Reactions of Complex Ligands, LXIV[◇]

Synthesis of 5,5′-Diphenyl-2,2′-bifuran, a Biaryl Compound with Remarkable Fluorescence Properties

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The 2-oxacyclic α,β-unsaturated carbene complex **1** reacts with an excess of dimethylamine to give the diphenylbifuran **2**. The structure of **2** was established by independent synthesis from 2-phenylfuran (**4**) via regioselective lithiation and transmetalation to zinc and tin organometallics **6a–c** and final oxidative copper coupling reactions.

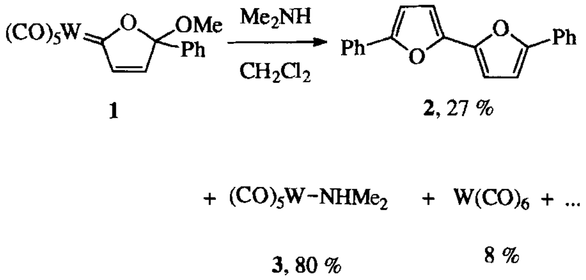
α,β-Unsaturated Fischer-type carbene complexes have become important reagents in synthetic organic chemistry[2]. Phenyl- and ethenyl-substituted representatives are valuable precursors of highly substituted and anellated hydroquinone derivatives[3]. An α,β-unsaturated alkoxycarbene complex may react with a primary or secondary amine either via attack of the nitrogen at the strongly electrophilic carbene carbon center yielding an aminocarbene ligand[4] or via a Michael-type 1,4-addition to the alkenyl or alkynyl functionality leading to a β-aminoalkyl or -alkenyl ligand[5]. We were interested in aminolysis reactions of α,β-unsaturated oxacyclic carbene ligands containing a cyclic acetal structure[6] such as **1** which was expected to generate a β-acylalkenyl aminocarbene system upon ring opening. Similar reactions are known for saturated cyclic carbene complexes[7] although they sometimes failed[8]. We now report on the aminolysis reaction of **1** revealing an unprecedented formation of the novel bifuran **2**. 2,2′-Bifuran[9] and a series of derivatives[10] including 5,5′-dialkyl compounds[11] are known some of which were synthesized by starting from carbene complexes[10a,10b,10c].

2,2′-Bifuran Formation via Aminolysis of Carbene Complex 1

Treatment of the cyclic tungsten carbene acetal **1** with an excess of dimethylamine resulted neither in a ring-opening reaction nor in a 1,4-addition to the α,β-double bond. Instead, cleavage of the metal-carbene bond occurred and the dimethylamine complex **3**[12] was isolated by column chromatography as the major product along with hexacarbonyl tungsten and identified by IR and NMR spectroscopy [ν(CO), PE: 2072 (A_1^1), 1932 (E), 1922 (A_1^2) cm^{-1}; $^1J(^{13}C,^{183}W)$ = 127 Hz (*cis* CO) and 147 Hz (*trans* CO).

The carbene ligand was incorporated into the novel 5,5′-diphenyl-2,2′-bifuran **2** (Scheme 1) which was characterized by spectroscopic methods and by elemental analysis. Bifuran **2** reveals a strong UV absorption band at λ_{max} = 364 nm (lg ε = 4.57) and a very strong fluorescence emission during exposure to UV radiation, especially when the 366-nm line of a mercury lamp is used. A blue fluorescence is observed both in solution and when **2** is absorbed on silica gel but is absent in the solid state. The UV/Vis emission spectrum of **2** (recorded upon irradiation at an angle of 90° with the 366-nm line of Hg; lower-energy lines were suppressed by using an appropriate filter) exhibits a strong emission band at 445 nm, accompanied by two shoulders at 420 and 475 nm. Several oligofurans display a similar absorption (e.g. bifuran: λ_{max} = 296 nm, terfuran: λ_{max} = 345 nm, quaterfuran: λ_{max} = 380 nm) and emission behavior[13].

Scheme 1



The mechanism of the bifuran formation remains obscure. One might speculate about a tungsten mediated redox process related to an Ullmann type coupling[14]. Such a sequence would require a 2-furyl tungsten(II) intermediate which might be formed from carbene complex **1** – after addition of dimethylamine – via elimination of methanol.

