Our study is the first reported demonstration that model lignins can be efficiently produced in vitro, in an aqueous environment, under homogeneous conditions; the presence of the micelles is able to keep in solution all the lipophilic reagents and reaction products, with practically no detriment to the catalytic efficacy of the enzyme. Moreover, since the activity of an enzyme under micelle conditions could be considered more similar to the cell system than in buffer alone,[12, 13] we propose that in our case the polymerization mechanism which drives oligolignol formation is closer to the natural process than are the other, well-established in vitro biosynthetic experiments. In conclusion, our results show that in lignin biosynthesis the ionic and the radical mechanisms operate effectively in parallel to the same extent, and they formally appear as strictly alternate steps. These results are also in favor of a more recent concept of a structural scheme for natural lignins which assumes an ordered structure with repeating units.[23, 24]

Experimental Section

In a typical experiment 20 mg of coniferyl alcohol are dissolved in 3.6 mL of sodium phosphate buffer (0.01M; pH 6.5) containing $(CTA)_2SO_4$ at a concentration of 2.7×10^{-2}M; to this solution are added sequentially 130 μL of 3% H_2O_2 and 20 μL of buffer containing seven purpurogallin units of horseradish peroxidase (type II, 200 U mg^{-1}, Sigma). The clear solution, where the substrate is at a concentration of 5.3 g L^{-1}, is stirred over a period of 5 min. After this time, which is sufficient for the substrate to be consumed (HPLC analysis), the reaction is stopped by the addition of a few drops of 5% $Na_2S_2O_7$, and the mixture thoroughly extracted with ethyl acetate. The organic layer is then washed with brine and dried, and the solvent evaporated under vacuo to give approximately 23 mg of product.

Received: October 15, 1998 [Z12529IE]
German version: *Angew. Chem.* **1999**, *111*, 1364 – 1367

Keywords: biosynthesis · enzyme catalysis · lignin · mass spectrometry · micelles

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Highly Substituted Spiro[4.4]nonatrienes from a β-Amino-Substituted α,β-Unsaturated Fischer Carbene Complex and Three Molecules of an Arylalkyne**

Heiko Schirmer, Michael Duetsch, Frank Stein, Thomas Labahn, Burkhard Knieriem, and Armin de Meijere*

Dedicated to Professor Klaus Kühlein on the occasion of his 60th birthday

In recent years α,β-unsaturated Fischer carbene complexes have established themselves as valuable functional building blocks in organic chemistry.[1] In particular, β-amino-substituted alkenylcarbene complexes exhibit a highly diverse reactivity depending upon the nature of the substituents and reaction conditions.[2] These complexes are readily available from alkynylcarbene complexes by 1,4-addition of amines to 1-metalla-1-en-3-ynes[3] and undergo inter alia formal [3+2],[4] [2+2+1],[5] and [4+2] cycloadditions[4c, 6] with alkynes. In contrast, (3-dimethylaminoalkenylidene)chromium complexes with sterically demanding substituents on the alkenyl terminus, and therefore normally with a *Z* configuration, react preferentially by sequential insertion of two alkyne units and carbon monoxide and only then undergo cyclization, that is, they give cyclopenta[*b*]pyrans by a formal [3+4+1] cycloaddition, frequently in high yields.[7] Although it also has a sterically demanding substituent and a *Z* configuration, the

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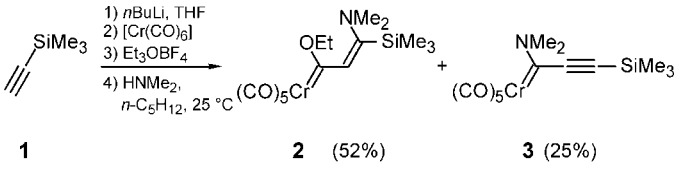
[**] This work was supported by the Volkswagen Stiftung, the Fonds der Chemischen Industrie, and by the companies BASF, Bayer, Degussa, and Hoechst (chemicals).

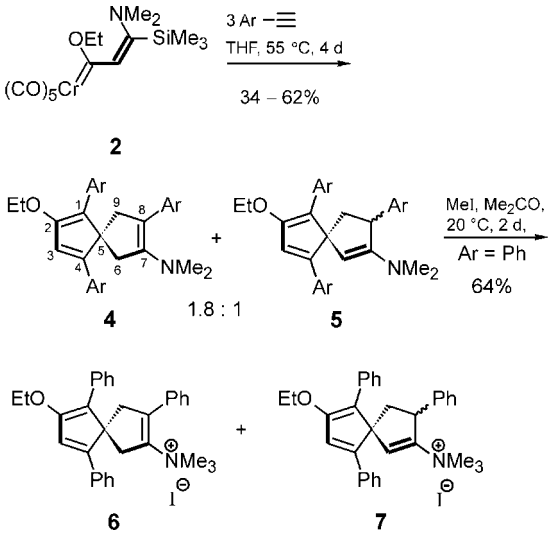
trimethylsilyl-substituted complex **2** reacts with formal insertion of three alkyne units in a manner not previously observed.[8a]

