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2-Acyl-3-morpholino-2-cyclopentenones from (1-Ethoxy-3-morpholino-alkenylidene)pentacarbonylchromium Complexes and Alkynes

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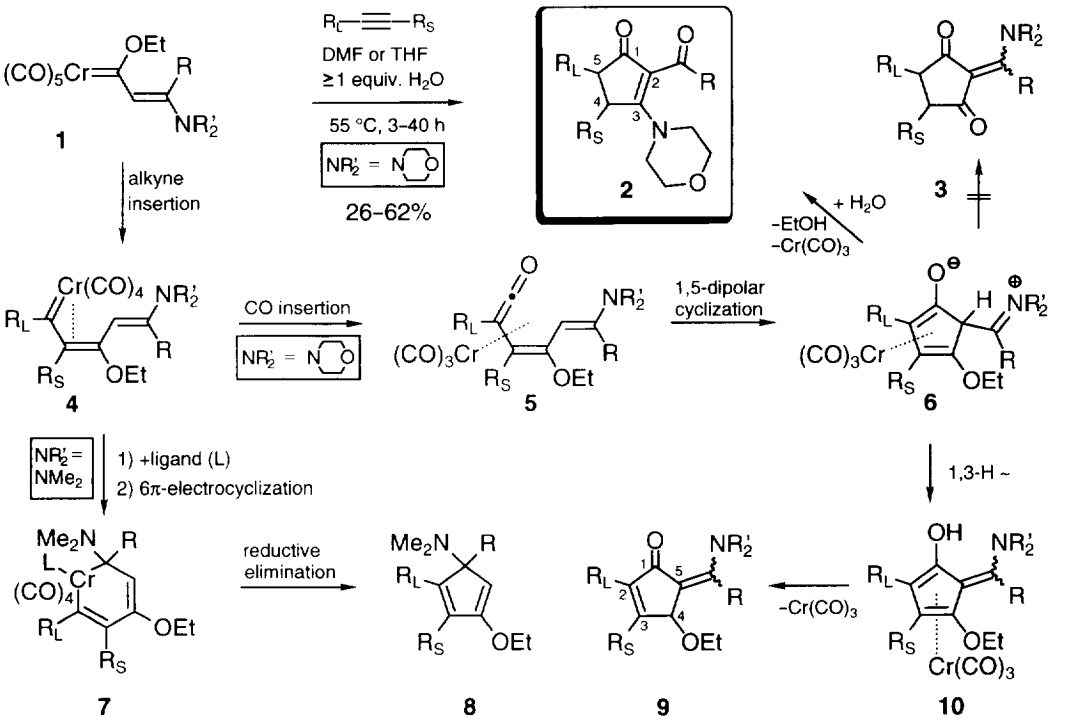
Abstract: (1-Ethoxy-3-morpholinoalkenylidene)pentacarbonylchromium complexes **1** react with terminal alkynes in DMF or THF in the presence of water to give 2-acyl-3-morpholino-2-cyclopentenones **2** in moderate to good yields (26–62%).

The template assemblies of carbene, carbonyl, and alkynyl ligands that result from reactions of carbene-pentacarbonylchromium complexes (Fischer carbenes) and alkynes offer remarkably efficient approaches to complex cyclic and polycyclic structures from simple, readily accessible starting materials.[1] The immediate product of these reactions is often a chromium π-complex, which is activated to undergo further transformations and manipulations.[2] The cycloaddition profile of (3-amino-1-ethoxyalkenylidene)pentacarbonylchromium complexes **1**[3] with alkynes[4] is quite different from that of other α,β-unsaturated carbene complexes without a β-amino substituent. The two major reaction modes of (*E*)-configurated complexes **1** are the formal [3+2]- with terminal alkynes, and [2+2+1]-cycloaddition with internal alkynes giving rise to cyclopentadienes **8**[4b] and 5-methylene-2-cyclopentenones **9**, respectively.[4d] We have now found that the [2+2+1]-cycloaddition can also take place between (1-ethoxy-3-morpholinoalkenylidene)pentacarbonylchromium complexes **1** and terminal alkynes and is followed by an interesting transformation to give 2-acyl-3-morpholino-2-cyclopentenones **2**.

A recently conducted exhaustive study directed at delineating between the reaction conditions and substituent requirements of the two major reaction modes of complexes of type **1** in order to establish each as a general cyclopentanellation procedure,[5] revealed that reactions of (1-ethoxy-3-morpholinoalkenylidene)-pentacarbonylchromium complexes of type **1a-c** with alkynes most often give exclusively the [2+2+1]-cycloadduct of type **9** as exemplified by the reaction of **1a** with 1-pentyne in anhydrous THF at 80 °C to give **9a** (entry 1, Table 1). However, when this reaction was conducted in DMF at 55 °C (entry 2, Table 1) neither the expected [2+2+1]-cycloadduct **9a** nor any of the other previously observed cycloadducts were obtained, rather a considerable amount of a single new product was isolated. The presence of a new carbonyl resonance in the ^{13}C NMR, the absence of ethyl group resonances in the ^{1}H NMR spectrum and the relative molecular mass of the product as well as some other spectral features initially led to the deduction of **3a** as the new structure. One doubtful aspect of this assignment was that only one set of resonances each in the ^{13}C and ^{1}H NMR spectrum was observed both at 25 °C and at –90 °C despite the expectation of both *E* and *Z* isomers of **3a** just as observed for compound **9a**.[6] A suspected involvement of water in the reaction was confirmed when an identical product was obtained in 1% aqueous THF (entry 3, Table 1).

Despite the uncertainties about the structural assignment of this new product a series of analogous derivatives was prepared by reacting three different complexes **1a,b,c** with a number of alkynes in either the same moist DMF at 55 °C or in 1% aqueous THF at 80 °C in a sealed vessel (entries 4-11). The only noticeable difference between the two conditions was that the higher reaction temperature substantially reduced the reaction time. Eventually, the cycloadduct of **1b** and *t*-butylacetylene (entry 6, Table 1) gave a suitable crystal for an X-ray structure analysis which revealed it as **2b-*t*Bu** (Fig. 1).[7] This structural assignment was consistent



Scheme 1. Compound **1**–**6**, **9**: **a**: NR'_2 = N⌀O, R = *n*Pr; **b**: NR'_2 = N⌀O, R = Ph; **c**: NR'_2 = N⌀O, R = $(CH_2)_3$OTBDMS. For further details see Table 1.

with the ^1H and ^{13}C NMR spectra of all other derivatives and the absence of *E,Z* isomers as compounds **2** have an endocyclic double bond.

