6-Phenyldibenzo[*b,d*]phosphinine

Pieter de Koe and Friedrich Bickelhaupt

Scheikundig Laboratorium, Vrije Universiteit,
De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

Reprint requests to Prof. Dr. F. Bickelhaupt. E-mail: bicklhpt@few.vu.nl

Z. Naturforsch. **58b,** 782 – 786 (2003); received April 14, 2003

The title compound (**2b**) was obtained in 7 steps from 2-phenylbenzhydrol (**5**). The phenyl substituent of **2b** confers thermal stability to the [5]phosphaphenanthrene system by steric protection; in addition, conjugative interaction is revealed by the UV spectrum. The analogy to the corresponding arenes is briefly discussed.

Key words: Aromatic Phosphorus Heterocycles, UV Spectroscopy

Introduction

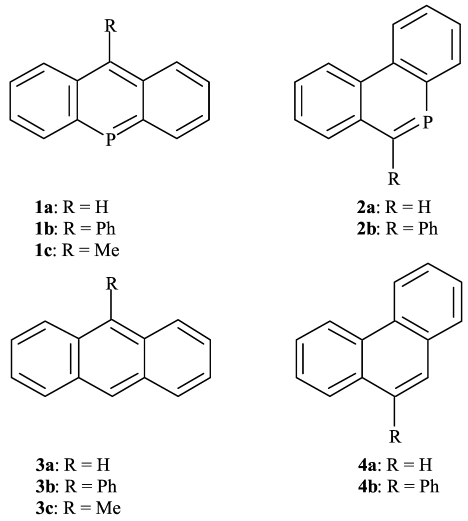
In contrast to benzene or pyridine and their derivatives, the phosphorus analogs, the phosphinines (or phosphabenzenes) [1 – 4] tend to be less stable both thermally and towards oxygen, in particular if additional aromatic rings are annelated to the central heterocycle. Thus, in the series of tricyclic phosphinines, both [9]phosphaanthracene **1a** [5] and [5]phosphaphenanthrene **2a** [6] were too unstable to be isolated in pure form (Scheme 1). However, introduction of a phenyl substituent as in **1b** increased the thermal stability sufficiently to allow isolation [7]. For that reason, we undertook the synthesis of **2b**, the phenyl derivative of the parent **2a**, in order to probe the general validity of this principle and to facilitate a comparison between **1** and **2** and their carbon analogues **3** and **4**, respectively.

Experimental details of our preparation of **2b** have so far not been published except in a thesis [2,8]. In the meantime, the photoelectron spectrum of **2b** [9] as well as an alternative synthetic approach to **2b** starting from 5-benzyldibenzophosphole [10] have been reported.

Results and Discussion

In analogy to the strategy which had proven successful in the case of **1a,b** and **2a**, we performed the synthesis of **2b** by base catalyzed elimination of hydrogen chloride from the immediate precursor **11** which was obtained as outlined in Scheme 2.

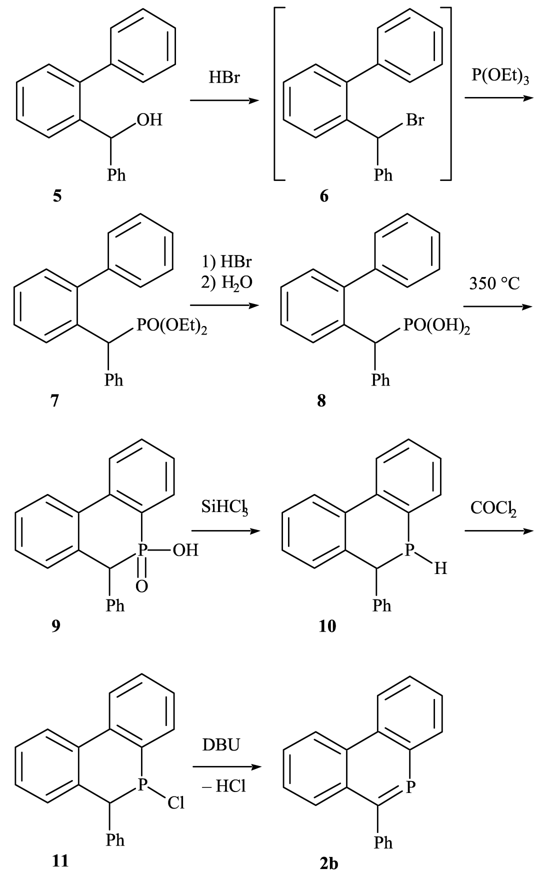
Passing gaseous hydrogen bromide into a benzene solution of 2-phenylbenzhydrol (**5**) afforded **6** as an unstable product with a high tendency toward cyclization to 9-phenylfluorene. However, heating freshly prepared **6** with triethyl phosphite furnished **7** in 58 % yield. Hydrolysis of **7** by heating under reflux, first in concentrated aqueous hydrogen bromide and then in water, gave **8**, which was cyclized to **9** by heating at 360 °C under vacuum. Reduction of **9** with trichlorosilane furnished **10** which on treatment with phosgene gave **11**.



