## Facile Syntheses of 1,8-Bis(diphenylphosphino)anthracene and 1,8-Bis(dimethylamino)anthracene by Nucleophilic Substitution of 1,8-Difluoroanthracene<sup>1</sup>

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Abstract: 1,8-Bis(diphenylphosphino)anthracene (1) was prepared in a three-step synthesis in 51 % overall yield starting from 1,8-dichloro-9,10-anthraquinone (8). Compound 8 was converted by chlorine-fluorine exchange and reduction with zinc into 1,8-difluoroanthracene (7) from which 1 was obtained by reaction with potassium diphenylphosphide. The conversion of 7 with lithium dimethylamide to 1,8-bis(dimethylamino)anthracene (10) clearly showed that in the case of 7 direct nucleophilic displacement (addition-elimination mechanism) dominates over aryne formation (elimination-addition mechanism). Single crystal X-ray structure analyses are reported for 1 and 10.

Previously of 1,8we reported the synthesis the bis(diphenylphosphino)anthracene (1) and its reaction with nickel or palladium dichloride forming cyclometallated and hence extremely stable complexes 2 and  $3^2$ . As a result of the cyclometallation at the anthracene C-9 atom, the diphosphine 1 is acting as a tridentate PCP ligand in these complexes. Whereas we first had failed to prepare the diphosphine 1 from either 1,8-dichloro- or 1,8-dibromoanthracene, 1 was obtained in moderate yield of 33 % by reaction of potassium anthracenedisulfonate (4) with two equivalents potassium diphenylphosphide (Ph2PK) in diethylene glycol diethyl ether (DEGDEE) under harsh reaction conditions (180°C, 20 h).<sup>2,3</sup> The disulfonate 4 needed for this conversion was prepared by zinc reduction of potassium 9,10-anthraquinone-1,8-disulfonate.<sup>4</sup> However, since the latter compound apparently is not commercially available anymore, it was desirable to search for a new and improved synthesis of the diphosphine 1.



In a recent paper we described the reaction of 4,5-difluoroacridine (**5**) with potassium diphenylphosphide (Ph<sub>2</sub>PK) giving 4,5bis(diphenylphosphino)acridine (**6**) in 79 % yield.<sup>5</sup> This prompted us to attempt the synthesis of **1** from 1,8-difluoroanthracene (**7**) and to investigate the use of fluoro substituted polycyclic aromatic hydrocarbons in nucleophilic aromatic substitution reactions with alkali metal phosphides and other nucleophiles.<sup>6</sup>



The unknown 1,8-difluoroanthracene (7) was prepared from the commercially available 1,8-dichloro-9,10-anthraquinone (8) in a two-

step synthesis. Following a literature procedure **8** was converted by reaction with cesium fluoride in dimethyl sulfoxide under anhydrous conditions into 1,8-difluoro-9,10-anthraquinone (**9**) [m.p. = 228°C (DSC, lit.<sup>7</sup> m.p. = 228-229°C), 71 %].<sup>7</sup> Reduction of **9** with zinc powder in aqueous ammonia (75°C, 4 h) followed by an acidic treatment (aqueous HCl, 2-propanol, reflux, 3 h) yielded **7** [yellow needles, m.p. = 142°C (DSC), 84%].<sup>8,9</sup> As anticipated compound **7** proved to be highly reactive for nucleophilic displacement of the fluoro substituents by alkali metal phosphides. Reaction with two equivalents potassium diphenylphosphide (Ph<sub>2</sub>PK, dioxane/THF 5:1 reflux, 3 h)<sup>10</sup> converted **7** in excellent yield to the diphosphine **1** [yellow needles, m.p. = 234°C (lit.<sup>2</sup> m.p. = 233-235°C), 86 %]. For the three-step synthesis starting from commercial **8** the overall yield of the diphosphine **1** was 51 %.



