5-Methylene-2-cyclopentenones as New Formal [2 + 2 + 1] Cycloadducts from [2-(Dibenzylamino)ethenyl]carbenechromium Complexes and Alkynes

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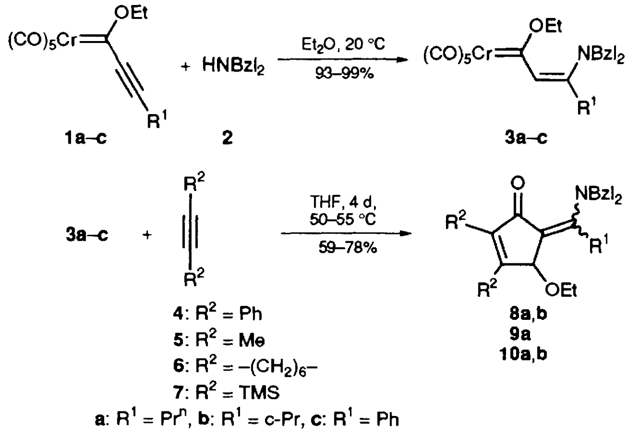
2-Alkylsubstituted pentacarbonyl{[2-(dibenzylamino)ethenyl]ethoxycarbene}chromium complexes **3a,b** react with diphenylethyne **4**, but-2-yne **5**, or cyclooctyne **6** to give 5-(dibenzylaminomethylene)-4-ethoxy-2-cyclopentenones **8a,b**, **9a**, **10a**, and **10b** in good yields (59–78%).

Cycloadditions of α,β-unsaturated Fischer carbenechromium complexes with alkynes are the best investigated and most outstanding reactions of these compounds.[1] A wide range of ethenyl alkoxycarbene complexes forms six-membered rings in [3 + 2 + 1] cycloadditions with alkynes and one inserted carbonyl ligand.[1,2] Chromium complexes with amino substituents at the carbene centre or the terminal vinylic position react with alkynes to give a totally different range of products. Benzo- or furano-fused, respectively, five-membered rings are obtained in formal [3 + 2] cycloadditions from aminoarylcarbenechromium complexes.[3] [2-(Dimethylamino)ethenyl]-ethoxycarbenechromium complexes give cyclopentadienes,[4] and fulvenes[5] in [3 + 2] or cyclopenta[*b*]pyrans[6] in formal [3 + 2 + 2 + 1] cycloadditions with monosubstituted alkynes. It is noteworthy that each of these products contains the C-1 to C-3 carbon chain of the carbene ligand in the ring. Because of their various reaction modes, the easily prepared[7,8] [2-(amino)ethenyl]ethoxycarbenechromium complexes are attractive starting materials in cycloadditions with alkynes, and we here report yet another unprecedent reaction mode.

As reported before,[8] [2-(dibenzylamino)ethenyl]ethoxycarbene complexes **3a–c** were prepared in almost quantitative yield by addition of dibenzylamine **2** to the alkynylcarbenechromium complexes **1a–c** (Scheme 1, Table 1). When **3a** was treated with diphenylethyne **4** in THF at 50–55 °C for 4 d, a yellow oil was isolated as the main product by column chromatography. The mass spectrum of this compound indicated that the carbene ligand, one molecule of **4**, and one carbonyl ligand were involved. NMR spectral data[†] revealed the product to be a mixture of two isomers, a fact which was incompatible with any of the above-mentioned known products. Finally, crystals suitable for X-ray diffraction were obtained by slowly evaporating a solution of the product in diethyl ether/hexane. The crystal structure analysis[‡] disclosed the product as 5-(dibenzylaminomethylene)-4-ethoxy-2-cyclopentenone (*Z*)-**8a** (Fig. 1).



Scheme 1 For detailed yields see Table 1

The reactions of **3a** with but-2-yne **5** and cyclooctyne **6** proceeded even more smoothly. The 2,3-dimethyl derivative **9a** and the bicyclo[6.3.0]undec-1^8-en-9-one **10a** were obtained in 78 and 75% yield, respectively, after heating the corresponding substrate mixtures for 4 d (Table 1). Bistrimethylsilylethyne **7** did not react with **3a**, 84% of the starting materials was recovered even after heating for 10 d. The cyclopropyl derivative **3b** gave **8b** and **10b** in 59 and 62% yield, whereas the phenyl counterpart **3c** did not afford any so far identified products in its reaction with **4**. In each case, the *Z*-configurated cyclopentenone was the main isomer (Table 1), and the cyclopropyl substituted derivative **8b** was solely obtained as the *Z*-isomer, according to the ^1H NMR spectra.

