CHEMISTRY
A EUROPEAN JOURNAL

An Efficient Three-Step Synthesis of Cyclopenta[*b*]pyrans via 2-Donor-Substituted Fischer Ethenylcarbenechromium Complexes

Armin de Meijere,*[a] Heiko Schirmer,[a] Frank Stein,[a] Frank Funke,[a] Michael Duetsch,[a] Yao-Ting Wu,[a] Mathias Noltemeyer,[b] Thomas Belgardt,[b] and Burkhard Knieriem[a]

Abstract: A wide range of cyclopenta[*b*]pyrans **4** has been synthesized in a one-pot reaction by treatment of different 2-donorsubstituted ethenylcarbenechromium complexes **2** with alkynes in THF in moderate to excellent yields (41–90% for 14 out of 25 examples). The starting materials **2** are readily available in good to excellent yields (76–99% for 25 out of 36 examples) by Michael addition of amines, alcohols and thiols, respectively, to the corresponding alkynylcarbenechromium complexes **1**. Due to their 10 π-electrons in a cross-conjugated bicyclic system, cyclopenta[*b*]pyrans have been termed pseudoazulenes, as they indeed have similar UV/Vis-spectroscopic properties.

Keywords: alkynes · carbenes · chromium · cycloadditions

Introduction

In recent years, Fischer carbene complexes have developed into readily accessible starting materials for the straightforward syntheses of numerous carbo- and heterocycles.[1] Depending on the substituents and reaction conditions they can be used to form hydroquinones[1b] and cyclohexadienones,[1g] cyclopentadienes,[1i,j,k] vinylcyclopropanes,[2a] cyclopentenones,[2b,c] pyrroles,[3a–d] pyridines,[3e] furans,[4a–c] γ-butyrolactones,[4d] β-lactams,[5] oxazolines,[6] phosphahydroquinones[7] as well as various azaoligocyclic systems.[8] In a preliminary communication we have previously reported the conversion of {[2-(dialkylamino)ethenyl]carbene}chromium complexes **2** to cyclopenta[*b*]pyrans **4**, in which twofold intermolecular insertion of an alkyne into the chromium–carbon double bond was observed only for the second time,[9] apart from an intramolecular example reported by Wulff et al.,[10] which led to indane derivatives. There are only a few preparative accesses to cyclopenta[*b*]pyrans **4**[11] which possess a 10π-electron system. As such, they are electronic analogues of azulene and have therefore been termed pseudoazulenes.[12] Here we report the full scope of the new synthesis of these interesting heterobicycles.

[a] Prof. Dr. A. de Meijere, H. Schirmer, F. Stein, F. Funke, M. Duetsch, Y.-T. Wu, B. Knieriem
Institut für Organische und Biomolekulare Chemie
der Georg-August-Universität Göttingen, Tammannstrasse 2
37077 Göttingen (Germany)
Fax: (+49) 551-399-475
E-mail: armin.demeijere@chemie.uni-goettingen.de

[b] M. Noltemeyer, T. Belgardt
Institut für Anorganische Chemie
der Georg-August-Universität Göttingen, Tammannstrasse 4
37077 Göttingen (Germany)

Results and Discussion

Previous results[9] indicated that increased yields of cyclopenta[*b*]pyrans were obtained from carbine-complexes **2** with more bulky substituents in the 3-position. Consequently, two possibilities to optimize the yields of formed cyclopenta[*b*]pyrans **4** were tested. On the one hand, the bulk of the substituents in the 3-position, and on the other hand the nature of the donor groups in the 1- and 3-positions of complex **2** were varied. For all these possibilities new β-donor-substituted ethenylcarbene complexes of type **2** had to be prepared, and this was readily achieved by Michael-type additions of nucleophiles to alkynylcarbene complexes **1** (see Table 1).[13]

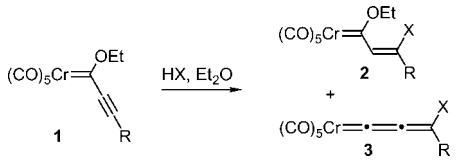
Systematic studies of the reaction conditions showed that (3-aminoallenylidene)chromium complexes of type **3** were found as by-products,[14] when secondary amines were added to the alkynylcarbene complexes. The access to the {[2-(dialkylamino)ethenyl]carbene}chromium complexes **2** was improved to give excellent yields at low temperatures (−115 to 20 °C) by exploring the temperature dependence of the ratio between the competing formation of the Michael adduct

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
DOI: 10.1002/chem.200500043

and the ethoxide elimination product.[14b] Room temperature was sufficient to give high yields of **2** (Table 1) from most of the complexes **1**. Numerous NOESY-NMR measurements indicated that the newly formed C=C double bond in most cases had (*Z*)-configuration, when R was a tertiary substituent, with the complexes **2bd**, **2bg**, **2bi**, and **2bl** being the only exceptions to the rule.