All of the related 2-acyl-3-morpholino-2-cyclopentenones **2** were obtained in moderate to good yields (26–62%, Table 1). The reactions of **1a** and **1b** with *t*-butyldimethylsilylacetylene are particularly interesting as they give α-silylketones **2a,b-TBDMS** that neither rearrange to the corresponding silyl enol ethers[8] nor protodesilylate under the aqueous reaction conditions (entries 8, 9, Table 1). These reactions of complexes **1**, however, may be limited to terminal alkynes since **1a** and 3-hexyne under these conditions did not give any isolable product.

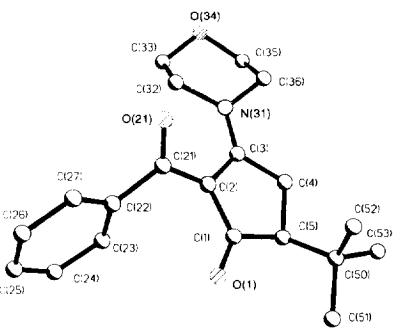
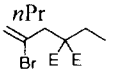


Fig. 1. Molecular structure of 2-benzoyl-5-*t*-butyl-3-morpholinyl-2-cyclopentenone **2b-*t*Bu** in the crystal.[7] Radii are arbitrary.

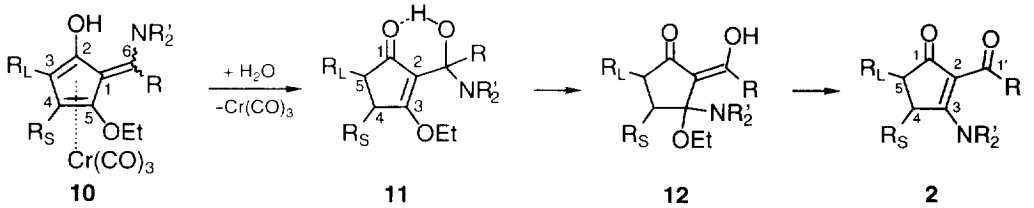
The [2+2+1]-cycloadditions of complexes **1** with alkynes to yield the 5-(aminomethylene)-2-cyclopenten-1-ones **9**[4d] probably follow a mechanism which is analogous to that previously proposed by Rudler et al.[2] for the cycloaddition of 1-aminoalkylidene complexes with alkynes to give pyrrolidinones. The intermediate vinyl-

Table 1. Reactions of (1-ethoxy-3-morpholinoalkenylidene)pentacarbonylchromium complexes **1a-c** with alkynes

Entry	Starting Complex	Alkyne R_L	Alkyne R_S	Equiv. of Alkyne	Solvent	Conditions[a]	Time [h]	Product	Yield (%)[b]
1	**1a**	*n*Pr	H	4	THF	A	3	**9a-*n*Pr**	56[c]
2	**1a**	*n*Pr	H	6	DMF	B	36	**2a-*n*Pr**	52
3	**1a**	*n*Pr	H	4	THF	C	3	**2a-*n*Pr**	54
4	**1a**	*t*Bu	H	3	THF	C	3	**2a-*t*Bu**	51
5	**1a**	*t*Bu	H	6	DMF	B	36	**2a-*t*Bu**	30
6	**1b**	*t*Bu	H	6	DMF	B	36	**2b-*t*Bu**	54
7	**1b**	*n*Pr	H	6	DMF	B	45	**2b-*n*Pr**	39
8	**1a**	TBDMS	H	3	THF	C	20	**2a-TBDMS**	62
9	**1b**	TBDMS	H	3	THF	C	12	**2b-TBDMS**	48
10	**1c**	*n*Pr	H	4	THF	C	3	**2c-*n*Pr**	50
11	**1a**		H	3	THF	C	7	**2a-E,E**	26[d]
12	**1a**	*n*Pr	H	3	THF	A/C	3	**9a-*n*Pr**	54[e]

[a] A: To a solution of the complex in anhydrous THF in a thick-walled pyrex bottle with a screw cap, 3–4 equivalents of alkyne was added and the sealed bottle heated at 80 °C until the consumption of complex was complete according to TLC (~3 h). – B: As in A except that the reaction was performed in moist DMF at 55 °C in the presence of 6 equivalents of alkyne. – C: As in A except that the reaction was performed in 1% aqueous THF. – [b] Isolated after column chromatography. – [c] Plus 13% of 3-ethoxy-2-(1'-morpholino-1'-butenyl)-5-*n*-propyl-2-cyclopentenone, see footnote 9. – [d] E = CO_2Et. – [e] Plus 10% **2a-*n*Pr**, see note c and footnote 9.

ketene complexes **5** resulting from consecutive alkyne and CO insertion do not undergo closure to a six-membered ring as in the Dötz reaction,[1a,10] but to a zwitterionic five-membered ring intermediate **6** due to their 1,5-dipolarity. A 1,3-proton shift can lead to a 1-hydroxy-6-aminofulvene complex **10**, and loss of the $Cr(CO)_3$ fragment leads to compounds **9**, on the other hand 1,4-addition of H_2O to **10** and loss of the $Cr(CO)_3$ fragment would then give **11**. Migration of the amino group from the exocyclic to the endocyclic 3-position to yield **12** most probably proceeds intermolecularly, as a cross-over experiment with a 1:1 mixture of the two complexes **1b**/**1d** and 1-pentyne gave a mixture (~30% yield) of all four possible 2-acyl-3-amino-2-cyclopentenones of type **2**. The latter must have eventually formed from intermediates **12** by 1,4-elimination of ethanol.



Scheme 2

In order to establish that the formation of **2** occurs by interception of an intermediate *en route* to **9** and not by a subsequent reaction of **9** with water, the reaction of **1a** with 1-pentyne in anhydrous THF was repeated, and after consumption of the starting complex **1a** was complete, 1% of water was added to the reaction mixture, and this mixture was stirred at 80 °C for another 3 h (entry 12, Table 1). No conversion of **9a-*n*Pr** to **2** was observed.[9] This corroborates that in the formation of **2**, the addition of water must occur before the $Cr(CO)_3$ group is irreversibly displaced from **10**.

This new method for the preparation of 2-acyl-3-(dialkylamino)-2-cyclopentenones **2** complements that of Herndon et al.[11] comprising a reaction of cyclopropylcarbenechromium complexes with alkynes and *in situ* reduction to give 3-alkoxy-2-cyclopentenones.