Scheme 1.

The tendency to eliminate hydrogen chloride from **11** under formation of **2b** was even higher than the analogous reaction in the linear series leading to **1b** [7]. This follows *e.g.* from the observation that attempted vacuum distillation of **11** gave a mixture of

0932–0776 / 03 / 0800–0782 $ 06.00 © 2003 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com



Scheme 2.

11 and **2b** containing 85–90% of the latter. Pure **2b** was prepared by treatment of **11** with DBU (1.5-diazabicyclo[5.4.0]undec-5-ene) in DMF at 20 °C; after the usual workup followed by vacuum sublimation, **2b** was obtained as colorless crystals. The identity of **2b** was established by elemental analysis and spectral data. Besides the phosphorus chemical shift ($\delta(^{31}P)$ = 186 [10]), the most convincing and informative indicator is the UV spectrum (Fig. 1).

Generally [2–4], the UV spectra of phosphaarenes are rather similar in shape and extinction coefficient to those of the parent arenes. However, the longest wavelength absorption λ_{max} is shifted even further when a CH group is replaced by phosphorus; for the combinations **3/1** and **4/2**, this shift is $\Delta\lambda_{max}$ = 30–50 nm (Table 1).

Of special interest is a comparison between the spectra of **1a/2a** on the one hand and of **1b/2b** on the other. In the anthracene series, introduction of a phenyl substituent in both the carbon and the phosphorus series (**3a**→**3b** and **1a**→**1b**, respectively) leads to a small bathochromic shift only ($\Delta\lambda_{max}$ = 6–8 nm) of the longest wavelength absorption. As in the anthracene derivatives the influence of the phenyl and the methyl substituent on the absorption spectra is practically the same (**1b**: λ_{max} = 432 nm, **1c**: λ_{max} = 431 nm [15]; **3b**: λ_{max} = 384 nm, **3c**: λ_{max} = 386 nm [16]), it is evident that the phenyl group has no conjugative interaction with the anthracene system, because presumably for steric reasons, it is forced into

Table 1. UV spectra of tricyclic arenes **1**–**4**.

Compound	λ_{max} [nm]	$\Delta\lambda_{max}$ [nm][a]	$\Delta\lambda_{max}$ [nm][b]	Solvent[c]
1a [5]	426		50	toluene
1b [7]	432	6	48	diethyl ether
1c [15]	431			diethyl ether
2a [6]	372		29	diethyl ether
2b[d]	339	−33	40	diethyl ether
3a [12]	376			hexane
3b [13]	384	8		ethanol
3c [16]	386			ethanol
4a [14]	343			hexane
4b [11]	299	−44		95% ethanol

[a] Shift of λ_{max} on replacement of hydrogen by phenyl (**a** → **b**); [b] shift of λ_{max} on replacement of carbon by phosphorus (**3** → **1** or **4** → **2**, respectively); [c] the solvent dependence of λ_{max} is generally small (λ_{max} [polar] < λ_{max} [apolar]) and in the order of 3–4 nm; [d] this work.