(3-Dimethylamino-1-ethoxy-3-trimethylsilylallylidene)-pentacarbonylchromium (**2**) may be prepared by the established procedure, but in diethyl ether a 0.9:1 mixture of **2** and **3** is formed in only modest yield (27 + 30 %).[3b, 8, 9] The best yield of **2** (52 % against 25 % **3**) is obtained when the addition of dimethylamine to the alkynyl complex (prepared from trimethylsilylethyne (**1**) by an improved method[4c, d]) is carried out in a one-pot reaction in pentane[9] at room temperature (Scheme 1).



Scheme 1. Synthesis of **2** from the trimethylsilylethyne **1** by the one-pot procedure.

Upon heating complex **2** with six equivalents (optimized, twofold excess) of phenylethyne in THF at 55 °C (complete conversion of **2** after four days according to thin-layer chromatography) a yellow solid which fluoresces strongly in solution is obtained after purification by column chromatography (Scheme 2). ^{1}H and ^{13}C NMR spectra indicated that it



Scheme 2. Synthesis of **4** and **5** and their conversion (Ar = Ph) into the quaternary ammonium salts **6** and **7**.

was a mixture of three isomers (ratio 3.6:1:1), none of which contained a trimethylsilyl group. Assuming that the highest peak in the mass spectrum of the mixture at *m/z* 433 corresponded to the molecular ion peak, a compound had been formed in this reaction in 62 % yield from the protiodesilylated carbene ligand and three molecules of phenylethyne without carbonyl insertion.

However, it was not possible to separate the three isomers by repeated column chromatography, nor was it possible to assign the correct structures from the NMR spectra of the mixture. All attempts at crystallizing the major isomer failed since the compound mixture dissolved in only a small volume of pentane and decomposed rapidly during slow evaporation. To increase the polarity of all isomers at their dimethylamino groups the mixture was treated with iodomethane in acetone at room temperature. The mixture of the three isomeric quaternary ammonium iodides obtained in 64 % yield after two days was considerably more stable in solution (Scheme 2). It was poorly soluble in ethanol, but readily soluble in acetone, and slow evaporation of a solution of the mixture in ethanol/acetone allowed the isolation of single crystals. According to X-ray structural analysis these consisted of the quaternary ammonium iodide **6** of 7-dimethylamino-2-ethoxy-1,4,8-triphenylspiro[4.4]nona-1,3,7-triene (**4a**).[10] An NMR spectrum of the single crystals showed that the product was the main isomer of the mixture (Figure 1).

A conclusive assignment of the other isomers in the mixture of products from **2** and phenylethyne was obtained by high-resolution 2D NMR correlation experiments,[11] according to which these two minor isomers consisted of a 1:1 diastereomeric mixture of the spiro[4.4]nona-1,3,6-triene **5a**. The

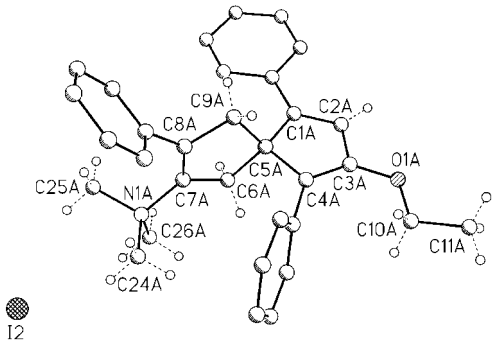


Figure 1. Crystal structure of the quaternary ammonium iodide **6**.[10] The hydrogen atoms and numbering of the phenyl rings have been omitted for clarity.

assumption that the isomers **4** and **5** existed in a dynamic equilibrium was not confirmed. ^{1}H NMR spectra measured at different temperatures showed that there were no changes in the characteristic signal intensities.

To elucidate the scope of this new reaction, **2** was allowed to react with a series of alkynes. This showed that only arylethynes yielded the spiro[4.4]nonatrienes **4** and **5**. The isomeric ratio of the products thus obtained varied according to the substitution pattern of the arylethyne employed (Table 1). Terminal alkynes such as 1-pentyne and internal alkynes such as 2-butyne reacted in the known manner[2, 4] to give the respective substituted cyclopentadienes.[12]

The conspicuously intense fluorescence of these spiro[4.4]-nonatrienes must be attributed to the conjugation of the diarylcyclopentadiene moiety in **4** and **5**. The mixture of the

Table 1. Formation of spiro[4.4]nonatrienes **4** and **5** from **2** and three equivalents of arylethyne.

