could be in equilibrium with the allenecopper compound **11**. The two intermediates can undergo reductive elimination to produce the 1,4-addition product from **10** and the 1,6-adduct from **11**. The experimentally observed exclusive formation of the 1,6-addition product may indicate that the hypothetical equilibrium lies on the side of intermediate **11**, or that the reductive elimination of **11** occurs much faster than from **10**.[14]

In conclusion, it is noted that kinetic investigations provide useful insight into the mechanistic pathways of the cuprate additions. The activation parameters determined here for the first time indicate that strong analogies exist between the reactions of various Michael acceptors.

Experimental Section

The kinetic measurements were conducted under an argon atmosphere in a double-walled flask with a double-walled dropping funnel; both were cooled with a Kryomat RUK90 made by Lauda. The temperature in the reaction flask was measured using a PT-100 thermometer and held constant to within ±0.5 K. Me$_2$CuLi · LiI was prepared in the double-walled flask by addition of MeLi (2 equiv, salt-free; ca. 1.5 M solution in diethyl ether) to a suspension of CuI (1 equiv) in diethyl ether. The cuprate solution was cooled to the reaction temperature, and a solution of the Michael acceptor and the internal standard tetradecane was likewise cooled in the dropping funnel. At the timepoint $t = 0$ the substrate was added in one shot to the cuprate (end volume: 40 mL; starting concentration of substrate and cuprate: 0.02–0.10 M); warming due to the formation of the π complex could be held to within 0.5 K. Aliquots were withdrawn at specific time intervals with a pipet that was precooled in liquid nitrogen; the aliquots were immediately hydrolyzed and analyzed by gas chromatography.

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[10] Typical results for the 1,4-addition of Me$_2$CuLi · LiI to the enone **8** at 215 K with c_0(enone) = 0.025 M: $k = 0.012 \pm 0.001\ \mathrm{s^{-1}}$ (c_0(cuprate) = 0.025 M); $0.009 \pm 0.001\ \mathrm{s^{-1}}$ (c_0(cuprate) = 0.050 M); $0.0080 \pm 0.0005\ \mathrm{s^{-1}}$ (c_0(cuprate) = 0.075 M); $0.009 \pm 0.001\ \mathrm{s^{-1}}$ (c_0(cuprate) = 0.10 M).

[11] Rate constants k for the 1,4-addition of Me$_2$CuLi · LiI to the enone **8**: $0.0011 \pm 0.0002\ \mathrm{s^{-1}}$ (204 K), $0.0016 \pm 0.0005\ \mathrm{s^{-1}}$ (208 K), $0.0046 \pm 0.0003\ \mathrm{s^{-1}}$ (211 K), $0.009 \pm 0.001\ \mathrm{s^{-1}}$ (215 K), $0.0080 \pm 0.0005\ \mathrm{s^{-1}}$ (215 K), $0.009 \pm 0.001\ \mathrm{s^{-1}}$ (215 K), $0.012 \pm 0.001\ \mathrm{s^{-1}}$ (215 K).

[12] Rate constants k for the 1,6-addition of Me$_2$CuLi · LiI to the enyne **9**: $0.00012 \pm 0.00004\ \mathrm{s^{-1}}$ (208 K), $0.00052 \pm 0.00008\ \mathrm{s^{-1}}$ (211 K), $0.00067 \pm 0.00008\ \mathrm{s^{-1}}$ (215 K), $0.00145 \pm 0.00008\ \mathrm{s^{-1}}$ (219 K), $0.00154 \pm 0.00005\ \mathrm{s^{-1}}$ (221 K), $0.0036 \pm 0.0009\ \mathrm{s^{-1}}$ (223 K), $0.0078 \pm 0.0003\ \mathrm{s^{-1}}$ (230 K).

