g., LiCl, although their exact role is not always fully understood, and that the nature of the bonding interactions in organometallic complexes may strongly depend on the retention of an alkali metal in the structure.[3]

Scheme 1



In the course of our studies on heterofunctional P,O ligands and the reactivity of their metal complexes,[4] we noticed that, among the huge diversity of heterofunctional ligands, phosphines containing a phosphoryl function, i.e., phosphonate, phosphinate, or phosphate, have received relatively little attention, although it is established that the P═O group can coordinate to a metal center via the O atom.[5,6] The hemilabile nature of the latter interaction[4b] may play an important role during a catalytic cycle, as shown with methanol carbonylation catalysts based on rhodium phosphine−phosphonate complexes.[7] We have thus prepared new enolphosphato- and phosphonatophosphine ligands that associate P^{III} and P^{V} centers.[6a,b]

The new silyl-substituted β-phosphonatophosphine ligand **1** was prepared according to Scheme 1, via the intermediacy

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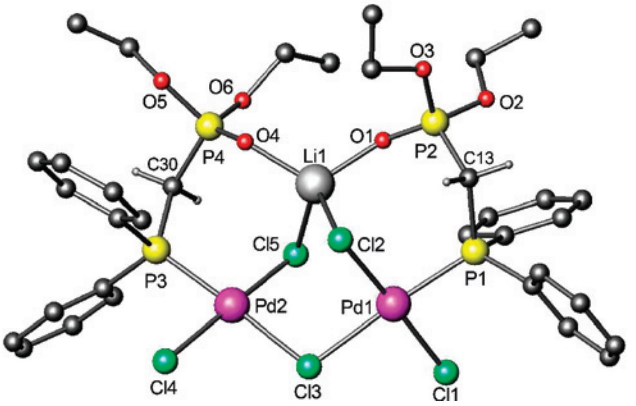
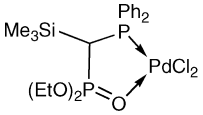
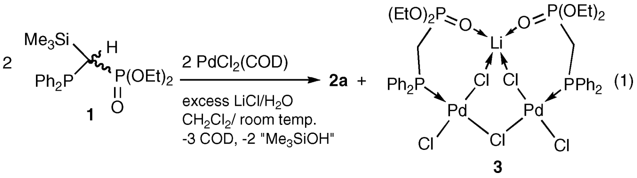


Figure 1. View of the molecular structure of **3** in **3**·3CH_2Cl_2. H atoms are omitted for clarity, except on the PCP carbons. Selected bond distances [Å] and angles [deg]: Pd1−P1 2.2323(10), Pd1−Cl1 2.2868(9), Pd1−Cl2 2.3327(9), Pd1−Cl3 2.4095(10), Pd2−P3 2.2214(10), Pd2−Cl3 2.3999(10), Pd2−Cl4 2.2967(9), Pd2−Cl5 2.3178(9), Li−O1 1.864(7), O1−P2 1.476(3), Li−O4 1.880(7), O4−P4 1.474(3), Li−Cl2 2.403(7), Li−Cl5 2.397(7); Cl1−Pd1−Cl2 175.41(4), Pd1−Cl2−Li 89.72(16), Cl4−Pd2−Cl5 173.98(4), Pd2−Cl5−Li 91.84(16), Pd1−Cl3−Pd2 106.21(4), P2−O1−Li 139.2(3), P4−O4−Li 127.3(3), O1−Li−Cl2 101.6(3), O1−Li−Cl5 114.0(3), O1−Li−O4 116.2(4), O4−Li−Cl2 118.9(3), O4−Li−Cl5 100.2(3), Cl2−Li−Cl5 106.0(3).

of $Me_3SiCH_2P(O)(OEt)_2$ (see the Supporting Information),[8,9] and it was reacted with [$PdCl_2$(COD)] to give after 1 h mainly complex **2a**, with a small amount of another complex, **3** (see below).[9] The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **2a** consists of two singlets at δ 9.7 and 23.8 for the PPh_2 and phosphonate groups, respectively. The ^1H NMR spectrum is consistent with the structure shown for **2a**.[9] The second, minor compound formed in this reaction (ca. 15% yield) could be crystallized as **3**·$CHCl_3$ and was shown by X-ray diffraction to be an anionic dinuclear Pd^{II} complex with a Li^+ cation encapsulated, resulting in the neutral molecule [$LiPd_2CI_5\{\mu\text{-}Ph_2PCH_2P(O)(OEt)_2\}_2$] (**3**). (Figure 1 shows the structure of this complex in **3**·3CH_2Cl_2; see below.[10]) Obviously, the LiCl present in this complex originated adventitiously from the ligand synthesis. The $SiMe_3$ group has been eliminated and the masked carbanion protonated, owing to the presence of traces of H_2O. We noted that when the reaction of **1** with [$PdCl_2$(COD)] was stopped after 10 min, additional ^1H NMR signals were observed, which could be consistent with the initial formation of **2b** ($^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 19.1 (d, $^{2+3}J(P,P) = 20.0$ Hz, PPh_2), 23.1 (d, $^{2+3}J(P,P) = 20.0$ Hz, PO), which progressively loses its silyl group to give **2a**. We have also noticed by $^{31}P\{^1H\}$ NMR monitoring that the hydrolysis of **2b** to give **2a** is significantly faster than that of the uncoordinated ligand **1**.



