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> SHORT COMMUNICATIONS

Synthesis of (2-X,3-Y-Phenyl)dimethylphosphanes (X, Y = Me₂P, H; Me₂P, F; Br, F) and Their Complexes with PdCl₂

L. I. Goryunov^a, J. Grobe^b, V. D. Shteingarts^a, and R. Mews^c

^aVorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia e-mail: shtein@nioch.nsc.ru ^bInstitut fur Anorganische und Analytische Chemie der Westfalischen Wilhelms-Universitat, Corrensstraβe 28/30, D-48149 Munster (Germany) e-mail: grobe@uni-muenster.de. ^cInstitut fur Anorganische und Physikalische Chemie, Universitat Bremen, Germany

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Earlier the trimethylsilyldimethylphosphane Me_2P -SiMe₃ (I) was utilized for the substitution of fluorine atom with PMe₂ groups in polyfluoroarenes C₆F₅X (X = H, F, Cl, CF₃, etc.) and pentafluoropyridine [1, 2], and also in 1,2,3and 1,3,5-trifluoro-, 1,2- and 1,3-difluorobenzenes [3, 4]. In this study the reagent was applied to the preparation of benzene-1,2-diylbis(dimethylphosphane) (II) and its new analog, 3-fluorobenzene-1,2-diylbis(dimethylphosphane) (III), chelating ligands for transition metal complexes as had been described for phosphane II [5, 6].

The reaction of *ortho*-difluorobenzene with exess phosphane I at relatively high temperature led to the formation (in keeping with the data of ¹⁹F and ³¹P NMR spectra) a mixture of dimethyl(2-fluorophenyl)phosphane (32%) [4] and diphosphane II (68%) isolated in 60% yield (Scheme 1). Lately diphosphane II was synthesized from dimethyl-(2-chlorophenyl)phosphane by metallation with lithium followed by the treatment with dimethylchlorophosphane [5] of by alkylation of 1,2-diphosphanobenzene

Scheme 1.



sodium salts with methyl iodide [7] in 11 and 68% yield respectively.

Phosphane IV obtained formerly by phosphanedebromination of 2,6- $F_2C_6H_3Br$ with lithium dimethylphosphide (V) [8] reacted with phosphane I under milder conditions affording in 96% yield diphosphane III that was isolated in 57% yield (path *a*, Scheme 2).

Phosphane I in contrast to phosphide V reacts with 2,6-F₂C₆H₃Br to give 92% of (2-bromo-3-fluorophenyl) dimethylphosphane (VI) and 7% of phosphane IV (Scheme 2, path b). The main product was isolated in 62% yield. The discovered difference in the results of the reaction between 2,6- $F_2C_6H_3Br$ and reagents I and V is probably due to the difference in the mechanism of reactions involving nucleophiles I and V: With Me₂PLi this is the mechanism S_{RN} initiated by the electron transfer from the nucleophile to the substrate (cf. [8]), and in the process with Me₂PSiMe₃ it is synchronic mechanism $A_N D_N$ apparently observed in its reactions with di- and trifluorobenzenes [4]. In this respect it is illustrative that the ratio (VI)–(IV) equal 13:1 indicates a weaker element-effect compared to reactions S_N Ar: In the products of reaction between bromofluorobenzenes with sodium methylate in a mixture DMSO-MeOH the Br-ions have not been found even in traces [9]. Probably the relatively low selectivity with respect to the nature of the substituted halogen is characteristic of the $A_N D_N$ mechanism combining in a cer-





Scheme 3.



R = H (II, VII), F (III, VIII).

tain way the properties of the mechanisms S_N Ar and S_N 2.

We prepared from phosphanes **II**, **III**, and **VI** new palladium complexes: [benzene-1,2-diylbis(dimethylphosphane)]palladium(II) chloride (**VII**), [3-fluorobenzene-1,2-diylbis(dimethylphosphane)]palladium(II) chloride (**VIII**), and bis[(2-bromo-3-fluorophenyl)dimethylphosphane)]palladium(II) chloride (**IX**) in 71–93% yield under the formerly described conditions [4] (Scheme 3).

The composition and the structure of first obtained compounds **III**, **VI–IX** were proved using ¹H, ¹⁹F, and ³¹P NMR spectra, for complexes, the data of high resolution mass spectrometry and elemental analyses. NMR spectra of phosphanes **III** and **VI** are in agreement with described spectra of their dimethyl- [7, 8] and diphenylphosphanyl [10] analogs. In the NMR spectra of the complex **VIII** solution in DMSO-*d*₆ alongside the peaks corresponding to proper structure **VIII** (Scheme 3) signals are present belonging evidently to the oligomeric form of this complex (content in the mixture ~15%). It is analogous to the previously described fact for poly(diphenylphosphanyl)benzene complexes of PdCl₂ and PtCl₂ [11]. Complex **IX** in the same solvent exists as a mixture of *cis- and trans*-isomers (cf. [4]).

Benzene-1,2-diylbis(dimethylphosphane) (II) was obtained from 0.057 g (0.5 mmol) of 1,2-difluorobenzene and 0.148 g (1.1 mmol) of phosphane I in 0.5 ml of C_6H_6 in an evacuated ampule under conditions indicated in Scheme 1. The volatile components were distilled off in a vacuum (0.08 mm Hg) at 20°C, from the residue by distillation under the same pressure at heating the bath to 100°C diphosphane II was isolated. Yield 0.061 g (60%), colorless fluid. ¹H and ³¹P{¹H} NMR spectra are in agreement with those published in [7].