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Experimental

All operations were performed under nitrogen. Diethyl ether and THF were dried by distillation from sodium or potassium/benzophenone. Column chromatography was performed on deactivated alumina. – ^{1}H NMR: Bruker AM 250 (250 MHz). – ^{13}C NMR: Bruker AM 250 (62.9 MHz), multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer) measurements. Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual solvent signals. – IR: Bruker IFS 66, Perkin-Elmer 298. – MS: Varian MAT CH 7, MAT 731. – HRMS: Varian MAT 311 A. – Melting points: Büchi 510, uncorrected. – Elemental analysis: Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Georg-August-Universität Göttingen. – Molecular composition and bulk purity were determined by microanalyses for representative examples of new compounds, for all others molecular masses were confirmed by high resolution mass spectrometry with preselected ion peak matching at R » 10000 to be within ±2 ppm of the exact masses.

General Procedure 1 (GP 1, Conditions B in Table 1) for Cycloadditions in Moist DMF: Alkyne (3.0 mmol) is added to a solution of complex **1** (0.5 mmol) in moist DMF (> 1 equiv. H_2O) (10 ml) in a screw cap pyrex bottle. The sealed bottle is heated to 55 °C (external temperature) for 40 h after which time the starting complex **1** is completely consumed according to TLC. After cooling to room temperature the solution is concentrated under vacuum and the residue is chromatographed on neutral alumina (II) eluting sequentially with pentane/CH_2Cl_2 (4:1), Et_2O, Et_2O/MeOH (100:1) to give **2**.

General Procedure 2 (GP 2, Conditions C in Table 1) for Cycloadditions in 1% Aqueous THF: Complex **1** (0.50 mmol) is reacted with alkyne (1.5–2.0 mmol) in a similar manner as described in GP 1 to give **2**, except that the reaction is conducted in 1% aqueous THF at 80 °C (3–20 h).

Pentacarbonyl[(2*E*)-1-ethoxy-3-morpholino-2-hexen-1-ylidene]chromium (**1a**): To a solution of pentacarbonyl(1-ethoxy-2-hexyn-1-ylidene)chromium (1.00 g, 3.16 mmol) in 20 ml of diethyl ether was added morpholine (0.28 g, 3.21 mmol). After 10 min the solvent was removed under vacuum. Washing the residue with 5 ml of methanol at 0 °C afforded **1a** (1.21 g, 95%) as orange crystals (m.p. 93 °C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00 (bs, 3 H, 6-H), 1.55 (bs, 5 H, OCH_2CH_3, 5-H), 2.62 (bs, 2 H, 4-H), 3.49 [bs, 4 H, $N(CH_2)_2$], 3.83 [bs, 4 H, $O(CH_2)_2$] 4.76 (bs, 2 H, OCH_2CH_3), 6.48 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.03 (+, OCH_2CH_3, $CH_2CH_2CH_3$), 21.74 (–, $CH_2CH_2CH_3$), 32.71 (–, $CH_2CH_2CH_3$), 47.48 [–, $N(CH_2)_2$], 66.38 [–, $O(CH_2)_2$], 74.18 (–, OCH_2CH_3), 118.33 (+, C-2), 157.34 (C_{quat}, C-3), 218.99, 224.15 (C_{quat}, C=O), 306.92 (C_{quat}, C-1). – IR (KBr): ν = 2962 cm^{-1}, 2928, 2045 (C=O), 1913 (C=O), 1724, 1510, 1437, 1117, 1027, 927, 660, 618. – Anal. Calcd for $C_{17}H_{21}CrNO_7$ (403.4): C 50.62, H 5.25, N 3.47; found: C 50.78, H 5.23, N 3.61.

Pentacarbonyl[(2*E*)-1-ethoxy-3-morpholino-3-phenylpropenylidene]chromium (**1b**): To a solution of pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)chromium (2.77 g, 7.91 mmol) in 30 ml of diethyl ether was added morpholine (0.69 g, 7.92 mmol). After 30 min the solvent was removed under vacuum. Washing the residue with 8 ml of methanol at 0 °C afforded **1b** (3.21 g, 93%) as orange crystals (m.p. 103 °C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.55 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 3.26 [bs, 4 H, $N(CH_2)_2$], 3.67 [bs, 4 H, $O(CH_2)_2$], 4.16 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 6.58 (s, 1 H, 2-H), 7.06–7.19 (m, 2 H, Ph-H), 7.32–7.35 (m, 3 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.84 (+, OCH_2CH_3), 48.76 [–, $N(CH_2)_2$], 66.40 [–, $O(CH_2)_2$], 73.50 (–, OCH_2CH_3), 119.57 (+, C-2), 128.32, 128.72, 129.10 (+, C-Ph), 136.71 (C_{quat}, C-Ph), 154.31 (C_{quat}, C-3), 218.72, 224.19 (C_{quat}, C=O), 301.71 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 437 (4) [M$^+$], 409 (5) [M$^+$ – CO], 381 (4) [M$^+$ – 2 CO], 353 (31) [M$^+$ – 3 CO], 297 (100) [M$^+$ – 5 CO], 241 (36), 155 (17), 52 (12) [Cr$^+$]. – Anal. Calcd for $C_{20}H_{19}CrNO_7$ (437.4): C 54.92, H 4.38; found: C 55.11, H 4.36.

Pentacarbonyl[(2*E*)-1-ethoxy-3-morpholino-6-(*tert*-butyldimethylsilyloxy)-2-hexen-1-ylidene]chromium (**1c**): *n*-Butyllithium (10 mmol, 2.3 M in hexane) was added to a solution of 5-(*tert*-butyldimethylsilyloxy)-1-pentyne (1.98 g, 10 mmol) in diethyl ether (50 ml) at –78 °C, and the solution was warmed to 0 °C. Hexacarbonylchromium (2.20 g,10 mmol) and THF (30 ml) were added and the reaction mixture was stirred at room temperature for 3 h, during which it turned to a clear bright yellow solution. Triethyloxonium tetrafluoroborate (2.09 g, 11 mmol) was added in several portions with vigorous stirring at 0 °C over 3 min, the