	Ar	Yield **4** + **5** [%]	**4**:**5**
a	C_6H_5	62	1.8:1
b	C_6H_4-4-C_6H_5	34	4.5:1
c	C_6H_4-4-OMe	37	2.5:1
d	C_6H_3-3,5-$(Me)_2$	48	1.6:1

  1433-7851/99/3809-1286 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **1999**, *38*, No. 9

(3,5-dimethylphenyl)-substituted isomers **4d**/**5d** (1.6:1) showed an absorption maximum in the UV spectrum at $\lambda_{max} = 237$ nm (isooctane) with $\varepsilon_{max} = 29\,500$. The absorption maximum in the fluorescence spectrum lay at $\lambda_{max} = 480$ nm (isooctane), and the relative fluorescence quantum yield was calculated to be 46%.

All previous speculations on the mode of formation of these new cocyclization products of arylethynes with the allylidene chromium complex **2** are poorly illuminating. It is particularly unusual that the original connectivity of the carbene ligand in **2** is lost in the products **4** and **5**. (Scheme 2). In contrast, the original connectivity is maintained in all previously known products from β-dialkylamino-substituted α,β-unsaturated carbene chromium complexes.[2] Attempts to shed light on the mechanism by introduction of terminally or internally ^{13}C-labeled phenylethynes are in progress. The possible triple insertion[13] of an alkyne with an alkenylcarbene chromium complex described herein for the first time once more extends the broad range of cycloadducts which can be selectively obtained from α,β-unsaturated Fischer carbene complexes.

Received September 24, 1998 [Z 12451 IE]
German version: *Angew. Chem.* **1999**, *111*, 1369 – 1371

