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Preliminary communication

Selective C–Cl versus P–Cl activation-syntheses of complexes with P–Cl functional phosphinomethyl bridges η^2,μ_2-{P(R)Cl–CH_2}

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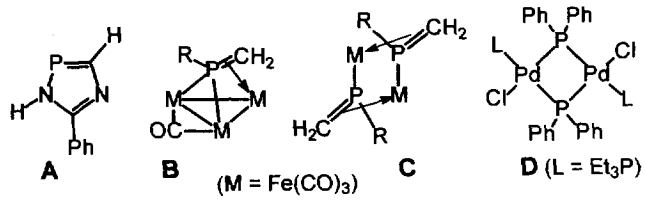
Abstract

On reaction of chloromethylchlorophosphines Cl(R)P–CH_2–Cl with $Pd(Ph_3P)_4$ the C–Cl bond is selectively activated by oxidative addition to Pd(0), unusual dipalladium complexes with P–Cl functional η^2,μ_2-{CH_2-P(R)Cl} bridges being formed with high diastereoselectivity. The X-ray structure of **3a** (R = *t*Bu) reveals a chair-shaped $Pd_2P_2C_2$ six-membered ring system with the substituents (Cl, *t*Bu) at the two m_2-P atoms in *cis*-position. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Chloromethylchlorophosphines; Selective C–Cl activation; η^2,μ_2-Phosphinomethyl bridges; Palladium; X-ray structure

1. Introduction

Chloromethylchlorophosphines Cl(R)P–CH_2–Cl [1–3] are multifunctional building blocks of great synthetic potential. The prototype of this class of chlorophosphines, Cl_2P–CH_2–Cl, has been employed for the syntheses of novel phosphorus containing heterocycles, e.g. 1,3,4-diazaphospholes **A**, by [3 + 2]-cyclocondensation reactions with amidine type compounds. Metal assisted reductive 1,2-dehalogenation of the derivatives Cl(R)P–CH_2–Cl with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ leads to phosphaalkenes stabilized by incorporation into cluster frameworks **B** [3,4] or bimetallic complexes **C** [3]. By analogy with the reductive dehalogenation of alkyl or arylchlorophosphines RR'PCl with transition metal carbonyls or carbonylates [5] μ_2-phosphido complexes, e.g. $(CO)_3Fe(\mu_2\text{-}PRR')(\mu_2\text{-}X)Fe(CO)_3$ (X = Cl, PRR'·R = Cl·R' = CH_2–Cl), are assumed to be formed as intermediates by oxidative addition of the P–Cl bonds to the low valent transition metal. The bis-μ_2-phosphido complex (X = PRR') has been obtained on reaction of Cl_2P–CH_2–Cl with $Fe_2(CO)_9$ [3]



In context of a program aimed at the syntheses of mono- and bicyclic phosphines by template assisted transformations of reactive metal stabilized phosphaalkenes we were interested in a further development of the synthetic procedure leading to clusters or complexes of type **B** or **C** containing transition metals other than iron, e.g. palladium.

2. Results and discussion

Reaction of the chloromethylchlorophosphine *t*Bu(Cl)P–CH_2–Cl (**1a**) [3,4] with an equimolar amount

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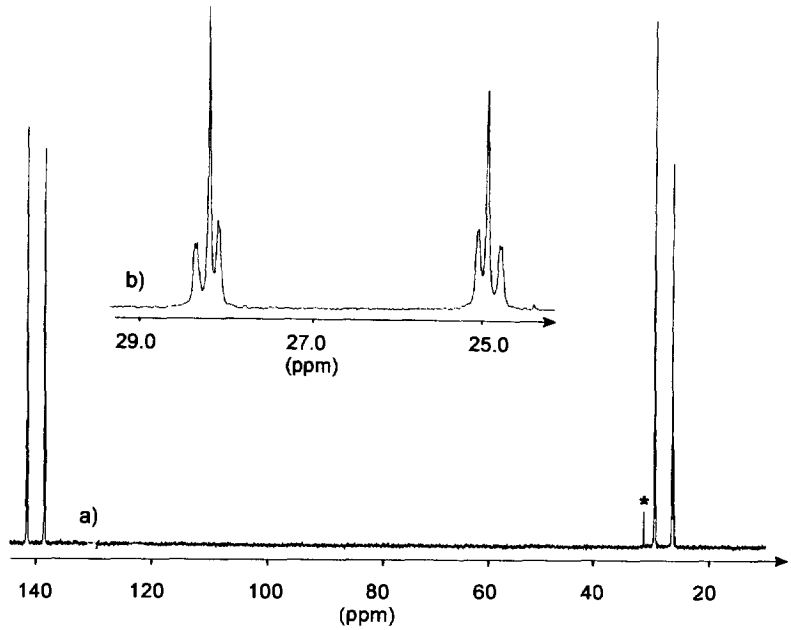