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **2ca** in a mixture of diethyl ether and hexane. This constitutes the first crystal structure analysis of a (*Z*)-configured β-donorsubstituted, α,β-unsaturated carbene complex (Figure 1). The bond lengths found for C(1)–C(2) 140.3, C(2)–C(3) 141.6 and C(3)–N(3) 132.7 pm indicate a significant delocalization of the double bond between C(1) and C(3). The interplanar angles C(1)-C(2)-C(3)-N(3) and C(1)-C(2)-C(3)-C(4) were found to be −42.1 and 140.8°, respectively.

Table 1. Reaction of (alkynylcarbene)chromium complexes **1a–k** with nucleophiles.



Starting material	R	X	*T* [°C]	Product[a]	Yield (%)	Product	Yield (%)	Ref.
1a	Ph	NMe_2	20	(*E*)-**2aa**	94	**3aa**	0	[14a, b]
1a	Ph	NBn_2	20	(*E*)-**2ab**	99	**3ab**	0	[14a, b]
1a	Ph		20	(*E*)-**2ac**	98	**3ac**	0	[14a, b]
1a	Ph		20	(*E*)-**2ad**	98	**3ad**	0	[14a, b]
1a	Ph	$N(iPr)_2$	20	(*E*)-**2ae**	44	**3ae**	53	[14a, b]
1b	CMe_2OEt	NMe_2	20	(*Z*)-**2ba**	80	**3ba**	13	[14a, b]
1b	CMe_2OEt	NBn_2	20	(*Z*)-**2bb**	23	**3bb**	74	[14a, b]
1b	CMe_2OEt		20	(*Z*)-**2bc**	30	**3bc**	64	[14a, b]
1b	CMe_2OEt		20	(*E*/*Z*)-**2bd**	92	**3bd**	0	[14a]
1c	CMe_2OSiMe_3	NMe_2	20	(*Z*)-**2ca**	87	**3ca**	12	[14b]
1c	CMe_2OSiMe_3	NBn_2	20	(*Z*)-**2cb**	41	**3cb**	59	new
1c	CMe_2OSiMe_3	NBn_2	−78	(*Z*)-**2cb**	91	**3cb**	4	new
1c	CMe_2OSiMe_3	NEt_2	20	(*Z*)-**2cf**	60	**3cf**	38	new
1d		NMe_2	20	(*Z*)-**2da**	85	**3da**	13	[14a]
1d		NBn_2	20	(*Z*)-**2 db**	53	**3 db**	45	[14b]
1e		NMe_2	20	(*Z*)-**2ea**	97	**3ea**	0	new
1f	$CHMe(OSitBuPh_2)$	NMe_2	20	(*E*)-**2fa**	95	**3fa**	3	new
1f	$CHMe(OSitBuPh_2)$	NBn_2	20	(*E*)-**2fb**	72	**3fb**	14	new
1g	$CHMe(OSitBuMe_2)$	NMe_2	20	(*E*)-**2ga**	96	**3ga**	0	new
1g	$CHMe(OSitBuMe_2)$	NBn_2	20	(*E*)-**2gb**	82	**3gb**	13	new
1h	$CHMe(OSiMe_3)$	NMe_2	20	(*E*)-**2ha**	98	**3ha**	0	new
1h	$CHMe(OSiMe_3)$	NBn_2	20	(*E*)-**2hb**	79	**3hb**	17	new
1h	$CHMe(OSiMe_3)$	NBn_2	−78	(*E*)-**2hb**	91	**3hb**	4	new
1i		NMe_2	20	(*Z*)-**2ia**	92	**3ia**	0	new
1i		NBn_2	−115	(*Z*)-**2ib**	88	**3ib**	0	new
1j	adamantyl	NMe_2	20	(*Z*)-**2ja**	90	**3ja**	0	[16b]
1j	adamantyl	NBn_2	20	(*Z*)-**2jb**	72	**3jb**	0	[16b]
1k	*t*Bu	NMe_2	20	(*Z*)-**2ka**	63	**3ka**	8	[8]
1b	CMe_2OEt	OEt	20	(*Z*)-**2bg**	76	**3bg**	0	[14a]
1b	CMe_2OEt	OPh	20	(*Z*)-**2bh**	91[b,c]	**3bh**	0	[14a]
1b	CMe_2OEt	OBn	20	(*E*/*Z*)-**2bi**	99[b]	**3bi**	0	new
1b	CMe_2OEt	O-*p*$NO_2C_6H_4$	20	**2bj**	0	**3bj**	0	new
1b	CMe_2OEt	O-*p*FC_6H_4	20	(*Z*)-**2bk**	98	**3bk**	0	new
1b	CMe_2OEt	SPh	20	(*E*/*Z*)-**2bl**	98[c]	**3bl**	0	[14a]
1b	CMe_2OEt	S-*p*$NO_2C_6H_4$	20	(*Z*)-**2bm**	17[d]	**3bm**	0	new
1b	CMe_2OEt	SEt	20	(*Z*)-**2bn**	93	**3bn**	0	new