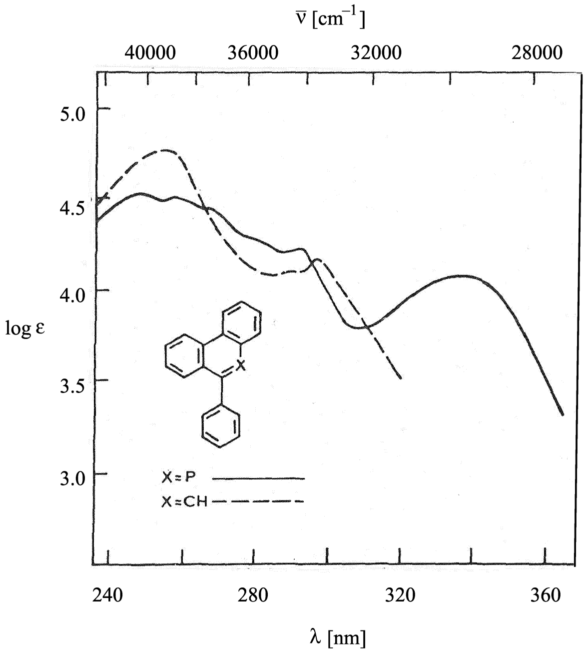
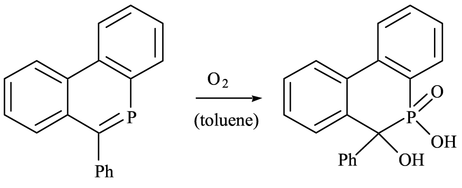


Fig. 1. UV Spectra of **2b** (———, in diethyl ether) and **4b** (– – –, in 95% ethanol).



2b **12**

Scheme 3.

an orientation perpendicular to the anthracene plane by the presence of two peri-hydrogen atoms at the adjacent benzene rings [13, 15]. By contrast, in the phenanthrene series, and again both for carbon and phosphorus (**4a**→**4b** and **2a**→**2b**, respectively), the shift on introduction of the phenyl substituent is quite large and hypsochromic ($\Delta\lambda_{max}$ = -33 to -44 nm). It is obvious that the seeming hypsochromicity is in reality due to the fact that in the parent and the phenyl substituted compounds, the longest wavelength absorptions are due to different transitions (**4a, 2a**: α-band, **4b, 2b**: *p*-band [17]). For both **4b** and **2b**, this means that conjugation between the phenyl substituent and the phenanthrene chromophore does occur because of a higher degree of coplanarity than in **1b** and **3b**, which is facilitated by reduced steric hindrance in the phenanthrene series as it has only one peri-hydrogen atom at the ring directly adjacent to the phenyl group.

With regard to thermal stability, the effect of the introduction of a phenyl substituent as in **1b** and **2b** is comparable. Contrary to the unsubstituted analogues of the **a**-series, both possess a strongly increased thermal stability which allows sublimation at 130 – 150 °C. However, the protective action of the phenyl group towards oxygen is insufficient. While in the solid state both **1b** and **2b** are reasonably stable towards air, they are prone to oxidation in solution so that preparation and handling had to be performed in a high vacuum system. When a sealed vessel containing a solution of **2b** in toluene accidentally broke and was kept standing under air overnight, subsequent extraction with aqueous ammonia and TLC analysis of the mixture revealed the formation of at least three (phosphorus) acids; crystallization from ethanol gave a colorless product in low yield to which on the basis of elemental analysis and IR data the structure of **12** (Scheme 3) was tentatively assigned.

Conclusion

Starting from 2-phenylbenzhydrol (**5**), the title compound **2b** was prepared in a 7 step synthesis. In comparison to the unsubstituted parent **2a**, the phenyl substituent increases the thermal stability considerably, but **2b** remains sensitive towards oxygen. The UV spectrum reveals conjugation between the [5]phosphaphenanthrene system and the phenyl group; it also again confirms the similarity between phosphaarenes (such as **2b**) and their carbon analogues (such as **4b**), except for the well-known trend of phosphaarenes to show a shift towards longer wavelength .

Experimental Section

The synthesis of **2b**, **10**, and **11** was performed under spectrally pure nitrogen in glassware which had been oven-dried at 150 °C. Solid starting materials were dried under vacuum, liquid starting materials were distilled under nitrogen. Solvents were distilled from $LiAlH_4$ (pentane, diethyl ether, cyclohexane, toluene) or from sodium/benzophenone (THF). Air sensitive compounds were handled in a Schlenk apparatus; melting points were determined in sealed glass capillaries. ^1H NMR spectra were obtained at 20 °C with a Varian A-60 spectrometer at 60 MHz (TMS as external standard), UV spectra with a Perkin-Elmer 137 spectrophotometer, IR spectra with a Perkin-Elmer 237 spectrometer, and mass spectra with an AEI-MS9 mass spectrometer. Elemental analyses were performed in our laboratory.

