Novel route to carbodiphosphoranes producing a new P,C,P pincer carbene ligand†

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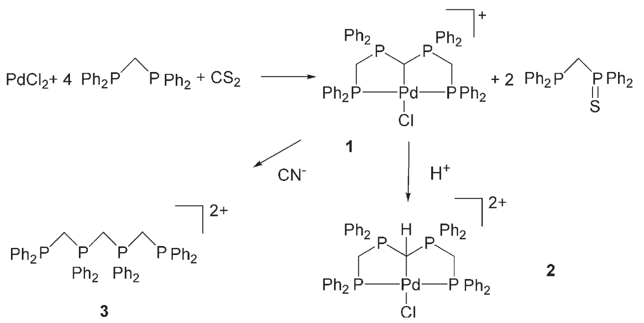
The reaction of $PdCl_2$, dppm and CS_2 in CH_2Cl_2/MeOH results in the palladium carbodiphosphorane complex [Pd($Ph_2PCH_2Ph_2PCPPh_2CH_2PPh_2$–P,C,P)Cl]Cl.

Pincer complexes are of current interest in relation to various catalytic functions such as polymerization,[1,2] dehydrogenation,[3,4] hydrogen transfer[5] and the activation of small molecules.[6,7] Among this large family, one pincer ligand containing a carbodiphosphorane function has previously been reported.[8] Carbodiphosphoranes R_3PCPR_3, are relatives of Bertrand- and Arduengo-type carbenes in that they are neutral, 2-e^- σ-donors, with bent structures in the solid state, and have betaine resonance forms with a negative charge on the carbenoid carbon.[8] Carbodiphosphoranes, can be seen as compounds of a zerovalent carbon atom and two phosphine ligands, which is also reflected in the synthetic routes described in the literature. The most frequently used carbodiphosphorane is the hexaphenyl compound Ph_3PCPPh_3, which was first prepared by Ramirez *et al.*[9]: Triphenylphosphine was treated with CH_2Br_2 to give the methylenebisphosphonium salt [$Ph_3PCH_2PPh_3$]Br_2, which was deprotonated in a stepwise fashion with Na_2CO_3 to the phosphoniumphosphoniomethylide [$Ph_3PCHPPh_3$]Br and with K to the carbodiphosphorane Ph_3PCPPh_3. Modifications of this route, using $NaNH_2$ or NaH still appear to be the state-of-the-art. An alternative, developed by Appel *et al.*,[10] consists in the reaction of PPh_3 with CCl_4 as C_1 source resulting in [$Ph_3PCClPPh_3$]Cl, which was converted to Ph_3PCPPh_3 by treatment with $P(NMe_2)_3$. We report here on the novel route to carbodiphosphoranes using CS_2 as C_1 source in the coordination sphere of palladium in protic medium. It is interesting to note that only the reverse reaction was described in the literature, *e.g.* treatment of Ph_3PCPPh_3 with S_8 has been reported to produce CS_2.[11]

The one pot reaction of $PdCl_2$, dppm and CS_2 in CH_2Cl_2/MeOH at ambient temperature gave the palladium carbodiphosphorane complex [Pd($Ph_2PCH_2Ph_2PCPPh_2CH_2PPh_2$–P,C,P)Cl]Cl **1** and dppmS as main products within an hour (Scheme 1).†‡



Scheme 1

In the absence of $PdCl_2$ there is no reaction between dppm and CS_2. The function of dppm as single sulfur acceptor seems to be selective: attempts to replace dppm by triphenylphosphine or dppmS were unsuccessful. The product **1** is formed in >60% yield based on ^{31}P NMR. The carbodiphosphorane ligand in **1** is formally composed of one carbon atom and two dppm ligands and represents a new class of P,C,P pincer ligands containing both a carbene and two phosphine donor groups. According to preliminary results, related reactions occur in the coordination sphere of other metal ions, *e.g.* Ni, Pt or Co. Protonation of **1** with hydrochloric acid gives the new P,C,P pincer bis(phosphonio)-methyl complex **2** (Scheme 1).†‡Treatment of **1** with aqueous cyanide results in the extrusion and protonation of the ligand, which was isolated as the new methylenebisphosphonium salt [$Ph_2PCH_2Ph_2PCH_2PPh_2CH_2PPh_2$]$Cl_2$ **3**. (Scheme 1)†‡

