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## 4,5-Bis(diphenylphosphino)acridine: A New Type of Tridentate Phosphorus-Nitrogen-Phosphorus Ligands<sup>1</sup>

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Abstract: Reaction of 4,5-difluoroacridine (8) with two equivalents of potassium diphenylphosphide (Ph<sub>2</sub>PK) yielded the title compound 3. Contrarily, diphenylphosphine (Ph<sub>2</sub>PH) reacted with 8 under addition, and 4,5-difluoro-9-diphenyl-9,10-dihydroacridine (12) was obtained. Compound 8 was prepared from 2-amino-3-fluorobenzoic acid (13) in a four step synthesis. As it is shown by the preparation of the metal complexes 4,5-bis(diphenylphosphino)-acridine-palladium dichloride (16) and 4,5-bis(diphenylphosphino)acridine-molybdenum tricarbonyl (17), compound 3 is capable of acting as a tridentate PNP ligand which coordinates transition metals in an approximately "T-shaped" planar coordination geometry. Single crystal X-ray structure analyses are reported for 3 and 17.

The importance and application of bidentate or polydentate phosphine ligands<sup>2</sup> in homogeneous catalysis is considerably extended by combining phosphorus centers and donors such as nitrogen or oxygen atoms in P/N ligands<sup>3</sup> or P/O ligands.<sup>4</sup> In the context of our concept of using polycyclic arenes and heteroarenes as rigid carbon skeletons for the construction of new bidentate and tridentate diphosphine ligands we previously described 1,8-bis(diphenylphosphino)anthracene (1)<sup>5</sup> and 4,6-bis(diphenylphosphino)dibenzofuran (2)<sup>6</sup> acting as tridentate PCP or POP ligands, respectively. In extending this concept to PNP ligands we now introduce 4,5-bis(diphenylphosphino)acridine (3, "acriphos").



The structure of 3 is related to the tridentate PNP ligand 2,6-bis(diphenylphosphinomethyl)pyridine (4).<sup>7-9</sup> However, the methylene groups connecting the phosphorus atoms and the pyridine ring make 4 less rigid than 3 and also involve some disadvantages. Apart from metal complexes 5 showing a tridentate coordination with a "T-shaped" planar geometry, apparently also complexes 6 exist which contain 4 as a bidentate ligand.<sup>8</sup> With basic reagents such as alkalimetal alkoxides complexes 5 react under elimination of benzylic hydrogen atoms to form delocalized phosphinomethanide structures 7.<sup>9</sup> As benzylic substituted tertiary phosphines the phosphorus atoms of 4 are considerably more sensitive towards oxidation than the triarylphosphine groups of 3.



For the synthesis of 3 we first prepared the unknown 4,5-dihalogenoacridines (8 - 10).<sup>10</sup> However, using 4,5-dichloro- and 4,5-dibromoacridine (9 and 10) the diphosphine 3 either was not obtained at all or was formed only in very low yields. On the other hand, the reaction of 4,5-difluoroacridine (8) with two equivalents of potassium diphenylphosphide (Ph<sub>2</sub>PK, dioxane/tetrahydrofuran 5:1, reflux, 1 h) yielded 3 (yellow crystals, dec.

255°C, 79 %).<sup>11,12</sup> This smooth reaction is remarkable in so far as acridine is known to be reactive towards nucleophilic addition at its C-9 position, and accordingly the phosphide Ph<sub>2</sub>PLi was reported to react with acridine under addition to 11.<sup>13</sup> When 8 was treated with the secondary diphenylphosphine Ph<sub>2</sub>PH instead of the phosphide Ph<sub>2</sub>PK, even mild reaction conditions (tetrahydrofuran, room. temp., 2 h) led to addition and 4,5-difluoro-9-diphenyl-9,10-dihydroacridine (12, m.p. 151°C, 46 %) was obtained (scheme 1).<sup>12</sup>



The necessary 8 (yellow crystals, m.p. 193-195°C) was prepared from 2-amino-3-fluorobenzoic acid  $(13)^{14}$  in a four step synthesis (scheme 2).<sup>11,12</sup> The crucial step is the selective removal of the chloro substituent from 9-chloro-4,5-difluoroacridine (15) without interfering with the fluoro substituents which are similarly reactive towards nucleophilic attack.



Scheme 2: a) 2-Fluoroiodobenzene, copper powder/K<sub>2</sub>CO<sub>3</sub>, cyclohexanol, reflux, 12 h (71 %); b) POCl<sub>3</sub>, reflux, 3.5 h (81 %); c) p-tosylhydrazine, CHCl<sub>3</sub>, 50°C, 30 min (87 %); d) NaOH/H<sub>2</sub>O/ethylene glycol, reflux, 2 h (62 %).

As shown by single crystal X-ray structure analysis (Figure 1a), compound 3 has the molecular structure expected with a planar acridine skeleton.<sup>15</sup> The planes between the outer benzene rings of acridine form an angle of  $177.9^{\circ}$ , and the P...P distance is found to be 4.338(1) Å.