*6-Phenyldibenzo[b,d]phosphinine (***2b***)*

The preparation and handling of **2b** was carried out in a closed glass vessel sealed under high vacuum [18,19]. A solution of **11** (1.50 g, 4.85 mmol) and DBU (0.84 g, 5.54 mmol) in DMF (45 ml) was kept overnight at 20 °C. The reaction mixture was evaporated and the residue was extracted 4 times with cyclohexane (250 ml total). The cyclohexane extract was evaporated and the residue crystallized from toluene, followed by vacuum sublimation (bath temperature of 130 – 140 °C). The yield could not be determined directly; titration according to Mohr of the DBU•HCl left after cyclohexane extraction indicated that 79% of DBU•HCl had been obtained. **2b**: M.p. 124 – 131 °C [20]. – UV/vis (Et_2O): λ_{max} [nm] (lg ε) = 247 (4.53), 257.5 (4.50), 265.5 (sh, 4.47), 279 (sh, 4.29), 291 (4.23), 339 (4.08). – ^1H NMR (CS_2): δ = 9.38 – 9.13 (m, 2 H), 9.05 – 8.6 (m, 1 H), 8.43 – 7.77 (m, 10 H). – MS (EI, 70 eV): *m/z* (%): = 272 (100) [M^+], 244 (3), 242 (4), 241 (5), 240 (4), 239 (10), 165 (2), 152 (0.5), 136 (6) [M^{2+}], 135 (6), 122 (8). – $C_{19}H_{13}P$: calcd. for [M^+] 272.0755; found 272.0749. – $C_{19}H_{13}P$ (272.27): calcd. C 83.81, H 4.81, P 11.38; found C 83.9, H 5.2, P 11.2.

*2-Phenylbenzhydryl bromide (***6***)*

At 20 °C, gaseous hydrogen bromide was introduced into a solution of **5** [21] (5 g, 19.2 mmol) in benzene (25 ml) until saturation was reached. The water formed was removed by pipettation, $CaCl_2$ was added, and hydrogen bromide was again introduced until saturation. After filtration (glass wool) and evaporation of the filtrate to dryness, the oily residue was crystallized from petroleum ether. The colorless white crystals of **6** were pure according to bromine analysis (boiling an aliquot of a solution in dioxane with a solution of KOH in ethanol, followed by neutralization with dilute H_2SO_4 and titration according to Mohr: $C_{19}H_{15}Br$ (323.23): calcd. Br 24.72; found Br 24.6). After standing overnight in a desiccator, the material was largely converted to 9-phenylfluorene [21].

*Diethyl 2-phenylbenzhydrylphosphonate (***7***)*

A mixture of freshly prepared **6** (23.9 g, 74 mmol) and triethyl phosphite (25 g, 150 mmol) was gradually heated to 50 °C and maintained at this temperature for 0.5 h. Then the reaction mixture was heated under reflux for 5 h. Afterwards, ethyl bromide and excess triethyl phosphite were distilled off, and the residue was subjected to vacuum distillation (1.3 *mu*bar), yielding 9-phenylfluorene (0.7 g, 3.9%, b.p. 125–162 °C) and **7** (16.2 g, 58%) as a colorless oil. **7**: B.p. 163 °C. – ^{1}H NMR (CCl_4): δ = 8.26 – 8.05 (m, 1 H), 7.5 – 7.0 (m, 13 H), 4.46 (d, $^2J_{P,H} = 25$ Hz, 1 H), 4.14 – 3.39 (m, 4 H), 1.06 (dt, $^3J_{H,H} = 7$ Hz, $^4J_{P,H} = 4$ Hz, 6 H). – $C_{23}H_{25}O_3P$ (380.41): calcd. C 72.61, H 6.62, P 8.14; found C 72.0, H 6.7, P 8.2.

*2-Phenylbenzhydrylphosphonic acid (***8***)*

A mixture of **7** (65.0 g, 171 mmol) and concentrated hydrobromic acid (1 l) was heated under reflux for 20 h. After cooling, the solid material was filtered off and boiled with water for 5 h; the precipitate was filtered off and recrystallized from ethanol (96%) to yield colorless crystals of **8** (50.4 g, 91%). **8**: M.p. 231.5 – 234 °C. – ^{1}H NMR ([D_6] DMSO): δ = 8.32 – 7.73 (m, 4 H), 7.43 – 6.8 (m, 12 H), 4.48 (d, $^2J_{P,H} = 24{,}5$ Hz, 1 H). – $C_{19}H_{17}O_3P$ (324.31): calcd. C 70.36, H 5.28, P 9.55; found C 70.7, H 5.8, P 9.6.