The structure of the cation of **1** is shown in Fig. 1. The geometries of the carbodiphosphorane complex **1** and of the corresponding bis(phosphonio)methyl complex **2** are compared in Fig. 2.[12,13] The environment of the C(1) atom of **1** is trigonal planar with a sum of the angles around C(1) of 360° and a deviation of C(1) from the least squares plane through P(2), P(3) and Pd(1) of 0.012(3) Å which is compatible with a sp^2 hybridization. In **2** the sum of the angles around C(1) amounts

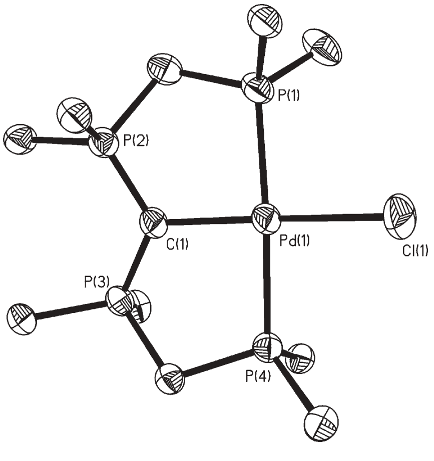


Fig. 1 Structure of the cation of **1**, only the *ipso*-carbon atoms of the phenyl groups are shown, a probability of 50% is chosen for the ellipsoids.

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† Electronic supplementary information (ESI) available: Complete X-ray diagrams of **1**–**3**. See DOI: 10.1039/b609723e

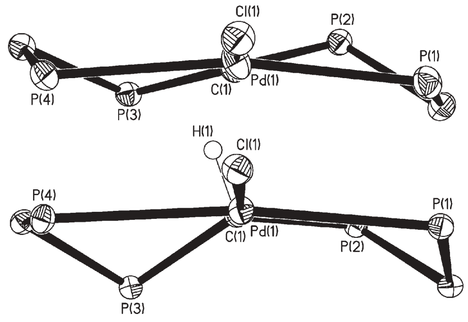
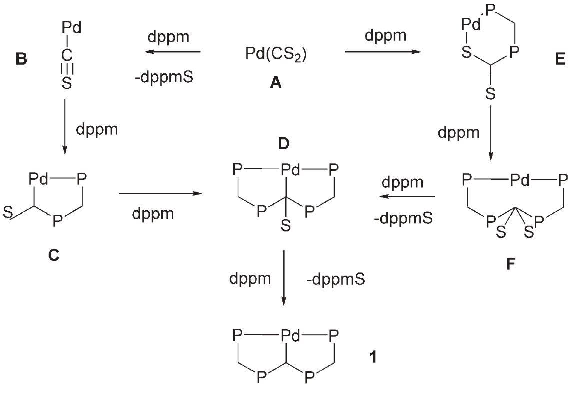


Fig. 2 Geometries of the cations of **1** and **2** in projections along Pd–C(1), the phenyl groups are omitted.

to 346.3°, the corresponding deviation of C(1) is 0.407(3) Å, which is slightly nearer to a trigonal planar than to a tetrahedral geometry. The Pd–C distance of **1** (2.062(2) Å) is distinctly longer compared with a palladium imidazolidene complex (1.999(13)).[14] A further increase is observed for **2** (2.102(3) Å) which is accompanied by a decrease of the Pd–Cl(1) bond length according to the concept of trans influence. The P–C(1)–P angle amounts 124.9(2)° in **1** and 121.9(2)° in **2** compared with the tetrahedral angle of 109.47°. The angles around H(1) (attached to C(1)), which was refined isotropically, vary within 100(2)° and 106(2)°. The cation of **3** has a crystallographically imposed centre of symmetry at the central carbon atom. The P–C(1)–P angle is larger (120.9(2)°) than the P(1)–C(2)–P(2) angle within the dppm parts of **3** (112.1(2)). The C(1)–P distance (180.4(2)) is very similar to that of **2** (mean 180.3(3)) but distinctly longer compared with **1** (mean 169.4(3)).