solution immediately turned red-brown and was then allowed to warm up to room temperature. After 15 min at room temperature, morpholine (1.13 g, 13 mmol) was added dropwise over 2 min to give a dark red solution. The reaction mixture was transferred to a separatory funnel, diluted with diethyl ether (50 ml), washed three times with water (200 ml) and the organic phase dried over magnesium sulfate. Solvents were removed under vacuum without heating and the crude material chromatographed on neutral alumina (I) eluting sequentially with pentane, pentane/CH_2Cl_2 (20 : 1), pentane/CH_2Cl_2 (1 : 1), and CH_2Cl_2 to give **1c** (4.27 g, 80%) as yellow crystals (m.p. 89–90 °C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.06 [s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $SiC(CH_3)_3$], 1.49 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.54 (m, 2 H, 5-H), 2.81 (m, 2 H, 4-H), 3.58 [bt, ^3J = 6.5 Hz, 4 H, $N(CH_2)_2$], 3.63 (t, ^3J = 7.0 Hz, 2 H, 6-H), 3.76 [bt, ^3J = 7.1 Hz, 4 H, $O(CH_2)_2$], 4.76 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 6.50 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.46 [$Si(CH_3)_2$], 15.56 (OCH_2CH_3), 18.18 [$SiC(CH_3)_3$], 25.87 [$SiC(CH_3)_3$], 27.48 (C-5), 31.50 (C-4), 47.47 [$N(CH_2)_2$], 62.03 (C-6), 66.42 [$O(CH_2)_2$], 74.13 (OCH_2CH_3), 118.48 (C-2), 157.57 (C-3), 219.05, 224.09 (C=O), 294.22 (C-1). – IR (KBr): ν = 2923 cm^{-1}, 2854, 2043, 1916 (C=O), 1889, 1508. – Anal. Calcd for $C_{23}H_{35}CrNO_8Si$ (533.6): C 51.77, H 6.61, N 2.62; found: C 51.74, H 6.51, N 2.70.

4-Ethoxy-2-*n*-propyl-5-(1'-morpholinobutylidene)-2-cyclopentenone (9a-*n*Pr) and 2-Butyryl-3-morpholino-5-*n*-propyl-2-cyclopentenone (2a-*n*Pr): Complex **1a** (178 mg, 0.44 mmol) and 1-pentyne (120 mg, 1.76 mmol) were treated in accordance with GP 2 except that the reaction was performed in anhydrous THF (8.0 ml, conditions A, Table 1) for 3 h to give **9a-*n*Pr** (76 mg, 56%, as a mixture of *E* and *Z* isomers) and **2a-*n*Pr** (16 mg, 13%) as tan oils after chromatography (**2a-*n*Pr** results from hydrolysis of the initially formed cycloadduct **13a-*n*-Pr**, identified in the ^{1}H NMR spectrum of the crude mixture, upon chromatography).[9] The same reaction was repeated with complex **1a** (178 mg, 0.44 mmol) and 1-pentyne (120 mg, 1.76 mmol), except that, after complete consumption of **1a** according to TLC, 1% water was added, and the reaction mixture heated at 80 °C for an additional 3 h (conditions A/C, Table 1), formation of **2a-*n*Pr** at the expense of 3-ethoxy-2-(1'-morpholino-1'-butenyl)-5-*n*-propyl-2-cyclopentenone was observed in the ^{1}H NMR spectrum of the crude mixture.[9] Purification yielded **9a-*n*Pr** (73 mg, 54%) and **2a-*n*Pr** (12 mg, 10%). ***E/Z*-9a-*n*Pr**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70–0.90 (m, 6 H, 2 × *n*Pr-CH_3), 0.95–1.20 (m, 3 H, OCH_2CH_3), 1.40–1.60 (m, 4 H, 2 × *n*Pr-CH_2CH_3), 2.12 (m, 2 H, $CH_2CH_2CH_3$), 2.22, 2.58 (2 × m, 2 H, 2'-H), 3.20–4.00 (m, 10 H, OCH_2CH_3, morpholino-CH_2), 4.92, 5.13 (2 × s, 1 H, 4-H), 6.62, 6.67 (2 × s, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.78, 13.86, 14.21 (2 × *n*Pr-CH_3), 15.60, 15.75 (OCH_2CH_3), 20.60, 20.66, 21.88, 22.63 (2 × CH_2CH_3), 27.19, 27.42 ($CH_2CH_2CH_3$), 30.07, 33.88 (C-2'), 48.41, 51.37 [$N(CH_2)_2$], 58.08, 60.69 [$O(CH_2)_2$], 67.12, 67.27 (OCH_2CH_3), 78.77 (C-4), 106.64, 106.69 (C-5), 140.31, 141.04 (C-2), 150.24, 150.38 (C-3), 160.28, 160.45 (C-1'), 188.34, 193.78 (C-1). – IR (film): ν = 3023 cm^{-1}, 2809, 1658, 1599, 1493, 1399. – MS (70 eV), *m/z* (%): 307 (5) [M^-], 278 (20) [$M^+ - CH_2CH_3$], 262 (35) [$M^+ - OCH_2CH_3$], 250 (15), 84 (100). – Anal. Calcd for $C_{18}H_{29}NO_3$ (307.4): C 70.32, H 9.51, N 4.56; found: C 70.37, H 9.75, N 4.63.

2a-*n*Pr: Variant A: A solution of complex **1a** (380 mg, 0.942 mmol) and 1-pentyne (386 mg, 5.67 mmol) in moist DMF (9.4 ml) was reacted according to GP 1 for 36 h. Purification yielded **2a-*n*Pr** (137 mg, 52%) as a yellow oil. – Variant B: A solution of Complex **1a** (194 mg, 0.48 mmol) and 1 pentyne (131 mg, 1.92 mmol) in THF (9.5 ml) containing 1% of water was reacted according to GP 2 to give **2a-*n*Pr** (72 mg, 54%) as a slightly yellow oil after chromatography. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 6.9 Hz, 6 H, 2 × $CH_2CH_2CH_3$), 1.31 (bs, 3 H, $CH_2CH_2CH_3$), 1.51 (m_c, 2 H, $CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 1.76 (bs, 1 H, $CH_2CH_2CH_3$), 2.25 (d, ^2J = 16.5 Hz, 1 H, 4-H), 2.39 (bs, 1 H, 5-H), 2.78 (dd, ^2J = 16.5, $^3J_{cis}$ = 8.1 Hz, 1 H, 4-H), 2.84 (t, ^3J = 8.1 Hz, 2 H, $CH_2CH_2CH_3$), 3.49 [bs, 4 H, $N(CH_2)_2$], 3.47 [bs, 4 H, $O(CH_2)_2$]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.91 (+, 2 × $CH_2CH_2CH_3$), 17.84 (–, $CH_2CH_2CH_3$), 20.47 (–, $CH_2CH_2CH_3$), 33.93 (–, $CH_2CH_2CH_3$), 34.38 (–, $CH_2CH_2CH_3$), 44.29 (+, C-5), 44.73 (–, C-4), 45.30 [–, $N(CH_2)_2$], 66.43 [–, $O(CH_2)_2$], 112.72 (C_{quat}, C-2), 175.72 (C_{quat}, C-3), 199.93, 202.54 (C_{quat}, C-1, C=O). – IR (film): ν = 2957 cm^{-1}, 2871 (C–H), 1639 (C=O), 1366, 1087, 973, 895, 824, 732. – MS (70 eV), *m/z* (%): 279 (38) [M^+], 250 (23) [$M^+ - C_2H_5$], 236 (60), 208 (17), 84 (100), 47 (8). – $C_{16}H_{25}NO_3$: calcd 279.1834 (correct HRMS). – Anal. Calcd for $C_{16}H_{25}NO_3$ (279.4): C 68.79, H 9.02; found: C 68.26, H 8.92.