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[14] Analogous mechanistic models can be designed for cuprate additions to any other Michael acceptor in which further rearrangement steps of the type **10** → **11** are necessary to produce the experimentally observed regioisomer.[1]

η^5-Phospholylgallium: The First Monomeric Polyhapto Compound between a Phospholyl Ligand and a Main Group Metal**

Andreas Schnepf, Gregor Stößer, Duncan Carmichael, François Mathey,* and Hansgeorg Schnöckel*

Metastable, donor-stabilized Ga$^{\mathrm{I}}$ halide solutions are important precursors for subvalent gallium species.[1] For instance, Ga$^{\mathrm{I}}$ chloride solutions have provided access to the first organometallic compounds of gallium(I), GaCp[2] and GaCp*[3] (Cp = C$_5$H$_5$, Cp* = C$_5$Me$_5$), which incorporate highly symmetrically bound η^5-Cp ligands. Simple neutral complexes involving main group elements bound to an aromatic

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[*] Prof. Dr. H. Schnöckel, Dipl.-Chem. A. Schnepf,
Dipl.-Chem. G. Stößer
Institut für Anorganische Chemie der Universität Karlsruhe (TH)
Engesserstrasse, Geb. 30.45, D-76128 Karlsruhe (Germany)
Fax: (+49) 721-608-4854
E-Mail: hg@achpc9.chemie.uni-karlsruhe.de

Prof. Dr. F. Mathey, Dr. D. Carmichael
DCPH-Ecole Polytechnique
F-91128 Palaiseau Cedex (France)
Fax: (+33) 1-69-33-39-90
E-mail: francoismathey@polytechnique.fr

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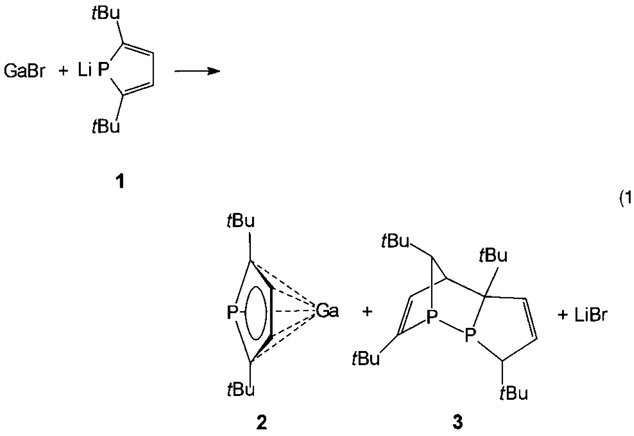
ligand containing one phosphorus atom are unknown, except for alkali metal compounds.[4] However, transition metals form many compounds of this type.[5] The absence of simple complexes containing the elements of Group 13 is surprising because such compounds could be interesting precursors for III–V semiconductors. An earlier attempt to employ indium as the group III component did not allow this problem to be resolved.[6] Consequently we were motivated to investigate the synthesis and characterization of the first η^5- phospholylgallium complex. We decided to use lithium 2,5-bis(*tert*-butyl)phospholide **1**, because the steric hindrance at its phosphorus lone pair tends to promote η^5 coordination.[7]

Cocondensation[1] of the high-temperature molecule GaBr with a toluene/THF mixture provides a metastable solution of Ga^I bromide, which was allowed to react with lithium 2,5-bis(*tert*-butyl)phospholide **1** at $-78\,^\circ C$ [Eq. (1)]. Slowly warming the reaction mixture to room temperature resulted in a black residue, which was formed from the excess gallium reagent, and a pale orange solution. After the solvent was removed in vacuo, the products were extracted with pentane.



(1)

The ^{31}P NMR spectrum of the pentane extract indicated that two products are formed in the reaction; a singlet at $\delta = 67$ for the principal product and two doublets at $\delta = -16.7$ and -30.2 with a coupling constant of 214 Hz for the by-product. Further workup of the pentane extract by fractional crystallization allowed colorless crystals of by-product **3** to be removed. The X-ray structure determination of these crystals shows this compound to be the Diels–Alder dimerization product of the protonated phosphole.[8] The major reaction product was obtained in the form of a pale yellow oil, which has precluded its characterization by X-ray diffraction to date. Its ^{69}Ga NMR spectrum gave a relatively sharp signal at $\delta = -653$ showing a half-height linewidth of 1926 Hz, indicative for η^5 coordination at gallium (GaCp*: ^{69}Ga NMR ([D$_8$]toluene): $\delta = -653$).[3]

Further support for this formulation was obtained from ab initio calculations,[9] the results of which are presented in Figure 1. An η^5-Ga^I-phospholyl structure **2** is obtained, in which the gallium atom is displaced from the axis perpendicular to the phospholyl centroid because of the greater van der Waals radius of phosphorus than carbon. NMR chemical shifts[9] were also calculated by the ab initio method, and these are in good agreement with the experimental data (Table 1).