2,2′-Bifuran Formation via Copper Coupling Reaction

The synthesis of bi- and oligoaryl compounds is generally based on coupling reactions of metalated arenes with transition metal(II) halides, especially $CuCl_2$[14]. In this case, the aryl-aryl bond is formed by reductive elimination from a bis(aryl)copper(II) complex. We also focussed on this meth-

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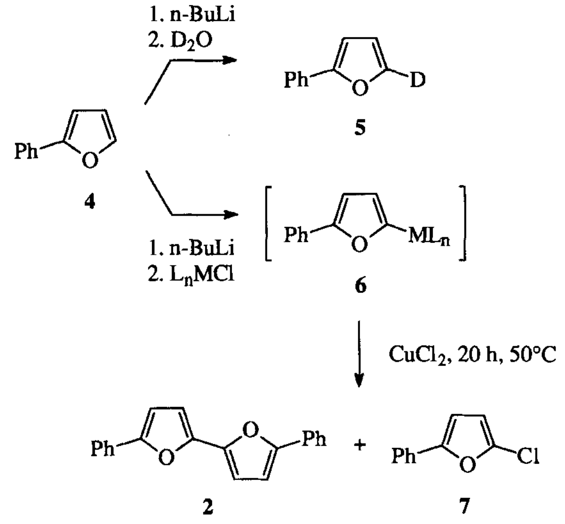
odology in order to gain a more satisfactory synthetic access to bifuran **2**. First, we worried about the regioselectivity of the deprotonation of the phenylfuran precursor **4** since *n*-butyllithium might deprotonate both the furan nucleus at C-5 and the phenyl ring at *o*-C; the latter reaction might be even favored by intramolecular coordination of the furyl oxygen to the lithium center. However, a deuteration experiment established that – after treatment of the lithiated intermediate **6a** with D_2O – the only deuterated phenylfuran isolated after chromatographic workup in 80% yield was the 5-deuterio derivative **5** (Scheme 2). The regioselective deuteration at C-5 was determined by ^{1}H- and ^{13}C-NMR spectroscopy: The signal of the furyl H-5 atom at $\delta = 7.33$ in **4** is completely missing in compound **5**. In addition, in the ^{13}C-NMR spectrum the C-5 ($\delta = 141.84$) and C-4 ($\delta = 111.39$) signals show a triplet pattern [$^1J(^{13}C,D) = 30.5$ Hz and $^2J(^{13}C,D) = 1.6$ Hz].

Scheme 2



6a: $ML_n = Li$
6b: $ML_n = ZnCl$
6c: $ML_n = SnBu_3$

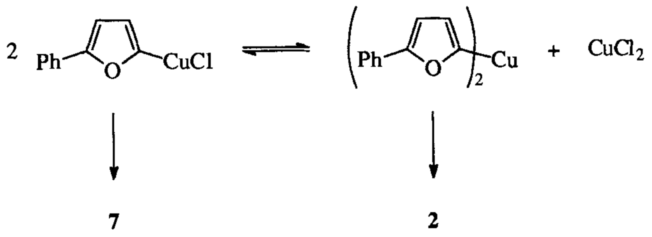
Table 1. Conditions of the copper coupling reactions for the formation of bifuran **2**

entry	L_nM	$CuCl_2$	T	**2**[a]	**7**[a]
1	Li	1.0 eq	20 °C	20 %	5 %
2	Li	1.0 eq	35 °C	34 %	26 %
3	Li	0.5 eq	35 °C	2 %	[b]
4	Li	[c]	[d]	26 %	[b]
5	ZnCl	1.0 eq	50 °C	45 %	55 %
6	$SnBu_3$	1.0 eq	67 °C	21 %	73 %

[a] Isolated yields. – [b] Not detectable. – [c] According to a literature procedure[17] using 1.0 eq of CuCN and subsequent oxidation of the cuprate with O_2. – [d] −78 °C, 1 h; 0 °C, 2 h; room temp., 5 h.

Lithiated phenylfuran **6a** reacts with one equivalent of $CuCl_2$ to give **2** in moderate yields (Table 1, entries 1, 2) along with a minor amount of the light-sensitive chlorofuran **7**[15]. The formation of **7**, which was separated by column chromatography, may be rationalized as the reductive elimination of a chloro(furyl)copper(II) intermediate which is in equilibrium with $CuCl_2$ and di(furyl)copper(II) as known for Grignard reagents[16] (Scheme 3).

