



0040-4039(94)02206-2

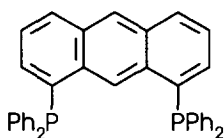
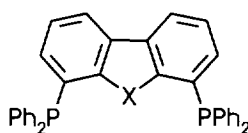
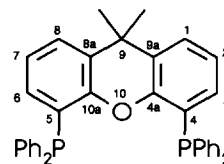
Bidentate Phosphines of Heteroarenes: 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene¹⁾

Stefan Hillebrand, Joachim Bruckmann, Carl Krüger and Matthias W. Haenel*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Federal Republic of Germany

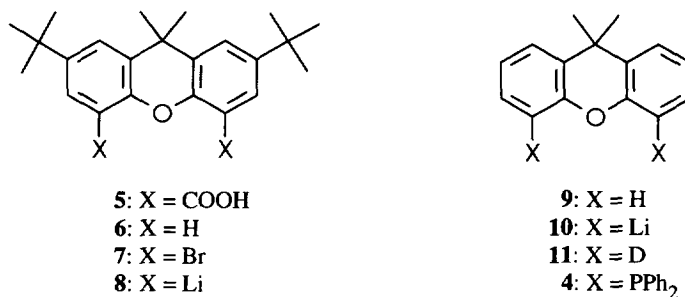
Abstract: Twofold lithiation of 9,9-dimethylxanthene with *n*-butyllithium and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in boiling *n*-heptane followed by reaction with chlorodiphenylphosphine (Ph_2PCl) yielded the title compound **4**. The phosphine ligand was characterised by ^1H NMR, ^{13}C NMR, ^{31}P NMR spectroscopy and single crystal X-ray structure analysis. The folded and deformed xanthene unit causes a remarkably short P...P distance of 4.1 Å which in turn results in a large coupling $^6J_{\text{PP}} = 27.3$ Hz.

Previously we reported the syntheses of 1,8-bis(diphenylphosphino)anthracene (**1**)²⁾, 4,6-bis(diphenylphosphino)dibenzofuran (**2**)³⁾ and 4,6-bis(diphenylphosphino)dibenzothiophene (**3**)^{3,4)}. These syntheses follow our concept of using polycyclic arenes and heteroarenes as rigid carbon skeletons for the construction of new bidentate phosphine ligands which might bear interesting features and new potentials with respect to catalytic processes. In this context we were interested also in the ligand 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (**4**) for which the 4,5-disubstituted xanthene (dibenzopyran) unit serves as a more or less rigid carbon skeleton⁵⁾. Recently we got knowledge of a conference abstract in which the ligand **4** also is mentioned⁶⁾. This prompts us to communicate briefly our synthesis of **4** and its characterisation by NMR spectroscopy and X-ray structure analysis.

**1****2:** X = O**3:** X = S**4**

In studies of molecular recognition, *Rebek, Jr., et al.*⁵⁾ have used the xanthene-4,5-dicarboxylic acid derivative **5** to construct molecular clefts. The desired 4,5-disubstitution pattern was accomplished by bromination of 2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene (**6**) which had been prepared from 9,9-dimethylxanthene (**9**) by electrophilic alkylation at its most reactive 2,7-positions. Subsequently the dibromo compound **7** could be converted easily *via* halogen-metal-exchange into the dilithium compound **8**, from which **5** was obtained by reaction with carbon dioxide⁵⁾. On the other hand, the protection of the xanthene 2,7-positions by alkylation should not be necessary if **9** is treated with strongly basic organoalkali-metal reagents in order to deprotonate the 4,5-carbon atoms. As we had shown previously, both the heteroarenes dibenzofuran and dibenzothiophene could be converted to their respective 4,6-dilithium compounds by twofold lithiation assisted and directed by the

heteroatoms^{3,4}). Hence we anticipated that a straightforward synthesis of the ligand **4** also might be possible via twofold metallation of **9** and subsequent reaction with Ph_2PCl .