Compounds III and VI were similarly obtained.

3-Fluorobenzene-1,2-diylbis(dimethylphosphane) (III) was obtained from 0.056 g (0.32 mmol) of phosphane VI and 0.052 g (0.38 mmol) of phosphane I under the conditions indicated in Scheme 2. Yield 0.039 g (57%), colorless fluid. ¹H NMR spectrum (C₆D₆), δ , ppm: 1.14 d (6H, CH₃, ²J_{PH} 4.1 Hz), 1.34 d (6H, CH₃, ²J_{PH} 4.1 Hz), 6.50–7.20 (3H, CH). ¹⁹F NMR spectrum, δ , ppm: –104.6 br.s. ³¹P{¹H} NMR spectrum, δ , ppm: –47.3 d.d (C²P, ⁴J_{PF} 4.2, ³J_{PP} 165.5 Hz), –52.2 d.d (C⁷P,

${}^{3}J_{\rm PF}$ 9.3, ${}^{3}J_{\rm PP}$ 165.5 Hz).

(2-Bromo-3-fluorophenyl)dimethylphosphane (VI) was obtained from 0.239 g (1.2 mmol) of 2,6- $F_2C_6H_3Br$ and 0.107 g (0.8 mmol) phosphane I under the conditions indicated in Scheme 2. The volatile components were distilled off in a vacuum (0.08 mm Hg) at 20°C, from the residue by double distillation under the same pressure at heating to 150°C phosphane VI was isolated. Yield 0.116 g (62%), colorless fluid. ¹H NMR spectrum (C₆D₆), δ , ppm: 0.97 d (6H, CH₃, ²J_{PH} 4.5 Hz), 6.50–6.80 m (3H, CH). ¹⁹F NMR spectrum, δ , ppm: –105.9 m. ³¹P{¹H} NMR spectrum, δ , ppm: –40.8 d (⁴J_{PF} 9.2 Hz).

[Benzene-1,2-diylbis(dimethylphosphane)] palladium(II) chloride (VII). A solution of 0.060 g (0.3 mmol) of diphosphane II and 0.116 g (0.3 mmol) of (PhCN)₂PdCl₂ in 1 ml of CH₂Cl₂ was stirred under an argon atmosphere in conditions indicated in Scheme 3. The precipitate was filtered off, washed with CH₂Cl₂ (2 ml), and dried in a vacuum (0.08 mm Hg) at 20°C. Yield 0.086 g (77%), yellow crystals. ¹H NMR spectrum (DMSO- d_6), δ , ppm: 2.11 s (12H, CH₃), 7.90 m (2H, CH), 8.30 m (2H, CH). ³¹P {¹H} NMR spectrum, δ , ppm: 37.5 s. Found [M-Cl⁻] + 336.945. C₁₀H₁₆³⁵ClP₂¹⁰⁴Pd. Calculated [M-Cl⁻] 336.945.

Compounds III and IX were similarly obtained.

[3-Fluorobenzene-1,2-diylbis(dimethylphosphane)]palladium(II) chloride (VIII) was obtained from 0.039 g (0.18 mmol)of diphosphane III and 0.069 g (0.18 mmol) of (PhCN)₂PdCl₂. Yield 0.051 g (71%), light-brown crystals. ¹H NMR spectrum (DMSO- d_6), δ , ppm: 2.13 m (6H, CH₃), 2.22 m (6H, CH₃), 7.70 m (1H, CH), 8.0 m (1H, CH), 8.20 m (1H, CH). ¹⁹F NMR spectrum, δ , ppm: -102.0 m. ³¹P {¹H} NMR spectrum, δ , ppm: 40.4 m (C¹P, C²P). Found [*M*-Cl⁻]+ 355.936. C₁₀H₁₅³⁵ClFP₂¹⁰⁵Pd. Calculated [*M*-Cl⁻] 355.937.

Bis[(2-bromo-3-fluorophenyl)dimethylphosphane)]-palladium(II) chloride (IX) was obtained from 0.116 g (0.49 mmol) of phosphane VI and 0.095 g (0.247 mmol) of (PhCN)₂PdCl₂. Yield 0.148 g (93%), light-yellow crystals, mp 197–202°C. ¹H NMR spectrum (DMSO- d_6), δ , ppm: 1.75 t (6H, CH₃, ²J_{PH} \approx $^{4}J_{PH} \approx$ 3.5 Hz, trans), 1.82 d (6H, CH₃, ²J_{PH} 10.6 Hz, *cis*), 7.28–7.42, 7.45–7.58 (CH; 3H *cis* and 3H *trans*). ¹⁹F NMR spectrum, δ , ppm: –104.5 m (*cis*), –105.60 m (*trans*). ³¹P{¹H} NMR spectrum, δ , ppm: 2.60 br.s (*trans*, 17%), 7.60 br.s (*cis*, 83%). Found, %: C 30.35; H 2.80. C₁₆H₁₈Br₂Cl₂F₂P₂Pd. Calculated, %: C 29.68; H 2.80.

¹H (200.13 MHz, internal references residual undeuterated benzene or DMSO), ¹⁹F (188.31 MHz, external reference CCl₃F), and ³¹P (81.02 MHz, external reference 85% H₃PO₄) were registered on a spectrometer Bruker AC200. Mass of molecular ions was determined on a high-resolution mass spectrometer Thermo Scientific DFS (70 eV). The preparation of Me₃SiPMe₂ (I) and its reactions with haloarenes were performed as previously described [1–4, 8].

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