2b



Having identified the nature of the unusual complex **3**, we performed the reaction of eq 1 in the presence of excess LiCl and obtained **3** in ca. 54% isolated yield, with the water responsible for the hydrolysis of the silyl group coming from the hygroscopic LiCl.

Single crystals of **3**·3CH_2Cl_2 were obtained, and the structure of the complex, determined by X-ray diffraction, is almost identical with that of **3**·$CHCl_3$ (Figure 1).[10] The molecule possesses almost a C_2 symmetry axis passing through the atoms Li and Cl3. Each Pd^{II} center has a square-planar coordination geometry [the sum of the angles around Pd1 and Pd2 is 360.3(2) and 360.0(7)°, respectively], and the bridging chloride Cl3 is trans to the phosphine donors P1 and P3. The phosphonate P═O atoms are bonded to the Li^+ cation [Li−O1 1.864(7) Å; Li−O4 1.880(7) Å], which

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(9) Selected data. $Me_3SiCH_2P(O)(OEt)_2$:[8b] yield 80%. ^1H NMR ($CDCl_3$): δ 0.14 (s, 9H, $SiCH_3$), 1.12 (2H, d, $^2J(P,H) = 22$ Hz, PCH_2Si), 1.28 (6H, t, $^3J(H,H) = 5.0$ Hz, OCH_2CH_3), 4.04 (m, 4H, OCH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.2 (s, PO). IR (CH_2Cl_2): ν(P═O) 1244 s cm^{-1}. $Ph_2PCH(SiMe_3)P(O)(OEt)_2$ (**1**): yield 78%. ^1H NMR (CD_2Cl_2): δ 0.05 (s, 9H, $SiMe_3$), 1.07 (t, 3H, $^3J(H,H) = 7.0$ Hz, CH_2CH_3), 1.15 (t, 3H, $^3J(H,H) = 7.0$ Hz, CH_2CH_3), 2.46 (dd, 1H, PCHP, $^2J(PO,H) = 21.6$ Hz, $^2J(P,H) = 1.1$ Hz, PCHP), 3.69 (m, 1H, OCH_2), 3.83 (m, 1H, OCH_2CH_3), 3.87 (m, 2H, OCH_2CH_3), 7.34−7.86 (m, 10H, aromatics). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −16.5 (d, $^2J(P,P) = 21.0$ Hz, PPh_2), 29.8 (d, $^2J(P,P) = 21.0$ Hz, PO). IR: ν(P═O) 1229 s cm^{-1}. [$PdCl_2\{Ph_2PCH_2P(O)(OEt)_2\}$-*P,O*] (**2a**): yield 78%. ^1H NMR ($CDCl_3$): δ 1.09 (t, 6H, $^3J(HH) = 6.7$ Hz, OCH_2CH_3), 3.18 (dd, 2H, $^2J(PO,H) = 20.6$, $^2J(P,H) = 4.0$ Hz, PCH_2P), 3.92−4.05 (m, 4H, OCH_2CH_3), 7.26−7.90 (m, 10H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.7 (s, PPh_2), 23.8 (s, PO). IR (KBr): 1236 s, 1166 m cm^{-1}. [$LiPd_2CI_5\{\mu\text{-}Ph_2PCH_2P(O)(OEt)_2\}_2$] (**3**): yield 54% based on Pd. ^1H NMR (CD_2Cl_2): δ 1.15 (t, 12H, $^3J(H,H) = 7.0$ Hz, OCH_2CH_3), 3.18 (dd, 4H, $^2J(PO,H) = 20.7$ Hz, $^2J(P,H) = 14.5$ Hz, PCH_2P), 3.86 (m, 4H, OCH_2CH_3), 3.96 (m, 4H, OCH_2CH_3), 7.49−7.97 (m, 20H, aromatics). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 16.3 (s, PPh_2), 24.7 (s, PO). ^7Li NMR (ref LiCl 1 M/D_2O): δ 0.15 (s). IR (pure): 1172 s, 1233 s cm^{-1}. IR (KBr): 1173 s, 1251 s cm^{-1}. Mass spectrum (MALDI-TOF$^+$): *m/z* 1030.91 [M − Cl].