Fig. 1. (a) $^{31}P\{^1H\}$ NMR spectrum of **3a** ($CDCl_3$, 303 K), * = impurity. (b) Extended high-field part.

of $Pd(Ph_3P)_4$ [6] in toluene at ambient temperature yields a yellow colored complex of composition {Pd(Ph_3P)**1a**}. Triphenylphosphine being formed could be separated by extraction of the crude reaction product remaining after all volatiles had been removed in vacuo. The molecular mass of the reaction product determined by osmometry on CH_2Cl_2 solutions (1070) indicated a dimeric structure [{Pd(Ph_3P)**1a**}]$_2$ for which a value of 1083.4 g mol^{-1} had to be expected. A product of identical composition was obtained, if **1a** was reacted with excess $Pd(Ph_3P)_4$ at ambient or higher temperature. In the $^{31}P\{^1H\}$ NMR spectrum of the reaction product (Fig. 1) the line pattern of an AA'XX' spin system (indication of the P atoms see formula) is observed, compatible with a phosphine substituted phosphido-bridged dipalladium complex of structure **2a**.

Its formation may be explained by oxidative addition of the P–Cl bond of **1a** to Pd(0) and subsequent dimerization of the intermediate **E** with elimination of Ph_3P (Eqs. (1a) and (2a)). By comparison of the δP values with those of *cis*- or *trans*-$PdCl_2L_2$ (L e.g. Ph_2PR; R = Me, Et, *n*Bu) [7] the high field part (δP = 26.6) of the $^{31}P\{^1H\}$ NMR AA'XX' spin system may be assigned to the Ph_3P ligands coordinated to Pd(II) ($P_{XX'}$). The strong deshielding of the central P atoms ($P_{AA'}$, $\delta P = 138.3$) was, however, not compatible with structure **2a** proposed for the reaction product. μ_2-Phosphido complexes of this type, e.g. **D**, have been investigated [8]. For the μ_2-phosphido bridges in these complexes the δP values are in the range between −120 and −180. The P–P coupling constants of the reaction product for which structure **2a** was assumed initially were calculated using iterative techniques ($J(AA') = 42.1$, $J(AX) = 517.1$, $J(AX') = -2.7$, $J(XX') = 3.7$ Hz). The coupling constants $J(AA')$ and $J(AX')$ obtained for the structurally related μ_2-phosphido complexes of type **D** are significantly greater, however ($J(AA') = 289.5$, $J(AX) = 405.9$, $J(AX') = 31.9$, $J(XX') = 2.9$ Hz). Taking into account the unusual δP values for the phosphido bridges and the pattern of the P–P coupling constants the unusual structure **3a** had to be assigned to the reaction product of composition {Pd(Ph_3P)**1a**}. Insertion of CH_2 groups between the P and Pd atoms reduces $J(AA')$ and $J(AX')$ while low-field $^{31}P\{^1H\}$ NMR resonances should be expected for the α-metalated chlorophosphine bridges μ_2-{CH_2–P(*t*Bu)Cl} in **3a**. The dipalladium complex **3a** with two asymmetrically substituted phosphorus atoms is formed with a high degree of diastereoselectivity the line pattern of only one AA'XX' spin system being observed in the $^{31}P\{^1H\}$ NMR spectrum. This is in agreement with the $^{13}C\{^1H\}$ NMR data which show only one higher-order triplet (X-part of ABNMX spin system; A, B = μ_2-P; N, M = P(Ph_3P)) at $\delta C = 9.6$ for the CH_2(P) group. As a consequence of the lower electronegativity of Pd versus Cl it is shifted to a high field compared with the δC value of the CH_2–Cl moiety in the starting material **1a** ($\delta C = 41.9$) [3]. $^{13}C\{^1H\}$ NMR signals at $\delta C = 42.4$ and 26.8 were assigned to the tertiary carbon and the Me groups of the *t*Bu substituents using DEPT spectra and the ^{13}C–^1H coupling fine structure in the ^{13}C NMR spectra.