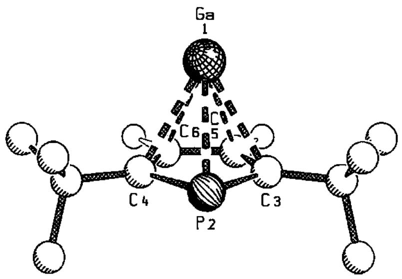


Figure 1. Sructure of **2** calculated by density functional theory: Ga–P 266.2, Ga–C3 256.7, Ga–C5 253.4, P–C 179, C3–C5 142.2, C5–C6 138.7 pm.

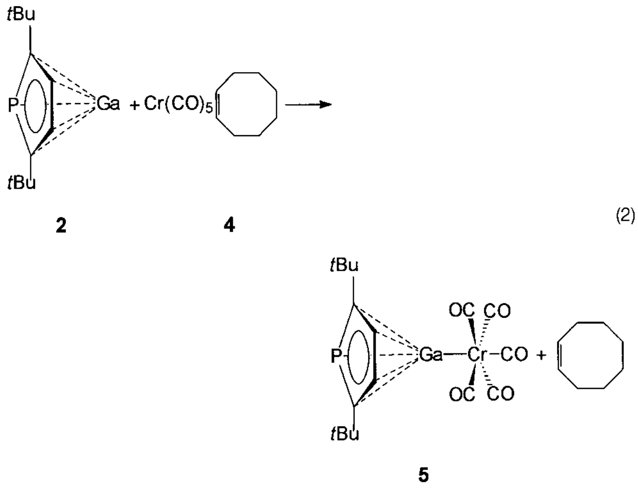
Table 1. Comparison of the calculated and observed NMR chemical shifts for **2**.

	δ Calculated	δ Experiment [ppm]
^{69}Ga	−655	−653
^{31}P	73	67
^{13}C	116.3, 176.4	118.9, 164.6

Further data supporting formulation **2** were obtained from the mass spectrum of the oil, whose molecular ion (m/z 266.1, 264.1 [M^+]) and base peak (m/z 251.1, 249.1 ([$M^+ - CH_3$]) show the anticipated $^{69}Ga/^{71}Ga$ isotope patterns.

To further substantiate these results by X-ray structure analysis, we attempted to synthesize a crystalline derivative. One possible target compound would be a transition metal carbonyl complex in which one CO ligand is replaced by the Ga^I compound. A series of analogous GaCp* derivatives have been described recently.[10]

Treatment of a solution of **2** in hexane with $Cr(CO)_5$–cyclooctene [Eq. (2)] furnished yellow crystals of the desired product in 80% yield. The results of the X-ray structure analysis (Figure 2) show the adduct to have the anticipated η^5-phospholylgallium(I) chromium pentacarbonyl structure **5**. A tilting of the phospholyl plane with respect to the Ga–Cr axis is clearly visible, and is reflected in the different gallium–ring distances. Thus, the Ga–P bond length of 248.9(1) pm is longer than the Ga–C lengths of 234.5(3) (C–*t*Bu) and 237.2(5) pm for (C–H). A comparison of the structures calculated for **5** and the uncomplexed phospholylgallium(I)



(2)