5-*tert*-Butyl-2-butyryl-3-morpholino-2-cyclopentenone (2a-*t*Bu): Variant A: A solution of complex **1a** (200 mg, 0.496 mmol) and *tert*-butylethyne (245 mg, 2.98 mmol) in moist DMF (4.9 ml) was stirred in accordance with GP 1 for 36 h. Purification yielded **2a-*t*Bu** (44 mg, 30%) as a dark yellow oil. – Variant B: A solution of complex **1a** (200 mg, 0.496 mmol) and 3,3-dimethyl-1-butyne (122 mg, 1.49 mmol) in 5.0 ml of THF containing 1% of water was treated in accordance with GP 2 for 3 h. Purification yielded **2a-*t*Bu** (74 mg, 51%) as a dark yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 0.99 [s, 9 H, $C(CH_3)_3$], 1.56 (tq, ^3J = 7.4, ^3J = 7.4 Hz, 2 H, $CH_2CH_2CH_3$), 2.27 (dd, $^3J_{trans}$ = 4.1, $^3J_{cis}$ = 8.1 Hz, 1 H, 5-H), 2.41 (dd, ^2J = 16.5, $^3J_{trans}$ = 4.1 Hz, 1 H, 4-H), 2.65 (dd, ^2J = 16.5, $^3J_{cis}$ = 8.1 Hz, 1 H, 4-H), 2.89 (t, ^3J = 7.4 Hz, 2 H, $CH_2CH_2CH_3$), 3.50 [bs, 4 H, $N(CH_2)_2$], 3.80 [bs, 4 H, $O(CH_2)_2$]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.98 (+, $CH_2CH_2CH_3$), 17.97 (–, $CH_2CH_2CH_3$), 27.43 [+, $C(CH_3)_3$], 31.65 [C_{quat}, $C(CH_3)_3$], 33.26 (–, $CH_2CH_2CH_3$), 44.93 (–, C-4), 45.47 [–, $N(CH_2)_2$], 53.87 (+, C-5), 66.57 [–, $O(CH_2)_2$], 114.42 (C_{quat}, C-2), 175.15 (C_{quat}, C-3), 200.17, 201.36 (C_{quat}, C-1, C=O). – IR (film): ν = 2959 cm^{-1}, 2869, 1634 (C=O), 1550, 1446, 1394, 1366, 1283, 1066, 1027, 961, 899. – MS (70 eV), *m/z* (%): 293 (4) [M^+], 273 (10), 267 (28), 251 (6) [$M^+ - C_3H_6$], 212 (6), 176 (7), 84 (100), 57 (7), 47 (12). – $C_{17}H_{27}NO_3$: calcd. 293.1990 (correct HRMS).

2-Benzoyl-5-*tert*-butyl-3-morpholino-2-cyclopentenone (2b-*t*Bu): A solution of complex **1b** (200 mg, 0.457 mmol) and 3,3-dimethyl-1-butyne (225 mg, 2.74 mmol) in moist DMF (4.6 ml) was stirred in accordance with GP 1 at 55 °C for 36 h. Purification yielded **2b-*t*Bu** (81 mg, 54%) as colorless crystals (m.p. 142 °C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.01 [s, 9 H, $C(CH_3)_3$], 2.36 (dd, $^3J_{trans}$ = 3.9, $^3J_{cis}$ = 7.9 Hz, 1 H, 5-H), 2.50 (dd, ^2J = 16.7, $^3J_{trans}$ = 3.9 Hz, 1 H, 4-H), 2.76 (dd, ^2J = 16.7, $^3J_{cis}$ = 7.9 Hz, 1 H, 4-H), 3.40 [bs, 4 H, $N(CH_2)_2$], 3.73 [bs, 4 H, $O(CH_2)_2$], 7.18–7.88 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 27.44 [+, $C(CH_3)_3$], 31.47 [C_{quat}, $C(CH_3)_3$], 33.20 (–, C-4), 49.55 [–, $N(CH_2)_2$], 53.77 (+, C-5), 66.17 [–, $O(CH_2)_2$], 116.80 (C_{quat}, C-2), 128.18, 129.56, 132.71 (+, C-Ph), 138.68 (C_{quat}, C-Ph), 173.21 (C_{quat}, C-3), 194.94, 200.82 (C_{quat}, C-1, COPh). – IR (KBr): ν = 2945 cm^{-1}, 2832 (C–H), 1565, 1449, 1113, 1033. – MS (70 eV), *m/z* (%): 327 (14) [M^+], 298 (22) [$M^+ - C_2H_5$], 271 (100), 216 (19), 151 (38), 105 (33), 67 (66), 41 (63). – Anal. Calcd for $C_{20}H_{25}NO_3$ (327.4): C 73.37, H 7.70; found: C 73.36, H 7.67.

Crystal Structure Analysis of 2-Benzoyl-5-*tert*-butyl-3-morpholino-2-cyclopentenone (2b-*t*Bu): Formula $C_{20}H_{25}NO_3$, molecular mass 327.41, monoclinic, space group $P2_1/c$, a = 1619.7(5), b = 917.9(3), c = 2531.1(7) pm, α = 90°, β = 108.10(2)°, γ = 90°, V = 3.577(2) nm^3, $\rho_{calcd.}$ = 1.216 Mg/m^3, μ(Mo-K_α) = 0.081 mm^{-1}, crystal dimensions 1.00 × 0.40 × 0.20 mm, 6261 unique reflections were measured with a Stoe-Siemens four-circle diffractometer and graphite-monochromated Mo-K_α radiation at 153(2) K, Θ-range: 3.56–25.00°. The structure was solved by direct methods (SHELXS-90[7b]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-93[7c]). All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were included in calculated positions and refined using a riding model. R values: $R_1 = \Sigma \mid Fo-Fc \mid / \Sigma Fo$ = 0.1233 (for $F > 4\sigma(F)$), $wR_2 = [\Sigma w(Fo^2-Fc^2)^2 / \Sigma w(Fo^2)^2]^{0.5}$ = 0.3157 (for all data) with 439 parameters and 0 restraints. Largest difference peak 1415 $e^- nm^{-3} \times 10^3$, largest difference hole –638 $e^- nm^{-3} \times 10^3$.