When 2.5 equivalents of *n*-butyllithium in *n*-hexane were added to a solution of one equivalent **9** and 2.5 equivalents of TMEDA in *n*-heptane at room temperature and subsequently the mixture was heated to reflux for 10 min, a greenish-brown reaction mixture was obtained. The lithium compounds formed were characterised first by their reaction with deuterium oxide: 82% of the 9,9-dimethylxanthene could be reisolated, which by mass, ^1H NMR and ^{13}C NMR spectra were shown to consist of about 94% of (4,5- D_2)-9,9-dimethylxanthene (**11**)⁷. This proves the extensive formation of 4,5-dilithio-9,9-dimethylxanthene **10** on reaction of **9** with *n*-BuLi/TMEDA. Reaction of **10** with two equivalents Ph_2PCl in *n*-heptane at 0°C yielded the diphosphine **4** which was isolated after aqueous work-up and repeated crystallisation from chloroform/2-propanol as colourless crystals (39%, m.p. $230\text{--}232^\circ\text{C}$)⁸.

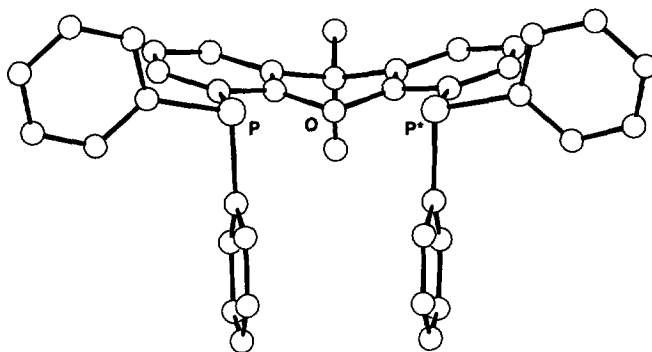


Figure 1: Molecular structure of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (**4**) crystallized from the solution in dichloromethane: front view on the oxygen side of the xanthene unit.

The diphosphine **4** shows one signal at $\delta = -17.9$ in the ^{31}P NMR spectrum (CD_2Cl_2 , 81 MHz) and one ABCXX' system (X and X' = ^{31}P) of twofold intensity at $\delta = 7.45$, 6.98 and 6.57 for the three neighbouring xanthene protons in the ^1H NMR spectrum (CD_2Cl_2 , 200 MHz)⁸. In the ^{13}C NMR spectrum (CD_2Cl_2 , 100 MHz)⁸ the multiplets, which are observed for the xanthene C-4, -5, the phenyl C_{ipso} and the phenyl C_{ortho} ,

could be analysed as AA'X-systems ($A = A' = {}^{31}\text{P}$, $X = {}^{13}\text{C}$) from which a large coupling between the two phosphorous nuclei with ${}^6J_{\text{PP}} = 27.3 \text{ Hz}$ could be extracted⁹⁾. This much larger coupling in **4** as compared to that in **3** (${}^6J_{\text{PP}} \cong 0 \text{ Hz}$)⁴⁾ apparently results from the much shorter P...P distance (*vide supra*).

The X-ray structure analysis, which was performed with a single crystal of **4** grown from the solution in dichloromethane, shows **4** in a conformation having a crystallographic mirror symmetry (Figure 1)¹⁰⁾. The xanthene unit is folded along the connecting line through the oxygen atom and the xanthene carbon atom C-9 so that the planes of the two benzenoid rings of the xanthene unit form an angle of 156.58° [angle between the plane O–C4a–C9a–C9 and its mirror related plane: 151.53°]. In addition, the xanthene unit shows deformed valence angles at the carbon centres C-4, -5 [C4a–C4–P : $118.4(2)^\circ$; C3–C4–P : $125.1(3)^\circ$] which apparently are caused by the repulsive interaction of the xanthene unit with the bulky phenyl substituents at the phosphorous atoms. Both the folding and the deformation result in a remarkably short P...P distance of $4.045(1) \text{ \AA}$.

A second X-ray analysis of **4** was performed with a single crystal which had been grown from the solution in THF and which contained solvent molecules (Figure 2)¹¹⁾. The molecular framework of both structures is essentially identical with the exception of some torsion angles involving the C–P bonds, presumably as a result of the incorporated solvent molecule. In this case a P...P distance of $4.155(1) \text{ \AA}$ is found. Presently the ligand properties of **4** are investigated.