Keywords: alkynes · carbene complexes · insertions · spiro compounds

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[10] Crystal structure analysis of **6** ($C_{32}H_{34}INO + C_2H_6O$): $Z = 2$, $M_r = 621.57$, crystal dimensions: $0.6 \times 0.6 \times 0.5$ mm, triclinic, space group $P\bar{1}$, $a = 988.95(14)$, $b = 1589.04(10)$, $c = 1033.17(18)$ pm, $\alpha = 103.842(5)$, $\beta = 96.126(10)$, $\gamma = 97.561(10)^\circ$, $V = 3.0435(5)$ nm^3, $\rho_{calcd} = 1.357$ Mg m^{-3}, $F(000) = 1280$, $\lambda = 71.073$ pm, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 1.082$ mm^{-1}. $2.10 \le 2\theta \le 22.50^\circ$; of 30 634 reflections collected, 7953 are independent and were used for structure refinement of 729 parameters with the help of 73 restraints. The R values are $R1 = 0.0445$ ($I > 2\sigma(I)$) and $wR2 = 0.1099$ (all data); min./max. residual electron density $-725/1323$ e nm^{-3}. The data were collected with a Stoe – Siemens – Huber four-circle diffractometer with a Siemens CCD area detector. The intensities were measured with ϕ and ω scans. Data integration was carried out with the SAINT program. The structure was solved by direct methods (SHELXS-90/97) and refined by the least-squares procedure against F^2. All non-hydrogen atoms were anisotropically refined.[14] All hydrogen atoms were positioned with ideal geometries and included in the refinement. All disorders were resolved with distance and ADP restraints and anisotropically refined. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-410 149. Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] Spectroscopic data for compounds **4** and **5**: IR (KBr): $\tilde{\nu} = 3053$ cm^{-1} (C–H), 2976 (C–H), 2850 (C–H), 2790, 1609 (C=C), 1595 (C=C), 1494, 1442, 1375, 1191, 1142, 1047, 999, 910, 846, 771, 697. **4**: ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.47$ (t, $^3J = 6.9$ Hz, 3H; OCH_2CH_3), 2.65 (s, 6H; $N(CH_3)_2$), 2.96 (AB, dd, $^2J = 17.1$, $^4J = 2.4$ Hz, 1H; 9-H), 3.03 (AB, dd, $^2J = 17.1$, $^4J = 2.4$ Hz, 1H; 9-H), 3.09 (AB, dd, $^2J = 17.1$, $^4J = 2.4$ Hz, 1H; 6-H), 3.18 (AB, dd, $^2J = 17.1$, $^4J = 2.4$ Hz, 1H; 6-H), 4.24 (q, $^3J = 6.9$ Hz, 1H; OCH_2CH_3), 4.25 (q, $^3J = 6.9$ Hz, 1H; OCH_2CH_3), 6.95 (s, 1H; 3-H), 7.28 – 7.34 (m, 9H; Ph), 7.42 (dd, $^3J = 7.6$, $^4J = 0.7$ Hz, 2H; Ph), 7.66 (dd, $^3J = 7.6$, $^4J = 0.7$ Hz, 2H; Ph), 7.90 (dd, $^3J = 7.6$, $^4J = 0.7$ Hz, 2H; Ph); ^{13}C NMR (125.7 MHz, $CDCl_3$, plus DEPT): $\delta = 15.59$ (+, OCH_2CH_3), 42.30 (–, C-9), 42.57 (+, $N(CH_3)_2$), 44.55 (–, C-6), 53.11 (C_{quat}, C-5), 65.97 (–, OCH_2CH_3), 112.59 (C_{quat}, C-4), 119.46 (+, C-3), 124.70, 125.20, 125.59, 125.97, 127.20, 127.74, 127.98, 128.32, 128.69 (+, Ph), 134.01, 134.83, 138.97 (C_{quat}, Ph), 144.89 (C_{quat}, C-8), 147.04 (C_{quat}, C-1), 154.48 (C_{quat}, C-7), 156.37 (C_{quat}, C-2). **5** (1:1-diastereomeric mixture): ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.25$ and 1.23 (t, $^3J = 6.9$ Hz, 3H; OCH_2CH_3), 2.09 and 2.12 (AB, dd, $^2J = 13.5$, $^3J = 2.4$ Hz, 1H; 9-H), 2.37 and 2.38 (AB, dd, $^2J = 13.5$, $^3J = 8.5$ Hz, 1H; 9-H), 2.48 and 2.52 (s, 6H; $N(CH_3)_2$), 3.40 and 3.61 (dt, $^3J = 8.5$, $^4J = 1.4$ Hz, 1H; 8-H) 3.92 and 4.04 (q, $^3J = 6.9$ Hz, 1H; OCH_2CH_3), 3.93 and 4.05 (q, $^3J = 6.9$ Hz, 1H; OCH_2CH_3), 4.48 and 4.49 (d, $^4J = 1.4$ Hz, 1H; 6-H), 6.43 and 6.59 (s, 1H; 3-H), 6.92 and 7.02 (d, $^3J = 7.6$ Hz, 2H; Ph), 7.14 – 7.26 (m, 9H; Ph), 7.56 and 7.58 (d, $^3J = 7.6$ Hz, 2H; Ph), 7.74 and 7.79 (d, $^3J = 7.6$, 2H; Ph); ^{13}C NMR (125.7 MHz, $CDCl_3$, plus DEPT): $\delta = 15.47$ and 15.52 (+, OCH_2CH_3), 40.87 and 40.88 (+, $N(CH_3)_2$), 41.58 and 42.81 (–, C-9), 50.96 (+, C-8), 65.78 and 65.91 (–, OCH_2CH_3), 66.23 (C_{quat}, C-5), 102.62 and 102.86 (+, C-6), 121.75 and 122.97 (+, C-3), 123.72 (C_{quat}, C-4), 125.38, 125.89, 127.03, 127.16, 127.34, 127.40, 127.42, 127.59, 127.62, 127.77, 127.80, 128.02, 128.09, 128.29, 128.30, 128.89, 129.55 (+, Ph), 135.73, 136.16, 136.17, 136.41, 136.48 (C_{quat}, Ph), 152.25 and 153.03 (C_{quat}, C-1), 153.79 and 155.09 (C_{quat}, C-7), 155.34 (C_{quat}, C-2). The assignments were verified with 2D correlation experiments. MS (70 eV): m/z (%): 433 (81) [M^+], 404 (100) [$M^+ - C_2H_5$], 398 (17) [$M^+ - N(CH_3)_2$], 356 (13), 202 (6), 103 (5). – $C_{31}H_{31}NO$ (433.6).

[12] Compound **2** yields 5-dimethylamino-3-ethoxy-1-propyl-5-trimethylsilyl-1,3-cyclopentadiene (25%) with 1-pentyne in THF after four days at 55 °C, and the analogous 1,2-dimethylcyclopentadiene derivative (44%) with 2-butyne in pyridine at 80 °C.

[13] The possible triple insertion can be considered as the start of an alkyne polymerization catalyzed by carbene complexes which takes place by multiple insertion into the metal – carbene carbon bond. See also: T. J. Katz, S. J. Lee, *J. Am. Chem. Soc.* **1980**, *102*, 422 – 424. However, as one referee has commented, it has not been confirmed whether or not the products **4** and **5** are formed in a sequence of double insertion of the arylethyne, [2+1] cycloaddition of the carbene to an arylethyne, and a subsequent transformation of the thus formed hexatrienylcyclopropene. However, an appropriate mechanism is not obvious.

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