*5,6-Dihydro-5-hydroxy-5-oxo-6-phenyldibenzo[b,d]phosphinine (***9***)*

Adapting a method described by Lynch [22], **8** (38.9 g, 120 mmol) was heated under vacuum at a bath temperature of 350 °C for 6 h. After cooling, the glassy residue was broken up and dissolved by boiling with NaOH (1N, 250 ml) for 10 min, followed by cooling and acidification with 2N HCl. The precipitate thus obtained was recrystallized from ethanol (96%) to yield colorless crystals of **9** (28.5 g, 78%). **9**: M.p. 244.5 – 251 °C. – ^{1}H NMR ([D_6]DMSO): δ = 8.18 – 6.83 (m, 14 H), 4.59 (d, $^2J_{P,H} = 24.0$ Hz, 1 H). – $C_{19}H_{15}O_2P$ (306.29): calcd. C 74.50, H 4.94, P 10.11; found C 74.4, H 5.0, P 10.1.

*5,6-Dihydro-6-phenyldibenzo[b,d]phosphinine (***10***)*

Trichlorosilane (46 g, 340 mmol) was gradually added to a boiling suspension of **9** (20 g, 65.3 mmol) in benzene (70 ml). The reaction mixture became homogeneous and was heated under reflux for 24 h. Under cooling and stirring in an ice bath, 20% aqueous NaOH (air-free, 100 ml) was added. The water layer was pipetted off and the organic layer was washed with 2N HCl (air-free) followed by water. The organic layer was dried ($MgSO_4$, air-free) and filtered under nitrogen pressure through a glass tube filled with glass wool into a distillation flak. The solvent was evaporated and the residue distilled to furnish **10** as a colorless viscous oil (8.5 g, 47%); according to the ^{1}H NMR spectrum, it consisted of a mixture (1.5 : 1) of the *E*/*Z* isomers **10A** and **10B**. **10**: B.p. 170 °C/13 *mu*bar). – ^{1}H NMR (CS_2): δ = 8.3 – 7.25 (m, 13 H); **10A**: 5.04 (dd, $^1J_{P,H} = 194$ Hz, $^3J_{H,H} = 2.5$ Hz, P*H*), 4.80 (dd, $^2J_{P,H} = {}^3J_{H,H} = 2.5$ Hz, C*H*); **10B**: 4.83 (dd, $^1J_{P,H} = 192$ Hz, $^3J_{H,H} = 11$ Hz, P*H*), 4.38 (dd, $^2J_{P,H} = 7$ Hz $^3J_{H,H} = 11$ Hz, C*H*). – $C_{19}H_{15}P$ (274.29): calcd. C 83.19, H 5.51, P 11.29; found C 83.5, H 5.2, P 11.6.

*5-Chloro-5,6-dihydro-6-phenyldibenzo[b,d]phosphinine (***11***)*

A solution of phosgene in toluene was prepared by condensing phosgene (1 ml) into a calibrated vessel cooled to −80 °C, followed by distillation into toluene (15 ml) cooled to −80 °C; the concentration (0.814 mmol/ ml) was determined after hydrolysis of an aliquot and titration of chloride according to Mohr. This phosgene solution (18.6 ml, 15.1 mmol) was added dropwise to a solution of **10** (3.95 g, 14.4 mmol) in toluene (25 ml) cooled to −80 °C. After warming to 20 °C, the colorless precipitate was removed by filtration under nitrogen pressure through a glass tube filled with glass wool. The filtrate was evaporated to dryness and the oily residue subjected to distillation (1.3 *mu*bar, bath temperature 170 – 180 °C) to furnish (rather) pure **11** (3.46 g, 78%) as a slightly yellowish viscous oil. **11**: ^{1}H NMR (CS_2): δ = 8.50 – 7.17 (m, 13 H), 5.22 (s, 1 H). – $C_{19}H_{14}ClP$ (308.74): calcd. C 73.91, H 4.57, P 10.03, Cl 11.49; found C 73.9, H 4.8, P 10.2, Cl 10.2.