In first experiments the coordination chemistry was studied by reacting the ligand 3 with different transition metal compounds. For instance the reactions of 3 with bis(benzonitrile)palladium dichloride in dichloromethane and of 3 with 2,5-norbornadiene-molybdenum tetracarbonyl in toluene yielded 4,5-bis(diphenylphosphino)-acridine-palladium dichloride [16, light-brown solid, dec. >185°C (DSC), 81 %] and 4,5-bis(diphenylphosphino)acridine-molybdenum tricarbonyl [17, dark-green solid, dec. >345°C (DSC), 15 %], respectively.<sup>12</sup>



In the complexes 16 and 17 both phosphorus atoms are coordinated to metal, as it is shown by the single signals in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra [81 MHz; 16:  $\delta = 32.7$  (CDCl<sub>3</sub>); 17:  $\delta = 58.6$  (CD<sub>2</sub>Cl<sub>2</sub>)]. The coordination of the nitrogen atom is suggested by the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra which in comparison with 3 show considerable shifts to lower magnetic field especially for 9-H, C-9 and C-4a,-10a [16:  $\Delta\delta(9-H) = 2.15$ ,  $\Delta\delta(C-9) = 11.2$ ,  $\Delta\delta(C-4a,-10a) = 4.2$ ; 17:  $\Delta\delta(9-H) = 0.18$ ,  $\Delta\delta(C-9) = 2.2$ ,  $\Delta\delta(C-4a,-10a) = 5.5$ ]. The ionic structure 16 proposed

corresponds with the mass spectrum (electrospray ionization: parent ion m/z = 688 for the complex cation  $[3+Pd+Cl]^+$ ) and with the conductivity, which in chloroform solution has a similar order as tetra-*n*-butylammonium perchlorate in comparable concentration. Finally, the single crystal X-ray structure analysis of 17 (Figure 1b) unambiguously shows that 3 really is capable of acting as a tridentate PNP ligand which complexes transition metal atoms with an approximately "T-shaped" planar coordination geometry.<sup>15</sup> In 17 the P…P distance is 4.732(1) Å and hence 0.4 Å longer than in the free ligand 3. The molybdenum atom is surrounded by a distorted octahedral ligand sphere formed by the tridentate ligand 3 and the three residual carbonyl ligands in *mer*-configuration [angles P1-Mo-P2: 156.8(1)°; C39-Mo-C40:170.5(2)°; N-Mo-C38: 176.9(2)°]. Since in 17 the P…Mo distances of 2.405(1) Å and 2.426(1) Å are in the upper range as determined for metal-phosphorus distances in transition metal phosphine complexes,<sup>16</sup> it can be assumed that the ligand 3 is capable of coordinating almost any transition metal in different oxidation states.

"Acriphos" **3** represents the first example of a new type tridentate PNP ligands. The synthesis via nucleophlic substitution of 4,5-difluoroacridine (**8**) makes it possible to prepare a series of other ligands containing different substituents at the phosphorus atoms, including chiral "acriphos" ligands.<sup>17</sup> Studies to investigate the possible application of the new PNP ligand **3** in catalysis are currently under way.



Figure 1: a) Molecular structure of 4,5-bis(diphenylphosphino)acridine (3), front view on acridine. b) Molecular structure of 4,5-bis(diphenylphosphino)acridine-molybdenum tricarbonyl (17).<sup>15</sup>

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## **References and Notes**

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- 11. 3: MS (EI, 70 eV): m/z (%) = 547 (100, M<sup>+</sup>), 360 (13), 284 (12), 283 (15). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>, external standard 85 % phosphoric acid):  $\delta = -14.7$  (s). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 8.82$  (s, 1 H, 9-H); 8.00 (dd), 7.40 (dd) and 7.15 (ddd) [ABCXX'-spin system with X = X' = <sup>31</sup>P, <sup>3</sup>J<sub>AB</sub> = 8.5 Hz, <sup>4</sup>J<sub>AC</sub> = 1.5 Hz, <sup>3</sup>J<sub>BC</sub> = 6.8 Hz,  $\Sigma^{n}J_{CX(X)} = 3.6$  Hz, each 2 H for 1-,8-H (A), 2-,7-H (B), 3-, 6-H (C)]; 7.30-7.20 (m, 20 H, phenyl H). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (multiplicity with respect to <sup>1</sup>J<sub>CH</sub>, coupling to <sup>31</sup>P with apparent multiplicity "m") = 149.5 (s, "t", C-4a,-10a), 138.7 (s, "t", C-4,-5 or phenyl C<sub>ipso</sub>), 138.6 (s, "t", C-4,-5 or phenyl C<sub>ipso</sub>), 137.0 (d, s, C-9), 135.8 (d, s, C-3,-6), 134.6 (d, "d" with  $\Sigma^{n}J_{CP} = 22.4$  Hz, phenyl C<sub>ortho</sub>), 129.2 (d, s, C-1,-8), 128.6 (d, "d" with  $\Sigma^{n}J_{CP} = 12.2$  Hz, phenyl C<sub>meta</sub>), 128.5 (s, "d" with  $\Sigma^{n}J_{CP} = 3.0$  Hz, phenyl C<sub>para</sub>), 126.9 (s, s, C-8a,-9a), 126.3 (d, s, C-2,-7).