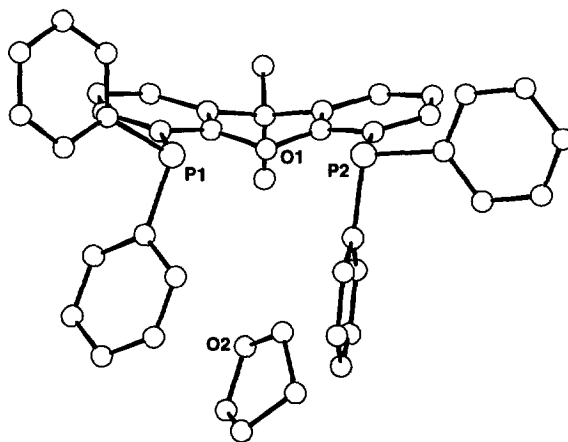


Figure 2: Molecular structure of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (**4** · THF) crystallized from the solution in tetrahydrofuran: front view on the oxygen side of the xanthene unit.

References and Notes:

- 1) Phosphine ligands, **4**; for part 3 see ref.⁴⁾. The work is part of the planned doctoral thesis of S. Hillebrand, to be submitted to the University of Düsseldorf.
- 2) Haenel, M.W.; Jakubik, D.; Krüger, C.; Betz, P. *Chem. Ber.* **1991**, *124*, 333-336.