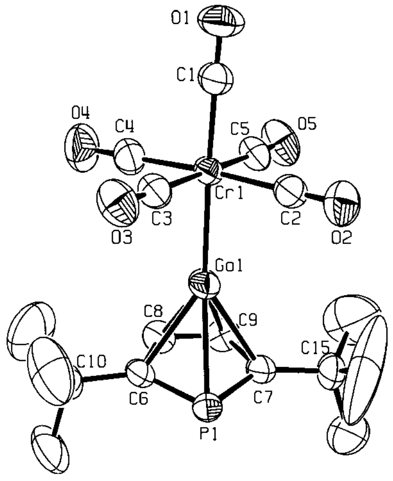


Figure 2. ORTEP diagram of the strucutre of **5**. For clarity, all hydrogen atoms except those of the phospholyl ligand have been omitted. Selected bond lengths [pm] and angles [°]: Ga1−P1 248.9(1), Ga1−C6 234.6(3), Ga1−C8 237.9(5), Ga1−Cr1 239.0(1), Cr1−C1 186.3(3), Cr1−C2 190.4(4), Cr1−C3 188.3(3) Cr1−C4 188.7(4), Cr1−C5 189.7(3), O1−C1 113.8(4), O2−C2 114.2(4), O3−C3 114.6(4), O4−C4 114.5(5), O5−C5 114.7(4), P1−C6 170.6(4), P1−C7 173.7(3), C6−C8 148.6(6), C7−C9 149.0(7), C8−C9 139.8(7); C1-Cr1-Ga1 177.5(1), C3-Cr1-C5 176.9(2), C6-P1-C7 95.6(2), C8-C6-P1 110.2(3).

compound **2** shows that the Ga–ring distances decrease by approximately 20 pm upon coordination to the $Cr(CO)_5$ fragment.[11] This is consistent with the trends observed for the corresponding Ga−Cp* compound which have been extensively discussed elsewhere.[12] Equally, the similarities between the Ga−Cr lengths in **5** (239 pm) and the corresponding Cp* complex (240 pm) illustrate that the bonding scheme which we have proposed previously[12, 13] can be extrapolated to **5**.

Consideration of the pentacarbonylchromium fragment reveals a close similarity between **5** and its Cp* analogue, which is apparent from the pattern of the IR spectrum in the carbonyl region. That the pattern is shifted to lower wavenumber in the phospholyl case may be attributed to the electron-donating properties of the phosphorus.[10, 13]

The results presented show that phospholylgsallium(I) compounds may be synthesized by the reaction of Ga^IBr with an appropriate lithium phospholide and that they are stable enough to be handled at room temperature. Additionally, mass spectrometric studies have confirmed that **2** is quite volatile. This property augurs well for the use of **2** as a CVD precursor for GaP.[14]

Experimental Section

2: Lithium 2-5-bis(*tert*-butyl)phospholide **1** (250 mg, 0.723 mmol) was dissolved in toluene (10 mL) and cooled to −78 °C. To this suspension, GaBr solution (2.5 mL, 0.3 M, 0.75 mmol GaBr) was slowly added at −78 °C. Allowing the mixture to warm slowly to room temperature produced a black precipitate and a pale orange solution which, when evaporated to dryness under high vacuum, yielded a black residue. This was extracted with pentane to give a pale orange solution from which the by-product **3** was separated by crystallization. This left the product **2** in the form of a light orange oil. Yield: 134 mg, 70 %. **2**: ^{69}Ga NMR (92 MHz, [D$_6$]benzene, 25 °C): $\delta = -653$ ($h_{1/2} = 1926$ Hz); ^{31}P NMR (100 MHz, [D$_6$]benzene, 25 °C): $\delta = 67.13$ (s, 1P); ^{13}C NMR (63 MHz, [D$_6$]benzene, 25 °C): $\delta = 32.6$ (2C), 34.96 (6CH$_3$), 118.86 (2CH), 164.6 (d, $J = 51$ Hz, 2C); ^{1}H NMR (250 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.32$ (s, 12H), 6.72 (d, $^2J = 4.1$ Hz, 2H); MS(70 eV): m/z (%): 266.1 (43, [M^+]), 264.1 (65, [M^+]), 251.1 (79, [$M^+ - CH_3$]), 249.1 (100, [$M^+ - CH_3$]), 196.1 (53), 181.1 (17), 140.1 (68), 125 (46), 103 (13), 70.9 (45), 68.9 (62), 57.1 (82). **3**: ^{31}P NMR (100 MHz, [D$_6$]benzene, 25 °C): $\delta = -30.20$ (d, $^2J = 214$ Hz, 1P), −16.70 (d, $^2J = 214$ Hz, 1P); ^{13}C NMR (63 MHz, [D$_6$]benzene, 25 °C): $\delta = 29.95$ (3CH$_3$), 30.35 (3CH$_3$), 32.59 (6CH$_3$), 33.57 (C), 35.50 (C), 37.56 (2C), 58.54 (CH), 60.92 (CH), 65.69 (CH), 75.75 (C), 133.385 (CH), 139.95 (CH), 151.07 (C); ^{1}H NMR (250 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.03$ (s, 9H), 1.07 (s, 18H), 1.21 (s, 9H), 2.23 (m, 1H), 2.54 (m, 1H), 3.21 (m, 1H), 5.67 (m, 2H), 6.08 (m, 1H); MS (70 eV): m/z (%): 392.4 (100, [M^+]), 335.3 (8, [$M^+ - t$Bu]), 196.2 (54, [$M^+/2$]), 140.1 (40, [$M^+/2 - t$Bu]), 57.1 (18, [tBu]).