Scheme 3



The use of decreasing amounts of $CuCl_2$ (Table 1, entry 3) or of CuCN followed by O_2 oxidation of the homocuprate[17] (Table 1, entry 4) did not improve the yield of **2**. When the lithium derivative **6a** is transmetalated to the more stable furylzinc compound **6b** and the furylstannane **6c** higher temperatures can be employed in the coupling reaction. Thus **6b** reacts with $CuCl_2$ at 50 °C to give the optimum yield of **2**. However, both in the zinc and in the tin series the yields of the chlorofuran **7** even increase to such an extent that it becomes the major product (Table 1, entries 5, 6). In summary, the oxidative copper coupling methodology (Table 1, entry 4) presently seems to be the method of choice for the preparative scale synthesis of the diarylbifuran **2** in order to explore its promising optical properties.

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Experimental

All operations were carried out in flame dried glassware under argon. Tetrahydrofuran (THF) was freshly distilled from potassium before use. – Column chromatography was accomplished with Merck silica gel (Type 60, 0.063–0.200 mm) and petroleum ether (PE) (fraction 40–60 °C). – ^{1}H and ^{13}C NMR: Bruker AM 400. – IR: Nicolet Magna 550. – MS: Concept 1H and Kratos MS 50 (HRMS). – Elemental analysis: Heraeus CHN-Rapid. – UV (absorption): Beckman DU 640. – UV/Vis (emission): excitation with the 366-nm line of a Hg lamp, all lines of lower energy were filtered out. – 2-Phenylfuran (**4**) was synthesized according to a literature procedure[18].

5,5'-Diphenyl-2,2'-bifuran (**2**) *from Carbene Complex* **1**: 6.5 ml (4.4 g, 97 mmol) of dimethylamine was added at −78 °C to a solution of 630 mg (1.26 mmol) of **1** in 10 ml of dichloromethane. The reaction mixture was allowed to warm to room temp. and then stirred for 1 d. After removal of the solvent chromatography of the residue on silica gel (PE/CH_2Cl_2, 3:1) yielded 50 mg (28%) of bifuran **2** as a yellow solid [m.p. 167.5–168.5 °C (dec.)] and 50 mg (8%) of hexacarbonyl tungsten. Further elution with PE/CH_2Cl_2 (1:1) gave complex **3** (yellow solid, 372 mg, 80%). – IR (KBr): $\tilde{\nu}$ = 1460 (s), 1022 (s), 922 (s), 909 (s), 788 (vs), 755 (vs), 691 (s), 655 (s) cm^{-1}. – UV (absorption, $CHCl_3$): λ_{max} (lg ε) = 269 (3.836), 354 sh (4.523), 364 (4.571), 381 sh (4.404) nm. – UV/Vis (emission, $CHCl_3$, $1.9 \cdot 10^{-3}$ mol/l): λ_{max} (I_{rel}) = 420 sh (17), 445 (100), 475 (50) nm. – ^1H NMR ($CDCl_3$): δ = 6.71 (d, J = 3.53 Hz, 1 H, furyl-H), 6.73 (d, J = 3.52 Hz, 1H, furyl-H), 7.24–7.28 (m, 1 H, *para*-H), 7.37–7.41 (m, 2H, *meta*-H), 7.71–7.73 (m, 2H, *ortho*-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 107.06 (furyl-CH), 107.43 (furyl-CH), 123.76 (phenyl-CH), 127.48 (phenyl-CH), 128.76 (phenyl-CH), 130.48 (phenyl-C), 145.98 (furyl-C), 153.25 (furyl-C). – MS (70 eV), *m/z* (%): 286 (100) [M^+], 181 (11) [M^+ – PhCO], 143 (14) [$(M/2)^+$], 115 (12) [$(M/2)^+$ – CO], 105 (17) [$PhCO^+$], 77 (15) [Ph^+]. – $C_{20}H_{14}O_2$ (286.3): calcd. C 83.90, H 4.93; found C 83.91, H 5.03. – Mol. mass calcd. 286.0994, found 286.0995 (HRMS).