Mechanistically the formation of **8a,b 9a**, **10a** and **10b** probably proceeds by insertion of the alkyne followed by insertion of a carbonyl ligand with formation of the coordinated butadienylketene **12** just as in the well established Dötz reaction.[2] With the dibenzylamino substituent, however, C-5 in **12** should be rather nucleophilic as usual for enamines and could attack C-1, which results in cyclisation to give **13**. A

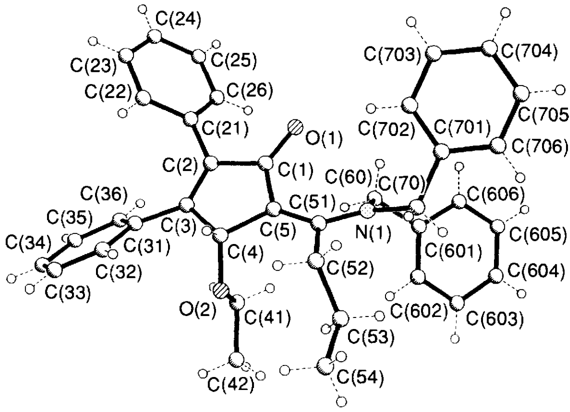
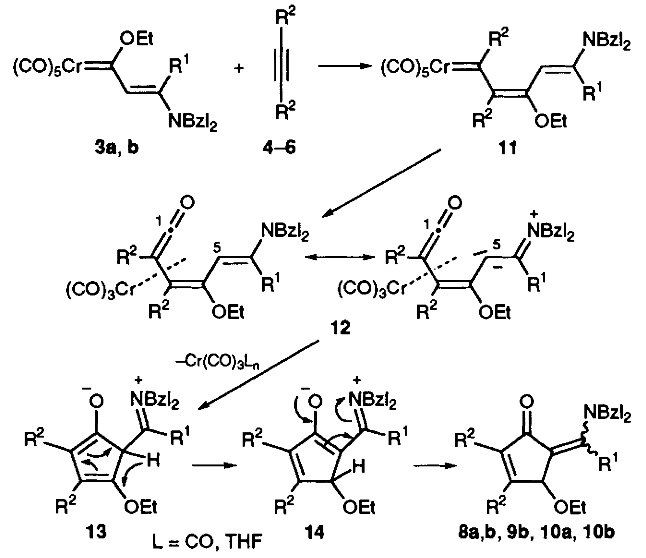


Fig. 1 Structure of (*Z*)-**8a** in the crystal[‡]

Table 1 Reaction of [2-(dibenzylamino)ethenyl]ethoxycarbene complexes **3a–c** with alkynes **4**, **5** and **6**

Starting material (% Yield)	R^1	Alkyne	R^2	Product[§]	*Z*-isomer (%)[a]	Yield (%)
3 (95)	Pr^n	**4**	Ph	**8a**	75	68
		5	Me	**9a**	64	78
		6	$-(CH_2)_6-$	**10a**	67	75
		7	$SiMe_3$	—	—	0[b]
3b (93)	c-Pr	**4**	Ph	**8b**	>95	59
		6	$-(CH_2)_6-$	**10b**	90	62
3c (99)[8]	Ph	**4**	Ph	—	—	0

[a] Established on the basis of ^1H NMR spectra; [b] 84% of starting material was recovered after 10 d.



Scheme 2

subsequent [1,5]-hydride-shift as known to be facile in cyclopentadienes,[9] would lead to **14** which is the zwitterionic form of the products **8a**,**b** **9a**, **10a** and **10b**.

This is the first case of a formal [2 + 2 + 1] cycloaddition¶ of α,β-unsaturated Fischer carbene complexes with alkynes, in which the cyclisation eventually occurs between the original carbon atoms C-1 and C-2. The resulting 5-methylene-2-cyclopentenones of types **8a**,**b**, **9a**, **10a** and **10b**, because of their highly functionalized nature, may be attractive materials for organic synthesis. They contain two Michael systems, an enamine and an allyl ether group.