(10) Crystal data for **3**·$CHCl_3$: Owing to strong disorder of the OEt groups on P2 and of one of the $CHCl_3$ molecules of solvation, a squeeze procedure (PLATON) was applied and only one molecule of $CHCl_3$ was considered. Analytical data are consistent, with a total of four molecules of $CHCl_3$ being present. $C_{34}H_{44}Cl_5LiO_6P_4Pd_2\cdot CHCl_3$, $M = 1188.93$, monoclinic, $C2/c$, $a = 34.6944(3)$ Å, $b = 13.0287(2)$ Å, $c = 23.0410(2)$ Å, $\beta = 90.557(1)°$, $V = 10414.6$ Å^3, $Z = 8$, $D_c = 1.517$ g cm^{-3}, μ(Mo Kα) = 1.261 mm^{-1}, $F(000) = 4752$. A Nonius-Kappa CCD diffractometer was employed for the collection of 11 896 unique reflections (Mo Kα, $\lambda = 0.710\,73$ Å, $T = 173$ K).[16] The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 (*SHELX97*[17]). The final R1 and wR2 are 0.0399 and 0.1157, respectively, for 511 parameters and 9517 reflections [$I > 2\sigma(I)$]. CCDC no. 669910. Crystal data for **3**·3CH_2Cl_2: $C_{34}H_{44}Cl_5LiO_6P_4Pd_2\cdot 3CH_2Cl_2$, $M = 1324.34$, triclinic, $P\bar{1}$, $a = 11.1497(5)$ Å, $b = 15.5662(6)$ Å, $c = 16.6267(8)$ Å, $\alpha = 110.906(2)°$, $\beta = 95.971(2)°$, $\gamma = 91.575(2)°$, $V = 2674.6(2)$ Å^3, $Z = 2$, $D_c = 1.644$ g cm^{-3}, μ(Mo Kα) = 1.381 mm^{-1}, $F(000) = 1324$. A Nonius-Kappa CCD diffractometer was employed for the collection of 12 149 unique reflections (Mo Kα, $\lambda = 0.710\,73$ Å, $T = 173$ K).[16] The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 (*SHELX97*[17]). The final R1 and wR2 are 0.0466 and 0.1036, respectively, for 554 parameters and 8525 reflections [$I > 2\sigma(I)$]. CCDC no. 669909.

has a tetrahedral coordination geometry, completed by the chloride ligands Cl2 and Cl5 [Li−Cl2 2.403(7) Å; Li−Cl5 2.397(7) Å]. The angles at the bridging chlorides are Pd1−Cl2−Li 89.72(16)° and Pd2−Cl5−Li 91.84(16)°. Some intramolecular nonclassical hydrogen bonds are present between the PCH_2 protons and the bridging chlorides, whereas intermolecular nonclassical hydrogen bonds involve the solvent molecules.[9]

An alternative description of this heterometallic complex is to view it as constituted of a LiCl unit trapped by a neural Pd_2Cl_4 moiety and the P,O ligands serving as bridges between the Pd and Li centers. In contrast to other examples where a Li cation is chelated by two M−Cl ligands,[11] there is no solvent molecule coordinated to Li (usually Et_2O or THF). Instead, intramolecular stabilization is achieved by bridging interactions with a functional ligand. This molecule appears to be of an unprecedented type, and we are aware of only one other report on fully characterized Li−Pd complexes.[12]

A recent illustration of the enhanced catalytic properties of a Li-containing dimetallic aggregate is provided by the alkyl complex $[(THF)_4Li_4Pd_2Me_8]$, which is very active and selective in the Heck coupling of 4-bromoacetophenone with *n*-butyl acrylate.[12] A complex with a Fe−Cl−Li unit stabilized by a bridging carboxylate ligand was recently shown to be an interesting precursor to novel cubane-type structures.[13] During the synthesis of a lithiated titanium phosphonate complex from $(MeO)_2P(O)CH_2SiMe_3$, it was found that traces of water also played an important role, but complete removal of the silyl group was not oberved.[14] Preliminary catalytic experiments have shown that **3** catalyzes the oligomerization of ethylene (296 K, 10 bar, C_2H_4, 4×10^{-5} mol of complex, 6 equiv of $EtAlCl_2$, total volume of toluene 15 mL)[15] with a poor activity [TOF = 90 mol of C_2H_4/(g pf Pd) h] but an interesting selectivity of 76% for decenes. When methylaluminoxane was used as a cocatalyst (similar conditions, 200 equiv, total volume of toluene 20 mL), the activity remained low [TOF = 340 mol of C_2H_4/(g of Pd) h] but decenes were again the major products (selectivity of 50%). These preliminary observations require further investigations.

The formation and structure of **3**, through a combination of serendipity and design, nicely illustrate the composition, properties, and structural changes that can result from the presence of LiCl in a reaction mixture. Preliminary experiments indicate that complex **2a** does not lead to **3** upon the addition of LiCl. This could be explained by the lower kinetic reactivity of the P,O chelate once formed toward ring opening. It can be anticipated that reactivity studies will show marked differences between **2a** or **2b** and **3**, and this is under study. Conversely, the typical solubility properties of LiCl are completely different when it is complexed by the dipalladium moiety.

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Supporting Information Available: Crystallographic details in the form of a CIF file and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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