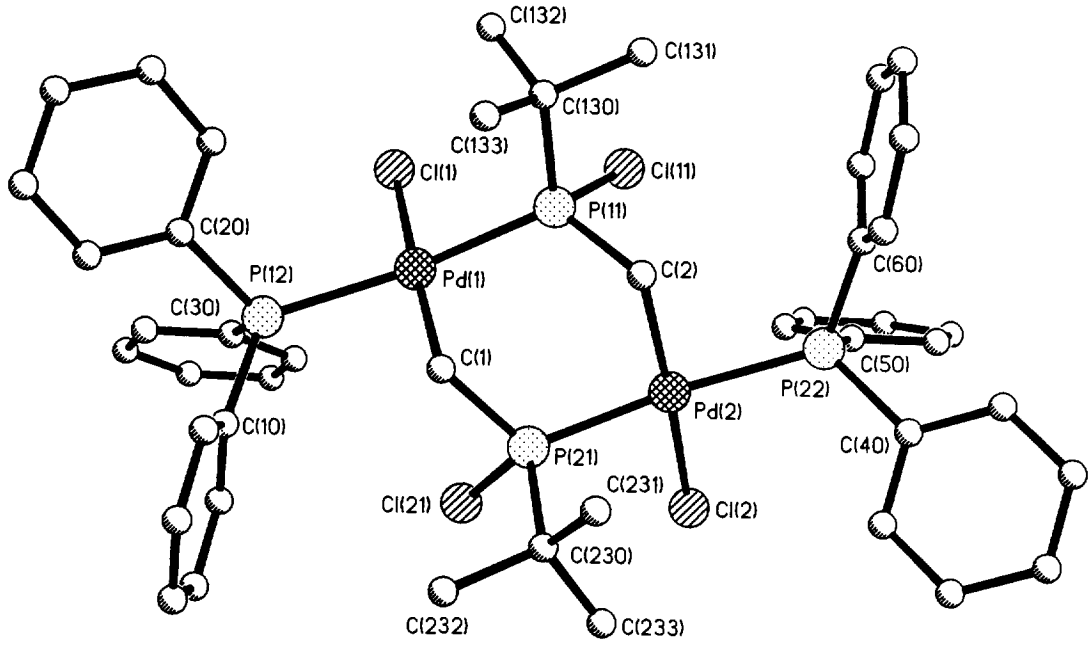
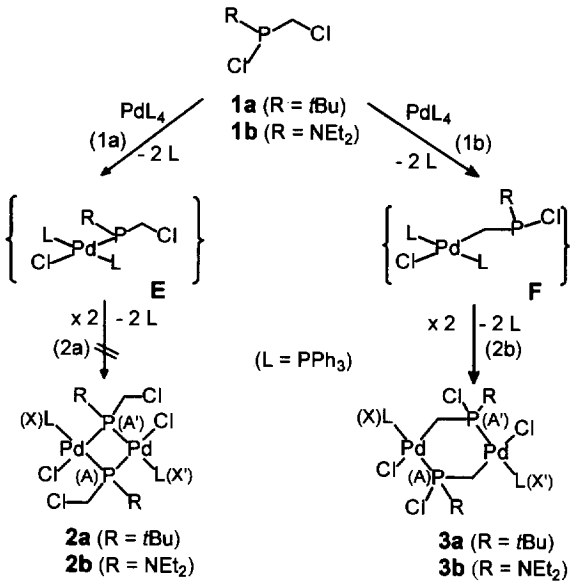