[a] (*E*/*Z*) ratio established on the basis of NOESY NMR measurements. [b] The products **2bh**, **2bi** were obtained only—yet within 5 s—when the reaction was carried out with 2 equiv of the alcohol in the presence of 0.1 equiv of the corresponding sodium alkoxide. [c] Ratio 5:1. [d] In addition to (*Z*)-**2bm**, tetracarbonyl[(1,4-diethoxy-4-methylpentyn-1-ylidene)-4-nitrothiophenol-*S*)chromium was isolated in 7% yield.

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

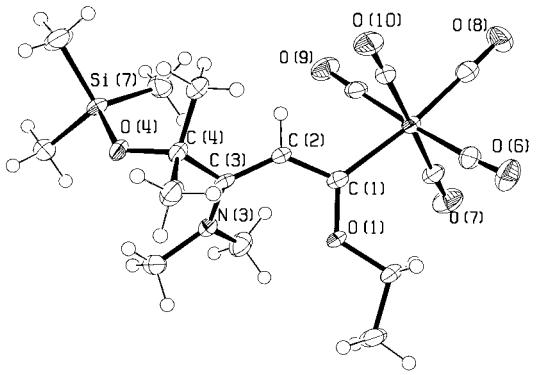


Figure 1. Structure of **2ca** in the crystal.[15]

The adamantyl-substituted complexes **2ja** and **2jb** were isolated in a four-step, single-pot operation directly from adamantylethyne.[16]

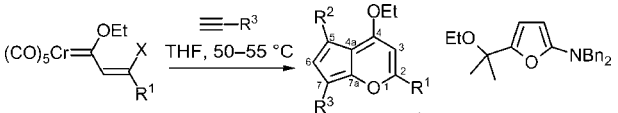
The aryloxy- and benzyloxyethenylcarbene complexes were obtained by reaction of the complexes **1** with a catalytic amount of sodium phenoxide and benzyloxide dissolved in phenol and benzyl alcohol, respectively.[14a] Whereas **2bh** was obtained as the pure (*Z*)-diastereomer as indicated by NOE measurements, **2bi** was a 5:1 mixture of (*E*)- and (*Z*)-diastereomers. The additions of arylthiols and alkylthiols to pentacarbonyl(1,4-diethoxy-4-methyl-2-pentyn-1-ylidene)chromium (**1b**) were performed in the same manner. A mixture of the diastereomeric adducts (*E*)- and (*Z*)-**2bl** (ratio 5:1) was also isolated in the case of added thiophenol.

Upon treatment of the complex **2da** with phenylethyne, a purple color appeared, and after the usual work-up, none of the expected 3-ethoxy-5-dimethylaminocyclopentadiene,[1i,j,l,16b] but a completely new type of product was isolated. The mass spectrum disclosed that this product must have been formed after incorporation of two molecules of the alkyne, and the molecular structure was eventually established as the cyclopenta[*b*]pyran **4d**-Ph by X-ray diffractometry.[9] After optimization of the conditions, that is, mainly by using a fourfold excess of phenylethyne, **4d**-Ph was accessible in 41% yield.

After this observation, a whole series of complexes of type **2** was treated with phenylethyne and 1-pentyne. In all cases, the correspondingly substituted cyclopenta[*b*]pyrans of type **4** were isolated in yields ranging from 5 to 90% (Table 2).

In several cases, the yields were higher when the starting material **2** contained a dibenzylamino or a diallylamino rather than a dimethylamino group (compare entries 1 with 2 and 3, 8 with 9, 18 with 19), but this is not a general trend (compare entries 14 with 15, 23 with 24). The highest yields of products **4** were obtained from starting materials **2** with the most bulky substituents R^1 at the alkenyl terminus, and phenylethyne as the alkyne. The record yield of 90% was reached for **4c**-Ph from pentacarbonyl(2*Z*)-3-dimethylamino-1-ethoxy-4-methyl-4-(trimethylsilyloxy)-2-penten-1-ylidene]chromium (**2ca**) (Table 2, entry 14). The diallylamino-substituted complexes **2ac** and **2bc** were observed to partly

Table 2. Cocyclizations of (*E*)- and [(*Z*)-2-(dialkylamino)ethenyl]carbenechromium complexes **2**, phenylethyne or 1-pentyne to yield cyclopenta[*b*]pyrans **4**-R^2.



