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4,5-Bis(diphenylphosphino)acridine: A New Type of Tridentate Phosphorus-Nitrogen-Phosphorus Ligands[1]

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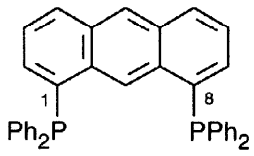
Abstract: Reaction of 4,5-difluoroacridine (**8**) with two equivalents of potassium diphenylphosphide (Ph_2PK) yielded the title compound **3**. Contrarily, diphenylphosphine (Ph_2PH) reacted with **8** under addition, and 4,5-difluoro-9-diphenyl-9,10-dihydroacridine (**12**) was obtained. Compound **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[2] in homogeneous catalysis is considerably extended by combining phosphorus centers and donors such as nitrogen or oxygen atoms in P/N ligands[3] or P/O ligands.[4] 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**)[5] and 4,6-bis(diphenylphosphino)dibenzofuran (**2**)[6] 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").



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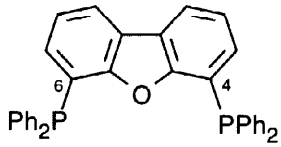

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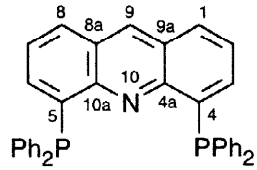
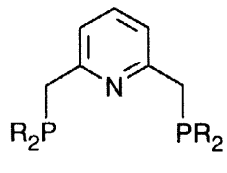


3

The structure of **3** is related to the tridentate PNP ligand 2,6-bis(diphenylphosphinomethyl)pyridine (**4**).[7-9] 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.[8] With basic reagents such as alkalimetal alkoxides complexes **5** react under elimination of benzylic hydrogen atoms to form delocalized phosphinomethanide structures **7**.[9] As benzylic substituted tertiary phosphines the phosphorus atoms of **4** are considerably more sensitive towards oxidation than the triarylphosphine groups of **3**.



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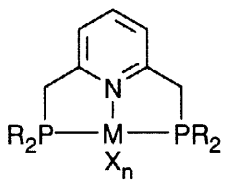

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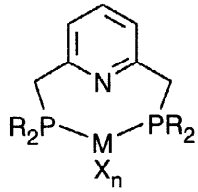

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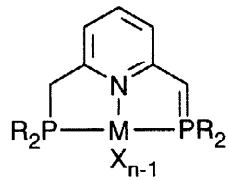

7

For the synthesis of **3** we first prepared the unknown 4,5-dihalogenoacridines (**8** - **10**).[10] 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_2PK, dioxane/tetrahydrofuran 5:1, reflux, 1 h) yielded **3** (yellow crystals, dec.

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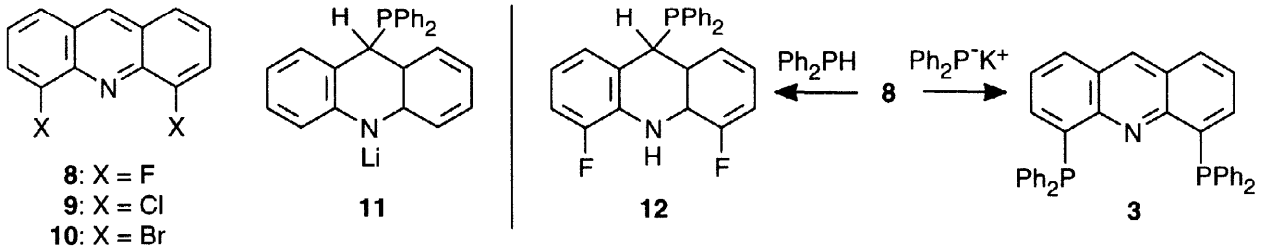
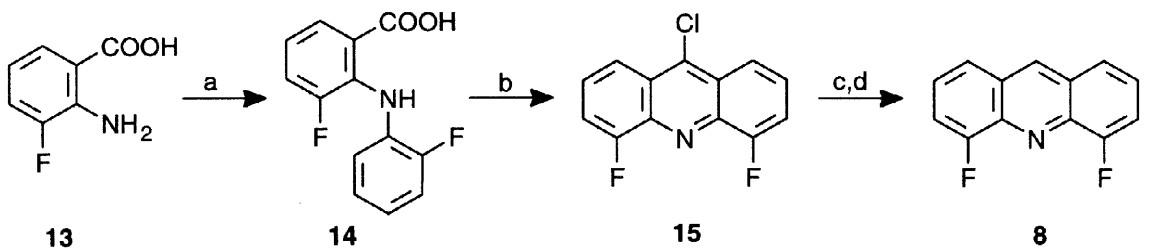
255°C, 79 %).[11,12] This smooth reaction is remarkable in so far as acridine is known to be reactive towards nucleophilic addition at its C-9 position, and accordingly the phosphide Ph_2PLi was reported to react with acridine under addition to **11**.[13] When **8** was treated with the secondary diphenylphosphine Ph_2PH instead of the phosphide Ph_2PK, 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).[12]