Fig. 2. Molecular structure of **3a**. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 2.051(12), Pd(1)–P(11) 2.284(4), Pd(1)–P(12) 2.356(4), Pd(1)–Cl(1) 2.383(4), Pd(2)–C(2) 2.075(11), Pd(2)–P(21) 2.287(4), Pd(2)–P(22) 2.359(4), Pd(2)–Cl(2) 2.379(4), Cl(11)–P(11) 2.049(5), Cl(21)–P(21) 2.040(5), C(1)–Pd(1)–P(11) 85.2(4), C(1)–Pd(1)–P(12) 91.5(4), P(11)–Pd(1)–P(12) 167.2(2), C(1)–Pd(1)–Cl(1) 176.4(4), P(11)–Pd(1)–Cl(1) 94.07(14), P(12)–Pd(1)–Cl(1) 89.98(13), C(2)–P(11)–C(130) 105.8(6), C(130)–P(11)–Cl(11) 102.9(5), C(2)–P(11)–Cl(11) 100.1(5), C(2)–P(11)–Pd(1) 120.3(5).



The formation of the dipalladium complex **3a** is quite surprising. It may be explained by a selective activation of the C–Cl bond in the chlorophosphine **1a** by $Pd(Ph_3P)_4$ (Eq. (1b)). Dimerization of the intermediate **F** involving elimination of Ph_3P yields the reaction product **3a** (Eq. (2b)). Activation of C–Cl bonds may be achieved under mild conditions (ambient temperature) by electron rich Pd(0) complexes, e.g. $Pd(tBu_2PH)_3$ [9](a) or $Pd(Cy_3P)_2(dba)$ (dba = dibenzylidene acetone) [9](b), even in CH_2Cl_2. In case of the reaction between **1a** and $Pd(Ph_3P)_4$ product formation is possibly controlled by the shielding effect of the bulky *t*Bu group directing the attack of the transition metal nucleophile towards the C–Cl bond at the periphery of the chlorophosphine.

Diethylaminochloromethylchlorophosphine **1b** reacted with $Pd(Ph_3P)_4$ in an analogous manner as **1a**. Based on the similarity of the $^{31}P\{^1H\}$ NMR spectra and the pertinent data ($\delta P(P_{AA'}) = 132.28$, $\delta P(P_{XX'}) = 27.06$, $N = |J(AX) + J(AX')| = 568.2$, $J(AA') = 116$ Hz) a structure analogous to that of **3a** may be assigned to the product **3b** formed concommitantly with Ph_3P. Due to the formation of side products which could not be separated from **3b** the product of this reaction could not be obtained analytically pure.

Crystals of composition **3a**·$2.5CHCl_3 \cdot 2H_2O$ obtained by recrystallization of **3a** from chloroform containing small amounts of water were used for a single crystal X-ray diffraction study. The asymmetric unit contains two independent molecules **3a** their structure being consistent with that derived from the analysis of the NMR spectra. As shown in Fig. 2 the Pd atoms and the the α-metalated chlorophosphine bridges, η^2,μ_2-{CH_2–P(*t*Bu)Cl}, form a chair shaped $Pd_2P_2C_2$ six-membered ring. In both cystallographically independent molecules in the asymmetric unit the substituents at the μ_2-phosphorus atoms P(11) and P(21) are in *cis*-position. The coordination geometry at the Pd atoms is distorted square planar. While the Pd–P distance

(Pd(1)–P(11) = 2.284(4), Pd(2)–P(21) = 2.287(4) Å) in **3a** is significantly shorter than in *trans*-$Cl_2Pd[Cl(tBu)–CH_2–Cl]_2$ (**G**) [10] (Pd(1)–P(1) = 2.3172(10) Å), the opposite is true for the Pd–Cl and P–Cl bond lengths (Pd(1)–Cl(1)/Pd(2)–Cl(2) = 2.383(4)/2.379(4) or P(11)–Cl(11)/P(21)–Cl(21) = 2.049(5)/2.040(5) Å) in **3a** versus Pd(1)–Cl(1) = 2.2898(10) or P(1)–Cl(2) = 2.0347(11) in **G**.