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Footnotes

† IR (neat): ν 3062 cm^{-1}, 2969, 2928, 2871, 1647, 1541, 1452, 1316, 1217, 1089, 1063, 732, 699.—^1H NMR (500 MHz, C_6D_6): (*Z*)–**9a**: δ 0.82 (t, ^3J 7.0 Hz, 3 H, $CH_2CH_2C\mathit{H}_3$), 1.12 (t, ^3J 7.0 Hz, 3 H, $OCH_2C\mathit{H}_3$), 1.53 (m_c, 2 H, $CH_2C\mathit{H}_2CH_3$), 1.72 (s, 3 H, 2-CH_3), 1.89 (s, 3 H, 3-CH_3), 2.29 (ddd, ^2J 15.0, ^3J 12.0, ^3J 5.0 Hz, 1 H, $C\mathit{H}_2CH_2CH_3$), 2.57 (ddd, ^2J = 15.0, ^3J = 12.0, ^3J = 5.0 Hz, 1 H, $C\mathit{H}_2CH_2CH_3$), 2.85 (dq, 1 H, ^2J 9.0, ^3J 7.0 Hz, $OC\mathit{H}_2CH_3$), 3.08 (dq, 1 H, ^2J 9.0, ^3J 7.0 Hz, $OC\mathit{H}_2CH_3$), 4.42 [d, ^2J 15.7 Hz, 2 H, $N(CH_2Ph)_2$], 4.71 [d, ^2J 15.7 Hz, 2 H, $N(CH_2Ph)_2$], 4.90 (s, 1 H, 4-H), 6.96–7.24 (m, 10 H, Ph-H).—(*E*)-**9a**: δ = 0.82 (t, ^3J 7.0 Hz, 3 H, $CH_2CH_2C\mathit{H}_3$), 1.09 (t, ^3J 7.0 Hz, 3 H, $OCH_2C\mathit{H}_3$), 1.55 (s, 3 H, 2-CH_3), 1.69 (m_c, 1 H, $CH_2C\mathit{H}_2CH_3$), 1.80 (s, 3 H, 3-CH_3), 1.91 (m_c, 1 H, $CH_2C\mathit{H}_2CH_3$), 2.89 (dq, 1 H, ^2J 9.0, ^3J 7.0 Hz, $OC\mathit{H}_2CH_3$), 3.02 (m_c, 1 H, $C\mathit{H}_2CH_2CH_3$), 3.33 (dq, 1 H, ^2J 9.0, ^3J 7.0 Hz, $OC\mathit{H}_2CH_2$), 3.87 (m_c, 1 H, $C\mathit{H}_2CH_2CH_3$), 3.95 [d, ^2J 17.0 Hz, 2 H, $N(CH_2Ph)_2$], 4.97 (s, 1 H, 4-H), 5.17 [d, ^2J = 17.0 Hz, 2 H, $N(CH_2Ph)_2$], 6.96–7.24 (m, 10 H, Ph-H).—^{13}C NMR (50.3 MHz, C_6D_6, plus APT): (*Z*)-**9a**: δ 8.87 (+, CH_3), 12.64, 14.62, 15.99 (+, $CH_2CH_2\mathit{C}H_3$, CH_3, $OCH_2\mathit{C}H_3$), 22.29 (−, $CH_2\mathit{C}H_2CH_3$), 34.57 (−, $\mathit{C}H_2CH_2CH_3$), 54.02, 56.60 [−, $N(CH_2Ph)_2$, $O\mathit{C}H_2CH_3$], 80.82 (+, C-4), 108.10 (−, C-2), 127.49, 127.52, 127.84, 128.00, 128.83 (C-Ph), 138.78 (−, C-5), 141.35, 152.63 (−, C-3, *C*NCH_2), 189.23 (−, C-1).—(*E*)-**9a**: δ 8.77 (+, CH_3), 12.42, 14.62, 15.76 (+, $CH_2CH_2\mathit{C}H_3$, CH_3, $OCH_2\mathit{C}H_3$), 23.53 (−, $CH_2\mathit{C}H_2CH_3$), 31.37 (−, $\mathit{C}H_2CH_2CH_3$), 55.78, 56.50 [−, $N(CH_2Ph)_2$, $O\mathit{C}H_2CH_3$], 80.09 (+, C-4), 103.00 (−, C-2), 126.89, 127.45, 128.30, 128.48, 128.98 (C-Ph), 138.95 (−, C-5), 140.83, 150.98 (−, C-3, *C*NCH_2), 193.52 (−, C-1).—MS (70 eV), *m/z* (%): 374 (23) [$M^+–C_2H_5$], 312 (100) [$M^+–C_7H_7$], 266(12), 238(4), 176(8), 136(20), 91(67) [$C_7H_7^+$].

‡ *Crystal data* for (*Z*)-**8a**: monoclinic, space group $P2_1$, $Z = 2$, a = 955.50(10), b = 1088.0(4), c = 1488.7(2) pm, β = 100.790(10°), V = 1.5203(6) nm^3, D_c = 1.153 Mg m^{-3}; 1933 observed (1893 unique) reflections with 7.40 ⩽ 2θ ⩽ 45°, Mo-Kα, R = 0.0378. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ All new compounds were fully characterized by spectroscopic methods (^1H NMR, ^{13}C NMR, IR, MS) and molecular formulas were confirmed by high resolution mass spectrometry. This assignment of *E*/*Z*-diastereoisomers is based on NOESY NMR measurements for compounds **8a** and **9a**.

¶ The formation of furans from Fischer carbene complexes[10] has also been designated as a [2 + 2 + 1] cycloaddition, but the rings of these products contain two atoms of the alkyne, both of a carbonyl ligand, and only the former carbene carbon.

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