5-*tert*-Butyldimethylsilyl-2-butyryl-3-morpholino-2-cyclopentenone (2a-TBDMS): A solution of complex **1a** (200 mg, 0.496 mmol) and *tert*-butyldimethylsilylethyne (209 mg, 1.49 mmol) in THF (5.0 ml) containing 1% of water was treated in accordance with GP 2 for 20 h. Purification yielded **2a-TBDMS** (108 mg, 62%) as a yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = –0.08 (s, 3 H, $SiCH_3$), –0.04 (s, 3 H, $SiCH_3$), 0.85 (t, ^3J = 7.1 Hz, 3 H, $CH_2CH_2CH_3$), 0.87 [s, 9 H, $SiC(CH_3)_3$], 1.53 (tq, ^3J = 7.1, ^3J = 7.1 Hz, 2 H, $CH_2CH_2CH_3$), 2.20 (d, $^3J_{cis}$ = 8.1 Hz, 1 H, 5-H), 2.53 (d, ^2J = 16.8 Hz, 1 H, 4-H), 2.71–3.01 (m, 3 H, $CH_2CH_2CH_3$, 4-H), 3.32 [bs, 2 H, $N(CH_2)_2$], 3.48 [bs, 2 H, $N(CH_2)_2$], 3.72 [bs, 4 H, $O(CH_2)_2$]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –7.34 (+, $SiCH_3$), –6.60 (+, $SiCH_3$), 13.84 (+, $CH_2CH_2CH_3$), 17.60 (–, $CH_2CH_2CH_3$), 17.82 [C_{quat}, $SiC(CH_3)_3$], 26.77 [+, $SiC(CH_3)_3$], 31.37 (–, $CH_2CH_2CH_3$), 36.07 (+, C-5), 44.48 (–, C-4), 45.21 [–, $N(CH_2)_2$], 66.40 [–, $O(CH_2)_2$], 113.74 (C_{quat}, C-2), 176.07 (C_{quat}, C-3), 199.49, 202.14 (C_{quat}, C-1, C=O). – IR (film): ν = 2957 cm^{-1}, 2857 (C–H), 1628 (C=O), 1390, 1066, 949, 938, 823, 638. – MS (70 eV), *m/z* (%): 351 (6) [M^+], 322 (13) [$M^+ - C_2H_5$], 238 (100), 205 (17), 182 (22), 139 (63), 75 (79), 57 (20). – $C_{19}H_{33}NO_3Si$: calcd. 351.2229 (correct HRMS).

2-Benzoyl-5-*tert*-butyldimethylsilyl-3-morpholino-2-cyclopentenone (2b-TBDMS): A solution of complex **1b** (200 mg, 0.457 mmol) and *tert*-butyldimethylsilylethyne (209 mg, 1.49 mmol) in THF (5.0 ml) containing 1% of water was treated in accordance with GP 2 for 12 h. Purification yielded **2b-TBDMS** (85 mg, 48%) as a yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.07 (s, 3 H, $SiCH_3$), 0.13 (s, 3 H, $SiCH_3$), 0.95 [s, 9 H, $SiC(CH_3)_3$], 2.31 (dd, $^3J_{trans}$ = 2.0, $^3J_{cis}$ = 8.0 Hz, 1 H, 5-H), 2.70 (dd, ^2J = 16.8, $^3J_{trans}$ = 2.0 Hz, 1 H, 4-H), 2.91 (dd, ^2J = 16.8, $^3J_{cis}$ = 8.0 Hz, 1 H, 4-H), 3.44 [bs, 4 H, $N(CH_2)_2$], 3.71 [bs, 4 H, $O(CH_2)_2$], 7.37–7.50 (m, 3 H, Ph-H), 7.78–7.81 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –7.27 (+, $SiCH_3$), –6.53 (+, $SiCH_3$), 17.66 [C_{quat}, $SiC(CH_3)_3$], 26.98 [+, $SiC(CH_3)_3$], 31.39 (–, C-4), 35.60 (+, C-5), 49.50 [–, $N(CH_2)_2$], 66.27 [–, $O(CH_2)_2$], 114.32 (C_{quat}, C-2), 128.12, 129.62, 132.73 (+, C-Ph), 138.73 (C_{quat}, C-Ph), 174.08 (C_{quat}, C-3), 194.76, 201.61 (C_{quat}, C-1, COPh). – IR (film): ν = 2925 cm^{-1}, 2854 (C–H), 1624, 1275, 1119, 904, 836, 666. – MS (70 eV), *m/z* (%): 385 (16) [M$^+$], 330 (10), 328 [M$^+$ – CCH_3] (100), 286 (5), 242 (3) [M$^+$ – $C(CH_3)_3$ – $N(CH_2CH_2)_2O$], 165 (2) [M$^+$ – $C(CH_3)_3$ – $N(CH_2CH_2)_2O$ – Ph], 105 (5), 75 (13), 47 (6). – $C_{22}H_{31}NO_3Si$: calcd. 385.2073 (correct HRMS).

5-Benzoyl-3-morpholino-5-propyl-2-cyclopentenone (2b-*n*Pr): A solution of complex **1b** (362 mg, 0.828 mmol) and 1-pentyne (338 mg, 4.96 mmol) in moist DMF (8.3 ml) was treated according to GP 1 for 45 h. Purification yielded **2b-*n*Pr** (101 mg, 39%) as a dark yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 1.35 (m_c, 3 H, $CH_2CH_2CH_3$, $CH_2CH_2CH_3$), 1.84 (m_c, 1 H, $CH_2CH_2CH_3$), 2.38 (dd, ^2J = 16.5, $^3J_{trans}$ = 3.5 Hz, 1 H, 4-H), 2.50 (m_c, 1 H, 5-H), 2.89 (dd, ^2J = 16.5, $^3J_{cis}$ = 7.7 Hz, 1 H, 4-H), 3.36 [bs, 4 H, $N(CH_2)_2$], 3.68 [bs, 4 H, $O(CH_2)_2$], 7.34–7.52 (m, 3 H, Ph-H), 7.77–7.80 (m, 2 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.90 (+, $CH_2CH_2CH_3$), 20.27 (–, $CH_2CH_2CH_3$), 33.87 (–, $CH_2CH_2CH_3$), 34.35 (–, C-4), 44.35 (+, C-5), 49.73 [–, $N(CH_2)_2$], 66.03 [–, $O(CH_2)_2$], 112.05 (C_{quat}, C-2), 128.07, 129.60, 132.74 (+, C-Ph), 138.32 (C_{quat}, C-Ph), 174.15 (C_{quat}, C-3), 194.54, 202.02 (C_{quat}, C-1, COPh). – IR (film): ν = 2958 cm^{-1}, 2929, 2869 (C–H), 1669 (C=O), 1624 (C=C), 1559, 1456, 1279, 1241, 1118, 924, 694. – MS (70 eV), *m/z* (%): 313 (11) [M$^+$], 284 (18) [M$^+$ – C_2H_5], 271 (100) [M$^+$ – CH_2C=O], 226 (8) [M$^+$ – $HN(CH_2CH_2)_2O$], 216 (16), 105 (26), 77 (20) [Ph$^+$]. – $C_{19}H_{23}NO_3$: calcd. 313.1677 (correct HRMS).