8: MS (EI, 70 eV): m/z (%) = 215 (100, M<sup>+</sup>), 214 (10). - <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>), external standard CFCl<sub>3</sub>):  $\delta = -123.7$  (s). - <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.79$  (t, <sup>5</sup> $J_{HF} = 1.5$  Hz, 1 H, 9-H), 7.80-7.74 (m, 2 H, 1-,8-H), 7.51-7.43 (m, 4 H, 2-,3-H and 6-,7-H). - <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  (multiplicity with respect to <sup>1</sup> $J_{CH}$ , coupling with <sup>19</sup>F) = 157.8 (s, d with <sup>1</sup> $J_{CF} = 259.8$  Hz, C-4,-5), 139.7 (s, d with <sup>2</sup> $J_{CF} = 14.0$  Hz, C-4a,-10a), 135.7 (d, t with <sup>4</sup> $J_{CF} = 6.1$  Hz, C-9), 128.0 (s, s br., C-8a,-9a), 125.6 (d, d with <sup>3</sup> $J_{CF} = 7.0$  Hz, C-2,-7), 123.8 (d, "t" with  $\Sigma^{n}J_{CF} = 6.1$  Hz, C-1,-8), 113.3 (d, d with <sup>2</sup> $J_{CF} = 19.2$  Hz, C-3,-6).

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- 15. Single crystal X-ray structure analyses: 3 (crystallized from dichloromethane): Empirical formula:  $C_{37}H_{27}P_2N$ , molecular mass: 547.6 g mol<sup>-1</sup>, crystal size: 0.04 x 0.08 x 0.10 mm, triclinic, PI [Nr.2], a = 10.524(1), b = 11.104(1), c = 13.322(1) Å,  $\alpha = 105.50(1)^{\circ}$ ,  $\beta = 103.22(1)^{\circ}$ ,  $\gamma = 97.85(1)^{\circ}$ ,  $V = 1427.7 Å^3$ , T = 293 K, d<sub>calcd</sub> = 1.27 g cm<sup>-3</sup>,  $\mu = 15.75$  cm<sup>-1</sup>, F(000) = 572 e, Z = 2,  $\lambda = 1.54178$  Å, analytical absorption correction (min.: 1.136, max.: 1.353), 6147 measured reflections [ $\pm h, \pm k, \pm l$ ], [sin $\Theta/\lambda$ ]<sub>max</sub> 0.63 Å<sup>-1</sup>, 5882 independent and 3967 observed reflexes [I>2 $\sigma$ (I)], 469 refined parameters, H atoms were found and included in the final refinement by least-squares, R = 0.049, R<sub>w</sub> = 0.056 [w=1/ $\sigma^2$ (F<sub>0</sub>)], residual electron density 0.36 e Å<sup>-3</sup>.

17 · CH<sub>2</sub>Cl<sub>2</sub> (crystallized from dichloromethane/*n*-pentane): Empirical formula: C<sub>40</sub>H<sub>27</sub>MoNO<sub>3</sub>P<sub>2</sub> · CH<sub>2</sub>Cl<sub>2</sub>, molecular mass: 812.5 g mol<sup>-1</sup>, crystal size: 0.46 x 0.42 x 0.28 mm, monoclinic, P2<sub>1</sub>/n [Nr.14], a = 9.63(1), b = 18.55(1), c = 20.08(6) Å,  $\beta$  = 90.25(3)°, V = 3945.4 Å<sup>3</sup>, T = 293 K, d<sub>calcd</sub> = 1.37 g cm<sup>-3</sup>,  $\mu$  = 0.70 cm<sup>-1</sup>, F(000) = 1648 e, Z = 4,  $\lambda$  = 0.71069 Å, 13902 measured reflexes [±h,±k,+l], [sinΘ/ $\lambda$ ]<sub>max</sub> 0.70 Å<sup>-1</sup>, 11526 independent and 5931 observed reflexes [I>2σ(I)], 478 refined parameters, H atoms were calculated and not included in the final refinement by least-squares, R = 0.071, R<sub>w</sub><sup>2</sup> = 0.207 [w = 1/(σ<sup>2</sup>(F<sub>0</sub><sup>2</sup>) + (0.100P)<sup>2</sup> + 0.000P) with P = (F<sub>0</sub><sup>2</sup>+2F<sub>c</sub><sup>2</sup>)/3], residual electron density 1.60 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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