Scheme 1

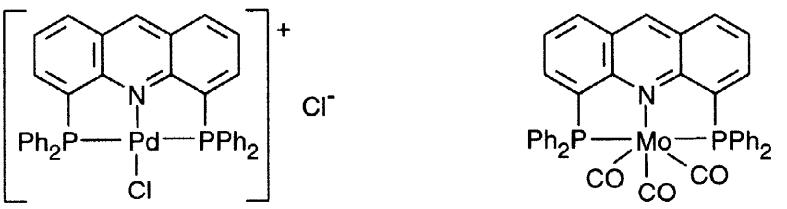
The necessary **8** (yellow crystals, m.p. 193-195°C) was prepared from 2-amino-3-fluorobenzoic acid (**13**)[14] in a four step synthesis (scheme 2).[11,12] The crucial step is the selective removal of the chloro substituent from 9-chloro-4,5-difluoroacridine (**15**) without interfering with the fluoro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



Scheme 2: a) 2-Fluoroiodobenzene, copper powder/K_2CO_3, cyclohexanol, reflux, 12 h (71 %); b) $POCl_3$, reflux, 3.5 h (81 %); c) *p*-tosylhydrazine, $CHCl_3$, 50°C, 30 min (87 %); d) NaOH/H_2O/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.[15] The planes between the outer benzene rings of acridine form an angle of 177.9°, 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.[12]



In the complexes **16** and **17** both phosphorus atoms are coordinated to metal, as it is shown by the single signals in the $^{31}P\{^1H\}$ NMR spectra [81 MHz; **16**: δ = 32.7 ($CDCl_3$); **17**: δ = 58.6 (CD_2Cl_2)]. The coordination of the nitrogen atom is suggested by the ^1H NMR and ^{13}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.[15] 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,[16] 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.[17] Studies to investigate the possible application of the new PNP ligand **3** in catalysis are currently under way.

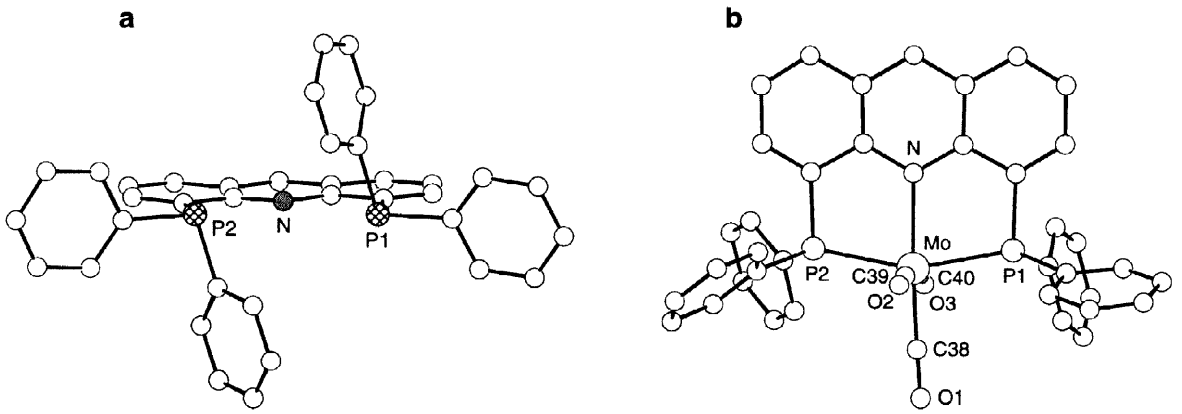


Figure 1: a) Molecular structure of 4,5-bis(diphenylphosphino)acridine (**3**), front view on acridine.
b) Molecular structure of 4,5-bis(diphenylphosphino)acridine-molybdenum tricarbonyl (**17**).[15]