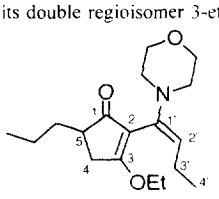
Diethyl 2-(2-Bromoallyl)-2-(3'-butyryl-4'-morpholin-4'-yl-2'-oxo-3'-cyclopentenylmethyl)malonate (2a-E,E): A solution of complex **1a** (200 mg, 0.496 mmol) and diethyl 2-(2-bromoallyl)-2-prop-2-ynylmalonate (472 mg, 1.49 mmol) in THF (5.0 ml) containing 1% of water was treated according to GP 2 for 7 h. Purification yielded **2a-E,E** (67 mg, 26%) as colorless crystals (m.p. 126 °C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 1.28 (t, ^3J = 7.2 Hz, 6 H, $CO_2CH_2CH_3$), 2.02 (m_c, 1 H, $CH_2CH_2CH_3$), 2.38–2.55 (m, 3 H, $CH_2CH_2CH_3$, 1-H), 2.69 (d, ^2J = 19.7 Hz, 1 H, 5'-H), 2.76–3.06 (m, 4 H, $CH_2CH_2CH_3$, 1'-H, 5'-H), 3.22 (s, 2 H, CH_2BrC=CH_2), 3.49 [bs, 4 H, $N(CH_2)_2$], 3.83 [bs, 4 H, $O(CH_2)_2$], 4.23 (m_c, 4 H, $COOCH_2CH_3$), 5.60 (s, 1 H, CH_2BrC=CH_2), 5.72 (s, 1 H, CH_2BrC=CH_2). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 11.86, 13.90 (+, $CH_2CH_2CH_3$, $COOCH_2CH_3$), 17.78 (–, $CH_2CH_2CH_3$), 34.71 (–, $CH_2CH_2CH_3$), 35.82 (–, C-1), 41.07 (+, C-1'), 44.46 (–, C-5', CH_2BrC=CH_2), 44.79 [–, $N(CH_2)_2$], 56.44 (C_{quat}, C-2), 61.77 [–, $O(CH_2)_2$], 66.55 (–, $COOCH_2CH_3$), 112.16 (C_{quat}, C-3'), 122.29 (–, CH_2BrC=CH_2), 126.71 (C_{quat}, CH_2BrC=CH_2), 170.67 (C_{quat}, $COOCH_2CH_3$), 175.67 (C_{quat}, C-4'), 199.71, 202.80 (C_{quat}, C-2', C=O). – IR (KBr): ν = 2955 cm^{-1}, 2926 (C–H), 1724 (C=O), 1636, 1113, 1039, 753, 618. – MS (70 eV), *m/z* (%): 529/527 (24/26) [M$^+$], 484/486 (13/10) [M$^+$ – C_3H_7], 448 (91) [M$^+$ – Br], 404 (37), 310 (100), 157 (18), 86 (35), 43 (32). – $C_{24}H_{34}BrNO_7$: calcd. 527.1518 (correct HRMS).

2-[4'-(*tert*-Butyldimethylsilyloxy)-butyryl]-3-morpholino-5-propyl-2-cyclopentenone (2c-*n*Pr): A solution complex **1c** (256 mg, 0.48 mmol) and 1-pentyne (131 mg, 1.92 mmol) in THF (9.5 ml) containing 1% of water was reacted in accordance with GP 2 to give **2c-*n*Pr** (98 mg, 50%) as a clear oil. – ^{1}H NMR (250 MHz, $CDCl_3$) δ = 0.00 [s, 6 H, $Si(CH_3)_2$], 0.83 [s, 9 H, $C(CH_3)_3$], 0.90 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.33 (m, 3 H, $HCHCH_2CH_3$), 1.78 (quint, ^3J = 7.1, ^3J = 7.1 Hz, 2 H, 3'-H), 1.81 (m, 1 H, $HCHCH_2CH_3$), 2.28 (dd, $^3J_{trans}$ = 4.5 Hz, ^2J = 16.3 Hz, 1 H, 4-H), 2.45 (m, 1 H, 5-H), 2.78 (dd, $^3J_{cis}$ = 6.1, ^2J = 16.3 Hz, 1 H, 4-H), 2.92, 2.98 (2 × t, 2 × ^3J = 6.9 Hz, 2 H, 2'-H), 3.47 [bm, 4 H, $N(CH_2)_2$], 3.61 (t, ^3J = 7.0 Hz, 2 H, 4'-H), 3.78 [bt, ^3J = 4.3 Hz, 4 H, $O(CH_2)_2$]. – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.37 [$Si(CH_3)_2$], 13.90 (CH_3), 17.89 [$SiC(CH_3)_3$], 20.27 (CH_2CH_3), 25.89 [$SiC(CH_3)_3$], 27.62 ($CH_2CH_2CH_3$), 34.00 (C-3'), 34.45 (C-4), 39.17 (C-2'), 44.33 (C-5),

49.25 [dynamically broadened s, $N(CH_2)_2$], 62.86 (C-4'), 65.70 [$O(CH_2)_2$], 112.75 (C-2), 175.62 (C-3), 199.37, 202.41 (C-1, C-1'). – IR (film): ν = 2987 cm^{-1}, 2845, 1675, 1636, 1559, 1448, 1270. – MS (70 eV), *m/z* (%): 409 (0.5) [M^+], 394 (3) [$M^+ - CH_3$], 352 (100) [$M^+ - C_4H_9$]. Anal. Calcd for $C_{22}H_{39}SiNO_4$ (409.6): C 64.51, H 9.60, N 3.42; found: C 64.58, H 9.63, N 3.52.