Reaction of **2b** *with air*

At one occasion, an evacuated vessel containing a solution of **2b** in toluene broke. After standing in air overnight, the solution was evaporated to dryness to give as a residue a colorless oil (1.24 g), 0.48 g of which dissolved in dilute ammonia. The ammonia extract contained at least three acids according to TLC (silica gel, propanol/25% ammonia 7 : 3). After acidification and three crystallizations from 96% ethanol, **12** was obtained (10.4 mg) as colorless crystals. **12**: M.p. 250 – 251 °C. – IR (KBr): 1185 cm^{-1} (P=O), 970 cm^{-1} (P-OH), 800 – 600 cm^{-1} (substitution pattern identical to that of **9**);

($CHCl_3$): 3660 cm^{-1} (C-OH); for similar characteristic data on monocyclic analogues of **12** see ref. [23]. – $C_{19}H_{15}O_3P$ (322.29): calcd. C 70.80, H 4.69, P 9.61; found C 70.3, H 5.1, P 9.8.

---

[1] K. Dimroth, Top. Curr. Chem. **38**, chapter 3 (1973); G. Märkl in Multiple Bonds and Low Coordination in Phosphorus Chemistry (Ed.: M. Regitz, O. J. Scherer), chapter 5, Thieme, Stuttgart (1990); Phosphorus: The Carbon Copy (Ed.:
K. B. Dillon, F. Mathey, J. F. Nixon), chapter 8.5, Wiley, Chichester (1998).

[2] P. Le Floch in Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain (Ed.: F. Mathey), Pergamon, Amsterdam, chapter 5.2 (2001).

[3] L. Nyulászi, Chem. Rev. **101**, 1229 (2001).

[4] F. Mathey, Angew. Chem. **115**, 1616 (2003); Angew. Chem. Int. Ed. **42**, 1578 (2003).

[5] P. de Koe, F. Bickelhaupt, Angew. Chem. **79**, 533 (1967); Angew. Chem. Int. Ed. **6**, 567 (1967).

[6] P. de Koe, R. van Veen, F. Bickelhaupt, Angew. Chem. **80**, 486 (1968); Angew. Chem. Int. Ed. **7**, 465 (1968).

[7] P. de Koe, F. Bickelhaupt, Angew. Chem **80**, 912 (1968); Angew. Chem. Int. Ed. **7**, 889 (1968).

[8] P. de Koe, Ph. D. Dissertation, chapter 4, Vrije Universiteit, Amsterdam (1969).

[9] W. Schäfer, A. Schweig, F. Bickelhaupt, H. Vermeer, Rec. Trav. Chim. Pays-Bas. **93**, 17 (1974).

[10] F. Nief, C. Charrier, F. Mathey, M. Simalty, Tetrahedron Lett. **21**, 1441 (1980).

[11] R. A. Friedel, M. Orchin, Ultraviolet Spectra of Aromatic Compounds, No. 383, Wiley, New York, Chapman and Hall, London (1951).

[12] H. H. Perkampus, I. Sandeman, C. J. Timmons, UV Atlas of Organic Compounds, Vol. II, E2/1, Butterworths, London, Verlag Chemie, Weinheim (1966).

[13] E. Clar, D. G. Stewart, J. Am. Chem. Soc. **74**, 6235 (1952).

[14] H. H. Perkampus, I. Sandeman, C. J. Timmons, UV Atlas of Organic Compounds, Butterworths, London, Verlag Chemie, Weinheim, Vol. III, E3/1 (1966).

[15] C. Jongsma, H. Vermeer, F. Bickelhaupt, W. Schäfer, A. Schweig, Tetrahedron **31**, 2931 (1975).

[16] R. A. Friedel, M. Orchin, Ultraviolet Spectra of Aromatic Compounds, Wiley, New York, Chapman and Hall, London, No. 389 (1951).

[17] M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der organischen Chemie, 4th ed., p. 16, Georg Thieme Verlag, Stuttgart (1991).

[18] A. D. Vreugdenhil, C. Blomberg, Recl. Trav. Chim. Pays-Bas **82**, 453 (1963).

[19] J. W. F. L. Seetz, B. J. J. van de Heisteeg, H. J. R. de Boer, G. Schat, O. S. Akkerman, F. Bickelhaupt in Organometallic Syntheses (Ed.: R. B. King, J. J. Eisch), Vol. 4, p. 392, Elsevier, Amsterdam (1988).

[20] The m.p. of 85 °C, reported for **2b** in ref. [10] is probably too low as it was determined on a Kofler bank *under air*: F. Nief, personal communication.

[21] C. F. Koelsch, J. Am. Chem. Soc. **56**, 480 (1934).

[22] E. R. Lynch, J. Chem. Soc. 3729 (1962).

[23] K. Dimroth, K. Vogel, W. Mach, U. Schoeler, Angew. Chem. **80**, 359 (1968); Angew. Chem. Int. Ed. **7**, 371 (1968).