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References and Notes

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11. **3**: MS (EI, 70 eV): *m/z* (%) = 547 (100, M^+), 360 (13), 284 (12), 283 (15). - ^{31}P NMR (81 MHz, $CDCl_3$, external standard 85 % phosphoric acid): δ = -14.7 (s). - ^1H NMR (400 MHz, CD_2Cl_2): δ = 8.82 (s, 1 H, 9-H); 8.00 (dd), 7.40 (dd) and 7.15 (ddd) [ABCXX'-spin system with X = X' = ^{31}P, $^3J_{AB}$ = 8.5 Hz, $^4J_{AC}$ = 1.5 Hz, $^3J_{BC}$ = 6.8 Hz, $\Sigma^nJ_{CX(X')}$ = 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). - ^{13}C NMR (75 MHz, CD_2Cl_2): δ (multiplicity with respect to $^1J_{CH}$, coupling to ^{31}P with apparent multiplicity "m") = 149.5 (s, "t", C-4a,-10a), 138.7 (s, "t", C-4,-5 or phenyl C_{ipso}), 138.6 (s, "t", C-4,-5 or phenyl C_{ipso}), 137.0 (d, s, C-9), 135.8 (d, s, C-3,-6), 134.6 (d, "d" with Σ^nJ_{CP} = 22.4 Hz, phenyl C_{ortho}), 129.2 (d, s, C-1,-8), 128.6 (d, "d" with Σ^nJ_{CP} = 12.2 Hz, phenyl C_{meta}), 128.5 (s, "d" with Σ^nJ_{CP} = 3.0 Hz, phenyl C_{para}), 126.9 (s, s, C-8a,-9a), 126.3 (d, s, C-2,-7).
8: MS (EI, 70 eV): *m/z* (%) = 215 (100, M^+), 214 (10). - ^{19}F NMR (188 MHz, $CDCl_3$, external standard $CFCl_3$): δ = -123.7 (s). - ^1H NMR (400 MHz, $CDCl_3$): δ = 8.79 (t, $^5J_{HF}$ = 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). - ^{13}C NMR (50 MHz, $CDCl_3$): δ (multiplicity with respect to $^1J_{CH}$, coupling with ^{19}F) = 157.8 (s, d with $^1J_{CF}$ = 259.8 Hz, C-4,-5), 139.7 (s, d with $^2J_{CF}$ = 14.0 Hz, C-4a,-10a), 135.7 (d, t with $^4J_{CF}$ = 6.1 Hz, C-9), 128.0 (s, s br., C-8a,-9a), 125.6 (d, d with $^3J_{CF}$ = 7.0 Hz, C-2,-7), 123.8 (d, "t" with Σ^nJ_{CF} = 6.1 Hz, C-1,-8), 113.3 (d, d with $^2J_{CF}$ = 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^{-1}, crystal size: 0.04 x 0.08 x 0.10 mm, triclinic, $P\bar{1}$ [Nr.2], a = 10.524(1), b = 11.104(1), c = 13.322(1) Å, α = 105.50(1)°, β = 103.22(1)°, γ = 97.85(1)°, V = 1427.7 $Å^3$, T = 293 K, d_{calcd} = 1.27 g cm^{-3}, μ = 15.75 cm^{-1}, F(000) = 572 e, Z = 2, λ = 1.54178 Å, analytical absorption correction (min.: 1.136, max.: 1.353), 6147 measured reflections [±h,±k,+l], $[\sin\Theta/\lambda]_{max}$ 0.63 $Å^{-1}$, 5882 independent and 3967 observed reflexes [I>2σ(I)], 469 refined parameters, H atoms were found and included in the final refinement by least-squares, R = 0.049, R_w = 0.056 [$w=1/\sigma^2(F_o)$], residual electron density 0.36 e $Å^{-3}$.
17 · CH_2Cl_2 (crystallized from dichloromethane/*n*-pentane): Empirical formula: $C_{40}H_{27}MoNO_3P_2 \cdot CH_2Cl_2$, molecular mass: 812.5 g mol^{-1}, crystal size: 0.46 x 0.42 x 0.28 mm, monoclinic, $P2_1/n$ [Nr.14], a = 9.63(1), b = 18.55(1), c = 20.08(6) Å, β = 90.25(3)°, V = 3945.4 $Å^3$, T = 293 K, d_{calcd} = 1.37 g cm^{-3}, μ = 0.70 cm^{-1}, F(000) = 1648 e, Z = 4, λ = 0.71069 Å, 13902 measured reflexes [±h,±k,+l], $[\sin\Theta/\lambda]_{max}$ 0.70 $Å^{-1}$, 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_w^2 = 0.207 [$w = 1/(\sigma^2(F_o^2) + (0.100P)^2 + 0.000P)$ with $P = (F_o^2+2F_c^2)/3$], residual electron density 1.60 e $Å^{-3}$. Atomic coordinates and e.s.d.'s have been deposited at the Cambridge Crystallographic Data Centre .
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