- 3) Haenel, M.W.; Jakubik, D.; Rothenberger, E.; Schroth, G. *Chem. Ber.* **1991**, *124*, 1705-1710.
- 4) Haenel, M.W.; Fieseler, H.; Jakubik, D.; Gabor, B.; Goddard, R.; Krüger, C. *Tetrahedron Lett.* **1993**, *34*, 2107-2110.
- 5) Nowick, J.S.; Ballester, P.; Ebmeyer, F.; Rebek, Jr., J. *J. Am. Chem. Soc.* **1990**, *112*, 8902-8906.
- 6) Kamer, P.C.J.; Kranenburg, M.; van Leeuwen, P.W.N.M. *Book of Abstracts, XVth International Conference Organometallic Chemistry*, University of Sussex, 10-15 July 1994, The Royal Society of Chemistry - Dalton Division, abstract no. OC.18.
- 7) **11** ($C_{15}H_{12}D_2O$): MS: 6% D_1 , 94% D_2 . - 1H NMR ($CDCl_3$, 25°C, 200 MHz): δ = 7.40, 7.18, 7.06 [ABCX with X = D, J_{AB} = 1.8, J_{AC} = 7.6, J_{BC} = 7.5, J_{BX} ($^3J_{HD}$) \approx 1 Hz, each 2 H for 1-, 8-H, 2-, 7-H, 3-, 6-H], 1.62 (s, 6 H, CH_3). - $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 50 MHz): δ = 150.4 (C-4a, -10a), 130.0 (C-8a, -9a), 127.2 (C-3, -6), 126.1 (C-1, -8), 123.0 (C-2, -7), 116.1 ($^1J_{CD}$ = 24.4 Hz, C-4, -5), 33.9 (C-9), 32.4 (CH_3).
- 8) **4**: $C_{39}H_{32}OP_2$ (578.63), calcd. C 80.95, H 5.57, P 10.71, found C 81.48, H 5.54, P 10.01. - MS: (70 eV): m/z (%) = 578 (100, M^+), 563 (21, $M^+ - CH_3$), 289 (6, M^{2+}), 281 (10). - 1H NMR (CD_2Cl_2 , 25°C, 200 MHz): δ = 7.45, 6.98, 6.57 [ABCXX' with X and X' = ^{31}P , J_{AB} = 7.5, J_{AC} = 1.4, J_{BC} = 7.5, $\Sigma J_{CX(X')} = 3.6$ Hz, each 2 H for 1-, 8-H, 2-, 7-H, 3-, 6-H], 7.32-7.15 [m, 20 H, phenyl H], 1.66 [s, 6 H, CH_3]. - $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 25°C, 100 MHz): δ [multiplicity with respect to $^1J_{CH}$, coupling to ^{31}P with apparent multiplicity ("m") or analysed as AA'X with A and A' = ^{31}P , X = ^{13}C] = 152.9 [s, $J_{PC} + P'C = 19.1$ Hz ("t"), C-4a, -10a], 137.8 [s, X-part of AA'X with $J_{PC} = 14.9$, $J_{P'C} = -2.5$, $J_{PP'} = 27.3$ Hz, phenyl C_{ipso}], 134.3 [d, X-part of AA'X with $J_{PC} = 19.6$, $J_{P'C} = 1.4$, $J_{PP'} = 27.3$ Hz, phenyl C_{ortho}], 132.4 [d, C-3, -6], 130.5 [s, C-8a, -9a], 128.8 [d, phenyl C_{para}], 128.6 [d, $J_{PC+P'C} = 6.7$ Hz ("t"), phenyl C_{meta}], 127.0 [d, C-1, -8], 126.0 [s, X-part of AA'X with $J_{PC} = 19.2$, $J_{P'C} = -0.1$, $J_{PP'} = 27.3$ Hz, C-4, -5], 123.8 [d, C-2, -7], 34.8 [s, C-9], 32.1 [q, CH_3]. - $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 25°C, 81 MHz): δ = -17.9 (s).
- 9) We thank Mrs. B. Gabor and Dr. R. Mynott for measuring the NMR spectra and for assistance in analysing the spin systems.
- 10) X-ray analysis of **4**: $C_{39}H_{32}OP_2$, $M_r = 578.6$ g mol $^{-1}$, colourless crystals, crystal size 0.21 x 0.46 x 0.49 mm, $a = 18.940(2)$, $b = 19.156(1)$, $c = 8.766(1)$ Å, $V = 3180.4$ Å 3 , $T = 293$ K, $d_{cal} = 1.21$ g cm $^{-3}$, $\mu = 1.60$ cm $^{-1}$, $Z = 4$, orthorhombic, space group Pnma [No. 62], Enraf-Nonius CAD4 diffractometer, $\lambda = 0.71069$ Å, scan mode ω -2 θ , 4109 measured reflections (+h, +k, +l) $[(\sin\theta)/\lambda]_{max} = 0.65$ Å $^{-1}$, 3744 independent reflections, 2164 observed reflections [$I > 2\sigma(I)$], structure solved by direct methods (SHELXS-86, Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467-473), final refinement by least-squares (GFMLX, a modified version of ORFLS, Busing, W. R.; Martin, K. O.; Levy, H. A. *Report ORNL-TM-305*, Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A. 1962), H atoms at the two C_{methyl} calculated and kept fixed in the final stage of refinement, $R = 0.063$, $R_w = 0.064$ for 235 refined parameters [$w = 1/\sigma^2(F_o)$], residual electron density 0.27 eÅ $^{-3}$. Atomic coordinates and e.s.d.'s have been deposited at the Cambridge Crystallographic Data Centre.
- 11) X-ray analysis of **4** · THF: $C_{43}H_{40}O_2P_2$, $M_r = 650.7$ g mol $^{-1}$, colourless crystals, crystal size 0.18 x 0.39 x 0.80 mm, $a = 11.069(2)$, $b = 20.202(5)$, $c = 15.189(1)$ Å, $\beta = 96.49(1)^\circ$, $V = 3374.8$ Å 3 , $T = 100$ K, $d_{cal} = 1.28$ g cm $^{-3}$, $\mu = 1.60$ cm $^{-1}$, $Z = 4$, monoclinic, space group $P2_1/n$ [No. 14], Enraf-Nonius CAD4 diffractometer, $\lambda = 0.71069$ Å, scan mode ω -2 θ , 8213 measured reflections ($\pm h, \pm k, \pm l$) $[(\sin\theta)/\lambda]_{max} = 0.65$ Å $^{-1}$, 7691 independent reflections, 6519 observed reflections [$I > 2\sigma(I)$], structure solved by direct methods (SHELXS-86, Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467-473), final refinement by least-squares (GFMLX, a modified version of ORFLS, Busing, W. R.; Martin, K. O.; Levy, H. A. *Report ORNL-TM-305*, Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A. 1962), H atoms refined isotropically, $R = 0.047$, $R_w = 0.057$ for 584 refined parameters [$w = 1/\sigma^2(F_o)$], residual electron density 0.52 eÅ $^{-3}$. Atomic coordinates and e.s.d.'s have been deposited at the Cambridge Crystallographic Data Centre.

(Received in Germany 27 October 1994; accepted 4 November 1994)