References and Notes

1. For reviews on the synthetic applications of Fischer carbene complexes see: (a) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587. – (b) Wulff, W. D.; Tang, P.-C.; Chan, K.-S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. – (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Transition Metal Chemistry*, University Science Books, Mill Valley, **1987**. – (d) Dötz, K. H. in *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field*; tom Diek, H.; de Meijere, A. (Eds.); Springer, Berlin, **1988**. – (e) Werner, H.; Erker, G. (Eds.), *Organometallics in Organic Synthesis 2*; Springer, Berlin, **1989**. – (f) Blystone, S. L. *Chem. Rev.* **1989**, *89*, 1663. – (g) Wulff, W. D. in *Adv. Met.-Org. Chem;* Liebeskind, L. S. (Ed.); JAI Press, Greenwich, CT, **1989**, Vol. 1, p. 209–393. – (h) Harrington, P. J. *Transition Metals in Total Synthesis*; Wiley, New York, **1990**, p. 346. – (i) Wulff, W. D. in *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I. (Eds.); Pergamon Press, Oxford, **1991**. – (j) Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381.
2. For examples see: Rudler, H.; Audouin, M.; Chelain, E.; Denise, B.; Goumont, R.; Massoud, A.; Parlier, A.; Pacreau, A.; Rudler, M.; Yefsah, R.; Alvarez, C.; Delgado-Reyes, F. *Chem. Soc. Rev.* **1991**, *20*, 503.
3. Complexes **1** are prepared in two steps from the corresponding terminal alkyne, $Cr(CO)_6$ and secondary amine, a one pot precedure was used in the preparation of **1c** (see experimental).. For the stepwise procedure see: Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051; Stein, F.; Duetsch, M.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Organometallics* **1993**, *12*, 2556.
4. (a) Duetsch, M.; Lackmann, R.; Stein, F.; de Meijere, A. *Synlett* **1991**, 324. – (b) Stein, F; Duetsch, M.; Noltemeyer, M.; de Meijere, A. *Synlett* **1993**, 486. – (c) Stein, F.; Duetsch, M; Lackmann, R.; Noltemeyer, M.; de Meijere, A. *Angew. Chem.* **1991**, *103*, 1669; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1658. – (d) Duetsch, M.; Vidoni, S.; Stein, F.; Funke, F.; Noltemeyer, M.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1679.
5. The previously reported[4a] formal [3+2]-cycloaddition to give highly substituted cyclopentadienes has indeed been generalized. Best conditions for a wide variety of starting materials **1** and alkynes were found to be performing the reaction in pyridine or by slow addition of the alkyne to a 0.05 M solution of complex **1** (R'_2 = alkyl, ≠ benzyl) in acetonitrile at 80 °C. Flynn, B. L.; Funke, F.; Duetsch, M.; Noltemeyer, M.; de Meijere, A. to be published.
6. Low temperature ^1H and ^{13}C NMR spectra of **3a** were recorded to ascertain that the room temperature spectra were not time averaged due to rapid interconversion of the *E* and *Z* isomer.
7. (a) Further details of this crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404067, the names of the authors, and the journal citation. – (b) Sheldrick G. M., *Acta Crystallogr. Sect. A*, **1990**, *46*, 467–473. (c) Sheldrick G. M., SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, **1993**.
8. *Cf.* Brook, A. G.; Bassindale, A. R. in *Rearrangements in Ground and Excited States*; de Mayo, P. (Ed.), Vol. 2, Academic Press, New York, **1980**, p. 149–227.
9. The reaction of complex **1a** with 1-pentyne in anhydrous THF (conditions A, Table 1, entry 1) gave a mixture of **9a-*n*Pr** and its double regioisomer 3-ethoxy-2-[(*E*)-1'-morpholino-1'-butenyl]-5-propyl-2-cyclopentenone. Under conditons C (Table 1) or chromatography (deactivated alumina), this compound hydrolysed with formal migration of the morpholino group, to give **2a-*n*Pr**. Addition of water to the enamine moiety in this compound gives an intermediate identical to **11a-*n*Pr**. In this work this compound was isolated as its hydrolysis product only, **2a-*n*Pr**, its formation was detected in the ^1H NMR spectrum of the crude mixture and has been subsequently isolated from a reaction selective for its formation (THF/CH_3CN, 9:1, alumina deactivated with hexamethyldisilazide). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.88 (m, 6 H, 3 H-4', $CH_2CH_2CH_3$), 1.30 (t, 3 H, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.35 (m, 1 H, $HCHCH_2CH_3$), 1.78 (m, 3 H, $HCHCH_2CH_3$, 2 × H-3'), 2.31 (dd, ^2J = 16.0, $^3J_{trans}$ = 2.0 Hz, 1 H, H-4), 2.46 (m, 1 H, H-5), 2.73 [bm, 5 H, 1 × H-4, $N(CH_2)_2$], 3.64 [t, ^3J = 2.8 Hz, 4 H, $O(CH_2)_2$], 4.40 (dynamically broadened s, 2 H, OCH_2CH_3), 4.61 (t, ^3J = 7.1 Hz, H-2'). – ^{13}C NMR (62.9 MHz, $CDCl_3$): = 13.94, 14.78, 14.34 (3 × CH_3), 20.33 ($CH_2CH_2CH_3$), 21.90 ($CH_2CH_2CH_3$), 33.90, 34.03 (C-4, C-3'), 44.50 (C-5), 48.66 [$N(CH_2)_2$], 66.10 (OCH_2CH_3), 66.94 [$O(CH_2)_2$], 109.73 (C-2'), 114.33 (C-2), 138.89 (C-1'), 153.49 (C-3), 206.27 (C-1'). – IR (film): = 3005 cm^{-1}, 2806, 1684, 1647, 1603, 1472, 1384, 1258, 1121. – MS (70 eV), *m/z* (%): 307 (12) [M^+], 278 (30) [$M^+ - C_2H_5$], 262 (17), 236 (25), 222 (100), 167 (45), 139 (40). – $C_{18}H_{29}NO_3$: calcd. 307.2147 (correct HRMS). *Cf.* Flynn, B. L.; Silveira, C. C.; de Meijere, A. *Synlett* **1995**, in press



10. (a) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9. – (b) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293. – (c) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organomet.* **1994**, *13*, 102. – (d) Harvey, D. F.; Grenzer, E. M.; Gantzel, P. K. *J. Am. Chem. Soc.* **1994**, *116*, 6719.
11. (a) Herndon J. W.; Tumer, S. U.; McMullen, L. A.; Matasi, J. J.; Schnatter W. F. K. *Adv. Met.-Org. Chem.*; Liebeskind, L. S. (Ed.); JAI Press, Greenwich CT, **1994**, *3*, 51–95. (b) Tumer, S. U.; Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1992**, *114*, 8394, and references cited therein on other organotransition-metal reagents in five-membered ring forming cycloaddition reactions.

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