The fact that 7 is converted efficiently into 1 without forming 1,7- or 2,7-substituted isomers rules out that the elimination-addition mechanism (aryne mechanism) is involved. Hence it must be assumed that the direct nucleophilic displacement  $7 \rightarrow 1$  proceeds by the addition-elimination mechanism.11 However, in the case of the nucleophilic substitution of 1-fluoronaphthalene by different alkali metal amides (amide, diethylamide, piperidide) the corresponding 1and 2-naphthylamines were formed in varying ratios which were interpreted by a competition of both mechanisms.<sup>11,12</sup> This gave us reason to attempt the nucleophilic substitution of 7 by alkali metal amides in order to see whether the direct nucleophilic displacement of the fluoro substituents is restricted to special nucleophiles such as alkali metal phosphides or represents a reaction of more general use. Treating 7 with 12 equivalents of lithium dimethylamide [(CH<sub>2</sub>)<sub>2</sub>NLi, prepared from dimethylamine and *n*-butyllithium] in dioxane/THF  $(1:1)^{10}$ yielded the unknown 1,8-bis(dimethylamino)anthracene (10, red crystals, m.p. =  $128^{\circ}$ C, 65 %).<sup>13,14</sup> As analysed by GC and GC-MS, the crude product of the reaction contained two isomers of the major component 10. Their yields with respect to 10 amounted to < 5 % and <0.5 %. Considering the relative ratios, it is tempting to assume that the two isomers possibly are 1.7- and 2.7-bis(dimethylamino)anthracene formed by a small contribution of the elimination-addition mechanism. However, no matter what their structures are, direct nucleophilic displacement also is found to be the major pathway in the reaction of 7 and lithium dimethylamide. The observation, that the direct nucleophilic displacement of fluoro substituents apparently is more favourable for anthracene than for naphthalene compounds, can be interpreted by considering the relative energies of the negatively charged  $\sigma$ -complexes which are formed as intermediates by the addition-elimination

301

When **7** was treated with only two equivalents of lithium dimethylamide under the same conditions as in the previous reaction,<sup>10</sup> a product mixture was obtained which according to GC and GC-MS analyses contained 50 % of a dimethylaminofluoroanthracene besides 36 % educt **7** and traces of **10**. Based on the structural characterisation of **10** it can be anticipated that the compound obviously is 1-dimethylamino-8fluoroanthracene (**11**). Using compound **11** the preparation of 1-amino-8-phosphinoanthracenes such as **12** is feasible by reaction with potassium diphenylphosphide. This will enable us to extend our investigations of the PCP ligand **1** to NCN and NCP ligands of types **10** and **12**.



In the context of our interest to use the diphosphine **1** and the diamine **10** as potential polydentate ligands in transition metal compounds, the molecular structures of both compounds were determined by single crystal X-ray structure analyses (Figure 1).<sup>16</sup>



Figure 1. a)Molecular structure of 1,8-bis(diphenylphosphino)anthracene (1, solvent molecule dichloromethane omitted). b) Molecular structure of 1,8-bis(dimethylamino)anthracene (10)<sup>16</sup>

As expected both ligands contain essentially planar anthracene skeletons. The bond distances between the heteroatoms and the substituted anthracene carbon atoms are 1.826(3) Å (P1-C1) and 1.813(3) Å (P2-C11) in **1** and 1.422(2) Å (N1-C1) and 1.424(2) Å (N2-C11) in **10**. The valence angles at the substituted anthracene carbon atoms show small deformations which cause the substituents to be inclined somewhat towards each other [**1**: C2-C1-P1: 122.8(2)°; C14-C1-P1: 118.2(2)°; C10-C11-P2: 122.9(2)°; C12-C11-P2: 117.3(2)°; **10**: C2-C1-N1: 123.4(2)°; C14-C1-N1: 117.1(1)°; C10-C11-N2: 122.9(2)°; C12-C11-P2: 117.7(1)°]. This results in distances P1…P2 of 4.925(5) Å for **1** and N1…N2 of 4.960(3) Å for **10**. The phosphorus atoms of **1** and the nitrogen atoms of **10** show tetrahedral geometries. Experiments are

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currently underway to further explore the coordination chemistry of the PCP ligand 1 and to investigate the properties of 10 as NCN-ligand in corresponding transition metal complexes.

In conclusion, we have shown that fluoro-substituted polycyclic arenes and heteroarenes such as **7** and **5** can serve as synthetically useful intermediates which are capable of direct nucleophilic displacement reactions by various strong nucleophiles.<sup>5,17</sup>

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303

with  ${}^{4}J_{CF} = 4.9$  Hz, C-4,-5), 122.8 (s, d with  ${}^{2}J_{CF} = 17.5$  Hz, C-8a,-9a), 113.2 (d, t with  ${}^{3}J_{CF} = 4.5$  Hz, C-9) 108.2 (d, d with  ${}^{2}J_{CF} = 19.7$  Hz, C-2,-7).