5: Phospholylgallium(I) **2** (132.5 mg, 0.5 mmol) dissolved in *n*-hexane (30 mL) was added to cyclooctene chromium pentacarbonyl **4** (150 mg, 0.5 mmol). The reaction mixture was refluxed for 1 h, whereupon a yellow solution was formed. After removal of the free cyclooctene in vacuo, a crystalline residue was obtained. Further crystallization from hexane gave yellow crystals of **5** (183 mg, 0.4 mmol 80 %). Phospholylgallium(I)chromium pentacarbonyl **5**: ^{31}P NMR (100 MHz, [D$_6$]benzene, 25 °C): $\delta = 41.97$ (s, 1P); ^{13}C NMR (63 MHz, [D$_6$]benzene, 25 °C): $\delta = 30.94$ (2C), 33.90 (6CH$_3$), 126.6 (2CH), 163.4 (d, $J = 54$ Hz, 2C); ^{1}H NMR (250 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.22$ (s, 12H), 6.90 (d, $^2J = 3.7$ Hz, 2H); IR (toluene): $\tilde{\nu} = 2022$ (m) [ν_s (CO)$_4$], 1936 (sh) [ν(CO)$_{ax}$], 1870 (vs) [ν_{as} (CO)$_4$] cm^{-1}; MS (70 eV): m/z (%): 457.9 (9, [M^+]), 455.9 (12, [M^+]), 444.1 (0.3, [$M^+ - CH_3$]), 442.2 (0.5, [$M^+ - CH_3$]), 402.0 (6.5, [$M^+ - 2CO$]), 399.9 (8.8 [$M^+ - 2CO$]), 317.9 (68, [$M^+ - 5CO$]), 315.9 (100, [$M^+ - 5CO$]), 196.1 (23), 140 (30), 70.9 (5.6), 68.9 (9).

Crystal structure data for **3**: $P_2C_{24}H_{42}$, $M_r = 392.52$; crystal dimensions $0.8 \times 0.7 \times 0.5$ mm, orthorhombic, space group $P2(1)2(1)2(1)$, $a = 11.9890(7)$, $b = 12.800(1)$, $c = 15.5492(8)$ Å, $V = 2386.2(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.093$ g cm^{-3}, $\mu_{Mo} = 1.88$ cm^{-1}, $2\theta_{max} = 559184$ observed reflections , 5485 unique reflections, absorption correction: semiempirical (min./max. transmission 0.2598/0.2185), $R_1 = 0.036$, $wR_2 = 0.084$. Stoe Stadi4 diffractometer (Mo$_{K\alpha}$ radiation, ($\lambda = 0.71073$ Å), 200 K). The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs: Shelxs and Shelxtl (G. M. Sheldrick, Universität Göttingen).