During the formation of **1**, no intermediates could be detected by ^{31}P NMR spectroscopy. The reaction probably starts with the coordination of CS_2 to Pd (**A**, Scheme 2). The active palladium complex (designated by Pd in Scheme 2) is unknown. It is thought not to be $Pd(dppm)_2Cl_2$, because the reaction of $Pd(dppm)_2Cl_2$/dppm/CS_2 takes much more time than an immediate mixture $PdCl_2$/dppm/CS_2. Since Pd(II) is readily reduced by phosphines, the active complex may involve a lower oxidation state of Pd, furthermore this complex may be oligonuclear because dppm is known to prefer a bridging bonding mode and readily locks together two or more metal centres.[15] The next step can be thought to involve the abstraction of S from the CS_2 ligand which would produce the thiocarbonyl complex **B** (Scheme 2). The abstraction of sulfur from metal–CS_2 complexes by use of phosphines which are converted to the corresponding phosphine sulfides, is an established route to thiocarbonyl complexes.[16] Subsequent nucleophilic attack of phosphorus atoms of dppm at the thiocarbonyl carbon centre in intermediate **B** may lead to **D** *via* **C**. The second sulfur atom is then transferred to dppm with concomitant formation of **1** and dppmS. A carbodiphosphorane–sulfur adduct related to the ligand in **D** has been reported: treatment of Ph_3PCPPh_3 with S_8 gives $Ph_3PC(S)PPh_3$ from which the carbodiphosphorane can be recovered by use of PEt_3.[11] A possible alternative pathway involves a nucleophilic attack of phosphorus atoms of dppm at the CS_2 carbon of **A** to give **E**. Although dppm, in contrast to the more basic trialkylphosphines,[17] does not give stable adducts with CS_2, a related reaction has been observed in the coordination sphere of manganese.[18] The reaction of **E** with dppm is likely to produce **F** in which sulfur atoms may coordinate to Pd. The formation of two P–C bonds between CS_2 and two tertiary phosphine functions related to the ligand of **F**, has been reported to occur in the coordination sphere of iron.[19] Two subsequent sulfur abstractions from the intermediate **F** by dppm may then lead to a final formation of **1** *via* the intermediate **D**. A catalytic transfer of sulfur atoms towards dppm *via* Pd-bound sulfide ligands may also play a role in the overall reaction pathway, since it is known that addition or abstraction of sulfur atoms may occur including easy oxidation/reduction of the involved Pd centres.[20,21]



Scheme 2

Notes and references

‡ *Synthesis of **1***: A mixture of 17.73 mg (0.1 mmol) $PdCl_2$, 153.76 mg (0.4 mmol) dppm, 50 μL (0.83 mmol) CS_2, 0.2 mL MeOH and 0.5 mL CH_2Cl_2 is stirred at ambient temperature until a clear solution is obtained (*ca.* 1 h). The product **1** is present in >60% yield based on ^{31}P NMR. The volatiles are removed *in vacuo* and dppmS is extracted with toluene. Single crystals are obtained from CH_2Cl_2/toluene. ^{31}P NMR (7.05 T, CH_2Cl_2, 298 K, ref: 85% H_3PO_4): $[AM]_2$ system, δP(1,4) 19.3; δP(2,3) 34.5 (labelling according to Fig. 1); Anal. Calcd. for $C_{51}H_{44}Cl_2P_4Pd$: C, 63.9; H, 4.6; Found: C, 63.7; H, 4.8.