- (10) A solution of  $Ph_2PK$  in THF or  $(CH_3)_2NLi$  in THF was added at room temp. to a solution of **7** in dioxane and subsequently the mixture was stirred under reflux for 3 h  $[Ph_2PK]$  or 1 h  $[(CH_3)_2NLi]$ , respectively.
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- (13) **10**:  $C_{18}H_{20}N_2$  (264.37 g mol<sup>-1</sup>): calcd. 81.78 % C, 7.63 % H, 10.60 % N; found: 80.83 % C, 7.38 % H, 10.41 % N. - MS (EI, 70 eV): m/z (%) = 264 (100, M<sup>+</sup>), 263 (8), 249 (12), 234 (14), 218 (11), 204 (5). - <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.18 (s, 1 H, 9-H), 8.34 (s, 1 H, 10-H); 7.62, 7.35, 6.97 [ABC spin system with <sup>3</sup>J<sub>AB</sub> = 8.5 Hz, <sup>3</sup>J<sub>BC</sub> = 7.2 Hz, each 2 H for 4-,5-H (A), 3-,6-H (B), 2-,7-H (C)], 3.00 (s, 12 H, CH<sub>3</sub>).- <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.3 (s, C-1,-8), 133.0 (s, C-4a,-10a), 127.0 (s, C-8a,-9a), 126.8 (d, C-10), 125.4 (d, C-3,-6), 122.6 (d, C-4,-5), 120.0 (d, C-9), 112.2 (d, C-2,-7), 45.3 (q, CH<sub>3</sub>).
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- (16) Single crystal X-ray structure analyses:  $1 \cdot CH_2Cl_2$  (crystallized from dichloromethane): Empirical formula:  $C_{38}H_{28}P_2 \cdot CH_2Cl_2$ , molecular mass: 631.47 g mol<sup>-1</sup>, crystal size: 0.21 x 0.35 x 0.80 mm, monoclinic,  $P2_1/n$  (no. 14), a = 8.3420(6) Å, b = 21.384(2) Å, c = 17.8822(13) Å,  $\beta$  = 963170(10)°, V = 3170.6(4) Å^3, T = 293 K, d<sub>calcd</sub> = 1.323 g cm<sup>-1</sup>,  $\mu$  = 0.333 mm<sup>-1</sup>, F(000) = 1312 e, Z = 4,  $\lambda$  = 0.71073 Å, 7880 measured reflections [±h,+k,+l], [sinθ/ $\lambda$ ]<sub>max</sub> = 0.65 Å<sup>-1</sup>, 7415 independent and 3977 observed reflections [I>2\sigma(I)], 388 refined parameters, H atoms were calculated and not refined in the final refinement by least squares, R = 0.0688, R<sub>w</sub> = 0.1839 [w = 1/\sigma^2(F\_o^2)+(0.100P)^2 + 0.000P) with P = (F\_o^2+2F\_c^2)/3], residual electron density 0.615 e Å<sup>-3</sup>.

**10** (crystallized from *n*-octane): Empirical formula:  $C_{18}H_{20}N_2$ , molecular mass: 264.36 g mol<sup>-1</sup>, crystal size: 0.12 x 0.38 x 0.47 mm, orthorhombic, *P*bca (no.61), a = 13.505(3) Å, b = 15.318(2) Å, c = 14.054(2) Å, V = 2907.5(8) Å<sup>3</sup>, T = 100 K, d<sub>calcd</sub> = 1.208 g cm<sup>-3</sup>,  $\mu = 0.071 \text{ mm}^{-1}$ , F(000) = 1132 e, Z = 8,  $\lambda = 0.71069$  Å, 3794 measured reflections [+h,+k,+l],  $[\sin\theta/\lambda]_{max} = 0.65$  Å<sup>-1</sup>, 3315 independent and 2153 observed reflections  $[I>2\sigma(I)]$ , 261 refined parameters, H atoms were found and refined in the final refinement by least squares, R = 0.0550,  $R_w = 0.1451$  [w = 1/ $\sigma^2(F_o^2)$ +(0.100P)<sup>2</sup> + 0.000P) with P =  $(F_o^2 + 2F_c^2)/3$ ], residual electron density 0.330 e • Å<sup>-3</sup>. Atomic coordinates and e.s.d.'s have been deposited at the Cambridge Crystallographic Data Centre.

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