Crystal structure data for **5**: $GaCrPO_5C_{17}H_{20}$, $M_r = 457.02$; crystal dimensions $0.8 \times 0.6 \times 0.46$ mm, triclinic, space group $P\bar{1}$, $a = 6.6462(13)$, $b = 9.929(2)$, $c = 15.670(3)$ Å, $\alpha = 88.88(3)$, $\beta = 79.51(3)$, $\gamma = 85.42(3)°$, $V = 1013.5(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.498$ g cm^{-3}, $\mu_{Mo} = 1.966$ cm^{-1}, $2\theta_{max} = 60°$, 9164 observed reflections, 5934 unique reflections, no absorption correction, $R_1 = 0.0484$, $wR_2 = 0.122$. Stoe Stadi4 diffractometer (Mo$_{K\alpha}$ radiation, ($\lambda = 0.71073$ Å), 200 K). The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs: Shelxs and Shelxtl (G. M.Sheldrick, Universität Göttingen).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-112168 (for **5**) and CCDC-112169 (for **3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] The ab initio calculations were performed with the TURBOMOLE[16] package using TZVP[17] (**2**) or SVP (**5**) basis sets.[18] Geometries were optimized by using the RI-DFT module [19] (BP-86-Functional[20]) in the C_s point group. NMR chemical shifts were calculated at the SCF level,[21] using geometries optimized at the RI-DFT level. **2**: $E = -2730.201229$ au, Ga–P 266.2, Ga–C 256.7 and 253.4, P–C 179, C–C 138.1, C–C 142.2 pm, C-P-C 90.9, P-C-C 110.4, C-C-C 114.1°. **5**: $E = -4346.064324$ au, Ga–P 249.9, Ga–C 246.3 and 242.1, Ga–Cr 241.4, P–C 184.9, C–C 138.7, C–C 143.4 pm, C-P-C 88.9°, P-C-C 110.9°, C-C-C 114.6°.

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[14] Whilst the preparation of the Ga^{I} halide solutions requires rather sophisticated equipment, the compound described here should be accessible through more classical techniques. One possible approach, by analogy with the successful synthesis of GaCp*,[10] involves the reduction of the corresponding phospholylgallium dihalide with potassium. Further synthetic investigations and preliminary CVD experiments aimed at the formation of GaP are in progress.

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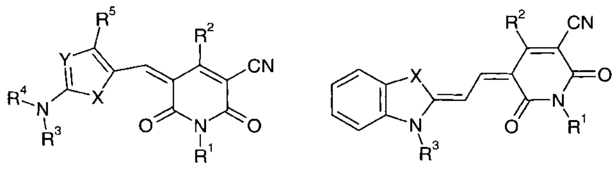
Design, Synthesis, and Evaluation of a Dye Library: Glass-Forming and Solid-State Luminescent Merocyanines for Functional Materials**

Frank Würthner,* Rüdiger Sens, Karl-Heinz Etzbach, and Günther Seybold

Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

In the development of functional dyes, after the identification of a suitable chromophore extensive variations of the substituents usually have to be carried out before a satisfactory product is obtained for the desired area of application. This optimization of the lead structure traditionally takes place according to combinatorial rather than rational principles, as stability, solubility, affinity, and compatibility properties are hard to predict.

Recently we reported on the dyes **1**–**4**,[1] which possess a very interesting chromogenic system for several high-technology applications.[2] These chromophores with an electronic structure at the mesomeric center between neutral and zwitterionic electron distribution have high polarizabilities, high dipole moments, and exhibit absorption spectra with sharp bands ($\varepsilon_{max} > 100000\,\mathrm{L\,mol^{-1}\,cm^{-1}}$, half widths $\Delta\tilde{\nu}_{1/2} < 1500\,\mathrm{cm^{-1}}$) that give rise to exceptionally brilliant magenta hues.[3] This resulted in hitherto unattainable refractive index modulations in photorefractive materials[1] as well as brilliant hues in thermal dye transfer printing and in electrophotography (color copiers).[2]



1: X = O, Y = CH
2: X = S, Y = CH
3: X = S, Y = N

4: X = CMe$_2$
5: X = S
6: X = O

High concentrations of colorant are necessary in photorefractive materials, ribbons for thermal dye transfer printing, and toners for color copiers, which leads to problems due to

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[*] Dr. F. Würthner,[+] Dr. R. Sens, Dr. K.-H. Etzbach, Dr. G. Seybold
BASF Aktiengesellschaft
ZDT – Farbenlaboratorium
D-67056 Ludwigshafen (Germany)

[+] New Address:
Abteilung Organische Chemie II der Universität
Albert-Einstein-Allee 11, D-89081 Ulm (Germany)
Fax: (+49) 731-50-22840
E-mail: frank.wuerthner@chemie.uni-ulm.de

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