*Crystal data for **1***: $C_{51}H_{44}Cl_2P_4Pd \cdot 2.5\ toluene \cdot MeOH$, M = 1220.42, triclinic, a = 10.2001(2) Å, b = 12.4004(2) Å, c = 24.4161(4) Å, α = 84.068(1)°, β = 82.649(1)°, γ = 89.914(1)°, V = 3046.28(9) Å^3, T = 233(2) K, space group $P\bar{1}$ (No. 2), Z = 2, radiation Mo-K$_\alpha$ (λ = 71.073 pm), 17 938 reflections measured, 12 411 reflections unique, reflections with $I > 2\sigma(I)$ 10 607, $R1$ ($I > 2\sigma(I)$) = 0.0411, $wR2$ ($I > 2\sigma(I)$) = 0.1042, goodness of fit 1.036. The structure was solved by direct methods (SHELXS-86),[22] and refined by full matrix least squares methods on F^2 (SHELXL-97).[23]

*Synthesis of **2***: **2** precipitates almost quantitatively upon treatment of a solution of **1** in CH_2Cl_2 with an excess of aqueous HCl (c = 10 mol L^{-1}). Single crystals were obtained by layering a CH_2Cl_2 solution of **1** with aqueous HCl (c = 2 mol L^{-1}). ^{31}P NMR (7.05 T, CH_2Cl_2/MeOH, 298 K, ref: 85% H_3PO_4): $[AM]_2$ system, δP(1,4) 10.2; δP(2,3) 42.4 (labelling according to Fig. 1); Anal. Calcd. for $C_{51}H_{45}Cl_3P_4Pd$: C, 61.6; H, 4.6; Found: C, 61.3; H, 4.7.

*Crystal data for **2***: $C_{51}H_{45}Cl_3P_4Pd \cdot 3\ H_2O$, M = 1048.55, triclinic, a = 9.2897(3) Å, b = 13.5853(6) Å, c = 19.9199(7) Å, α = 86.390(2)°, β = 89.649(2)°, γ = 72.822(2)°, V = 2396.84(16) Å^3, T = 233(2) K, space group $P\bar{1}$ (No. 2), Z = 2, radiation Mo-Kα (λ = 71.073 pm), 13 389 reflections measured, 8354 reflections unique, reflections with $I > 2\sigma(I)$ 6610, $R1$ ($I > 2\sigma(I)$) = 0.0420, $wR2$ ($I > 2\sigma(I)$) = 0.0755, goodness of fit 1.039. The structure was solved by direct methods (SHELXS-86),[22] and refined by full matrix least squares methods on F^2 (SHELXL-97).[23]

*Synthesis of **3***: a mixture of a solution of **1** (0.1 mmol) in CH_2Cl_2 (0.5 mL) and NaCN (1 mmol) in H_2O (0.5 mL) is stirred for 24 h. The CH_2Cl_2 phase is separated and the solvent is evaporated *in vacuo*. The residue is dissolved in MeOH and treated with a suspension of a strongly basic anion exchanger in the chloride form. The MeOH phase is separated, the solvent is evaporated *in vacuo* and the product is crystallized from toluene/$CHCl_3$. ^{31}P NMR (7.05 T, CH_2Cl_2/MeOH, 298 K, ref: 85% H_3PO_4): δP(1,4) 13.0;

δP(2,3) −34.0, (labelling according to Fig. 1) Anal. Calcd. for $C_{51}H_{46}Cl_2P_4$: C, 71.8; H, 5.4; Found: C, 71.3; H, 5.1.

*Crystal data for **3***: $C_{51}H_{46}Cl_2P_4 \cdot 1.5\ CHCl_3 \cdot 0.5$ *toluene*, M = 1078.78 , orthorhombic, a = 15.2377(6) Å, b = 20.5124(7) Å, c = 8.7621(4) Å, V = 2738.70(19) Å^3, T = 233(2) K, space group $P2_12_12$ (No. 18), Z = 2, radiation Mo-Kα (λ = 71.073 pm), 15 158 reflections measured, 4284 reflections unique, reflections with $I > 2\sigma(I)$ 3750, $R1$ ($I > 2\sigma(I)$) = 0.0498, $wR2$ ($I > 2\sigma(I)$) = 0.1229, goodness of fit 1.027. The structure was solved by direct methods (SHELXS-86),[22] and refined by full matrix least squares methods on F^2 (SHELXL-97)[23]

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609723e

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