[5-D$_1$]-2-Phenylfuran (**5**): 0.72 g (5.0 mmol) of 2-phenylfuran (**4**) was lithiated with 5.0 mmol (3.1 ml of a 1.6 M solution in hexane) of *n*-butyllithium in 5 ml of THF at –78 °C. After stirring at 0 °C for 1 h 5.0 ml (5.5 g, 0.28 mol) of D_2O was added, and the aqueous layer was extracted several times with Et_2O. The combined organic layers were washed with brine and dried with $MgSO_4$. Filtration, concentration of the filtrate and chromatography (PE, SiO_2) of the residue gave 0.58 g (4.0 mmol, 80%) of the deuterated furan **5** as a colorless oil. – MS (70 eV), *m/z* (%): 145 (100) [M^+], 116 (62) [M^+ – HCO], 115 (72) [M^+ – DCO], 77 (8) [Ph^+]. – ^1H NMR ($CDCl_3$): δ = 6.48 (d, J = 3.5 Hz, 1H, furyl-H), 6.66 (d, J = 3.1 Hz, 1H, furyl-H), 7.25–7.28 (m, 1H, *para*-H), 7.37–7.41 (m, 2H, *meta*-H), 7.68–7.70 (m, 2H, *ortho*-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 104.91 (3-furyl-CH), 111.39 [t, $^2J(^{13}C,D)$ = 1.6 Hz, 4-furyl-CH], 123.74 (phenyl-CH), 127.28 (phenyl-CH), 128.64 (phenyl-CH), 130.85 (phenyl-C), 141.84 [t, $^1J(^{13}C,D)$ = 30.5 Hz, 5-furyl-C], 153.93 (2-furyl-C). – $C_{10}H_7DO$ (145.17): Mol. mass calcd. 145.0638, found 145.0638 (HRMS).

5,5'-Diphenyl-2,2'-bifuran (**2**) *from Phenylfuran* (**4**): 5.0 mmol of **4** was lithiated as described for the synthesis of **5**. This solution was added to a solution of 0.68 g (5.0 mmol) of dry $ZnCl_2$ in 5 ml of THF at –78 °C. The mixture was stirred for 1 h at room temp. and then added to a suspension of 0.67 g (5.0 mmol) of $CuCl_2$ in 5 ml of THF at –78 °C. After stirring at room temp. for 1 h and at 50 °C for 20 h, the reaction mixture was partitioned between THF and 15 ml of a saturated solution of NH_4Cl in 10% aqueous NH_3. The aqueous layer was extracted several times with Et_2O, the combined organic layers were washed with brine and dried with $MgSO_4$. After filtration and evaporation of the solvent from the filtrate, the residue was purified by chromatography on silica gel (PE/CH_2Cl_2, 3:1). From the first fraction 0.49 g (2.7 mmol, 55%) of chlorofuran **7** was isolated as a colorless, light-sensitive oil which solidified at 10 °C. Further elution with the same solvent gave 0.32 g (1.1 mmol, 45%) of bifuran **2** as a yellow solid.

2-Chloro-5-phenylfuran (**7**): IR (film): $\tilde{\nu}$ = 1516 (vs), 1483 (s), 1205 (s), 1155 (s), 1016 (s), 941 (s), 783 (s), 758 (vs), 695 (s) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 6.24 (d, J = 3.52 Hz, 1H, furyl-H), 6.61 (d, J = 3.52 Hz, 1H, furyl-H), 7.25–7.29 (m, 1H, *para*-H), 7.36–7.40 (m, 2H, *meta*-H), 7.60–7.62 (m, 2H, *ortho*-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 106.82 (furyl-CH), 108.21 (furyl-CH), 123.33 (phenyl-CH), 127.60 (phenyl-CH), 128.67 (phenyl-CH), 129.84 (phenyl-C), 135.83 (furyl-C), 153.42 (furyl-C). – MS (70 eV, reg. ^{35}Cl), *m/z* (%): 178 (32) [M^+], 115 (100) [M^+ – COCl]. – $C_{10}H_7ClO$ (178.6): calcd. C 67.24, H 3.95; found C 67.00, H 3.93. – Mol. mass 178, 180 (MS).

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