3. Experimental section

All reactions were performed in an oxygen-free atmosphere using standard Schlenk technique. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 400.1, 100.6 and 162.0 MHz on a Bruker AC 400 instrument. The chloromethylchlorophosphines **1a** and **1b** were prepared by reaction of *t*BuMgCl or $Et_2N–SiMe_3$ with $Cl_2P–CH_2–Cl$ as reported earlier by us [3,4].

3.1. Preparation of $\{Cl(Ph_3P)Pd[\eta^2,\mu_2\text{-}CH_2–P(tBu)Cl]\}_2$ (3a)

To a suspension of 9.71 g (8.4 mmol) $Pd(Ph_3P)_4$ in 50 ml of toluene 1.45 g (8.4 mmol) of *t*-butylchloromethylchlorophosphine **1a** were added with magnetic stirring at ambient temperature. After 1 h the solvent was removed in vacuo and the remaining residue was dissolved in 10 ml of dichloromethane. The solution obtained was poured into 250 ml of petrolether 40/60 a yellow colored precipitate being formed. After filtration with a Schlenk frit the remaining yellow solid was washed with three aliquots of 5 ml of petrolether and dried in vacuo. The filtrate contained all the Ph_3P formed during the reaction. For a further purifcation **3a** was recrystallized from chloroform. Yield: 3.35 g (73.6%).

3.1.1. Spectroscopic and analytical data of 3a

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 303 K): [ppm] $\delta P(A,A') = 138.3$; $\delta P(XX') = 26.6$; $J(AA') = 42.1$, $J(AX) = 517.1$, $J(AX') = -2.7$, $J(XX') = 3.7$; $-$ $^{13}C\{^1H\}$ NMR ($CDCl_3$, 303 K): [ppm] $\delta C = 9.6$ (*t*, CH_2); 26.8 (m, $CH_3(tBu)$); 42.4 (s, C(*t*Bu)); 128.5 (d, 10.2 Hz, C3-aryl); 130.5 (s, C4-aryl); 131,0 (d, 39.7 Hz, C1-aryl); 135.6 (d, 11.2 Hz, C2-aryl); $-$ ^1H NMR ($CDCl_3$, 303 K): [ppm] = 0.9 (m, CH_2, 2 H) 1.12 (d, 16.3 Hz. $CH_3(tBu)$, 9 H); 7.45 (m, Ph, 9 H), 7.78 (m, Ph, 6 H) ($^nJ(C,P)$ and $^nJ(H,P)$ in parentheses). Analysis found: C, 50.85; H, 4.94; Cl, 13.34. $C_{46}H_{52}Cl_4P_4Pd_2$ (1083.46). Calculation: C, 50.99; H, 4.84; Cl, 13.09%.

3.2. X-ray structure analysis of 3a

Empirical formula: $\mathbf{3a}\cdot 2.5CHCl_3\cdot 2H_2O$, crystal size 0.52 × 0.44 × 0.30 mm, space group monoclinic, $P2_1/n$ (Nr. 14), $a = 19.283(7)$, $b = 31.641(9)$, $c = 21.811(5)$ Å, $\beta = 94.81(2)°$, $V = 13261(7)$ Å^3, $Z = 8$, $F(000) = 5704$, $D_{calc} = 1.420$ g × cm^{-3}, $\mu(MoK_\alpha) = 1.135$ mm^{-1}. Data collection was performed on a Siemens P4 Diffractometer, $T = 293$ K, ω-scan, 17206 independent reflections with $\theta \leq 22.51°$, $R_1 = 0.080$ for 7875 reflections with $|F^2| > 2\sigma(F^2)$, $wR_2 = 0.199$, $S = 0.896$. The structure was refined by full matrix least square techniques using the SHELXL-93 program system [11]. Hydrogen atoms were placed in calculated positions and all other atoms were refined anisotropically with exception of the oxygen atoms of the water molecules. Full details of data collection, structure refinement, thermal parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre [12].

Acknowledgements

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[12] Copies of these data may be obtained under the deposit number 100356 free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (Fax: int. code + 44(0)1223/336-033, e-mail: deposit @ chemcrys.cam.uk).