2a–e,j,k-X **4a–e,j,k-R^2** **5**

Entry	Starting material	R^1	X	R^2	Product	Yield (%)	Ref.
1	**2aa**	Ph	NMe_2	Ph	**4a**-Ph	24	[9]
2	**2ab**	Ph	NBn_2	Ph	**4a**-Ph	48	
3	**2ac**	Ph	$N(\sim\!\!\sim)_2$	Ph	**4a**-Ph	43	
4	**2ad**	Ph	N⟨ ⟩	Ph	**4a**-Ph	5	
5	**2ae**	Ph	$N(iPr)_2$	Ph	**4a**-Ph	17	
6	**2aa**	Ph	NMe_2	*n*Pr	**4a**-*n*Pr	19	[9]
7	**2ae**	Ph	$N(iPr)_2$	*n*Pr	**4a**-*n*Pr	11	
8	**2ba**	CMe_2OEt	NMe_2	Ph	**4b**-Ph	51	
9	**2bb**	CMe_2OEt	NBn_2	Ph	**4b**-Ph	68	
10	**2bc**	CMe_2OEt	$N(\sim\!\!\sim)_2$	Ph	**4b**-Ph	42	
11	**2bd**	CMe_2OEt	N⟨ ⟩	Ph	**4b**-Ph	7	
12	**2ba**	CMe_2OEt	NMe_2	*n*Pr	**4b**-*n*Pr	59	[9]
13	**2bb**	CMe_2OEt	NBn_2	*n*Pr	**4b**-*n*Pr	23[a]	
14	**2ca**	CMe_2OSiMe_3	NMe_2	Ph	**4c**-Ph	90	
15	**2cb**	CMe_2OSiMe_3	NBn_2	Ph	**4c**-Ph	78	
16	**2cf**	CMe_2OSiMe_3	NEt_2	Ph	**4c**-Ph	87	
17	**2cf**	CMe_2OSiMe_3	NEt_2	*n*Pr	**4c**-*n*Pr	25	
18	**2da**		NMe_2	Ph	**4d**-Ph	41	[9]
19	**2db**		NBn_2	Ph	**4d**-Ph	47	
20	**2da**		NMe_2	*n*Pr	**4d**-*n*Pr	33	[9]
21	**2ea**		NMe_2	Ph	**4e**-Ph	84	
22	**2ea**		NMe_2	*n*Pr	**4e**-*n*Pr	5	
23	**2ja**	adamantyl	NMe_2	Ph	**4j**-Ph	56	
24	**2jb**	adamantyl	NBn_2	Ph	**4j**-Ph	47	
25	**2ka**	*t*Bu	NMe_2	Ph	**4k**-Ph	52	[9]
26	**2ka**	*t*Bu	NMe_2	*n*Pr	**4k**-*n*Pr	43	[9]

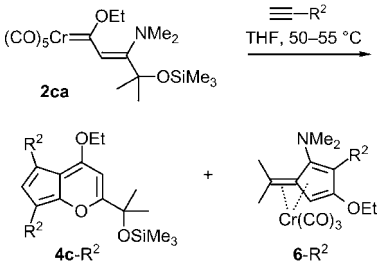
[a] In addition to **4b**-*n*Pr, 2-dibenzylamino-5-(1′-ethoxy-1′-methylethyl)furan (**5**) was isolated in 50% yield.

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

decompose before they reacted. The (ethoxyisopropyl)-substituted complex **2bb** upon treatment with 1-pentyne gave 2-dibenzylamino-5-(1′-ethoxy-1′-methylethyl)furan (**5**) as an interesting product in 50% yield in addition to the expected cyclopenta[*b*]pyran **4b**-*n*Pr (23%).

Another interesting second product was isolated in 38% yield from the reaction of (trimethylsilyloxyisopropyl)-substituted complex **2ca** with 1-pentyne and was identified by X-ray diffraction as the tricarbonyl(fulvene)chromium complex **6**-*n*Pr.[17] Analogous reactions of **2ca** with propyne and cyclopropylethyne (Table 3) also gave the corresponding fulvene complexes **6**-Me and **6**-*c*Pr (7 and 14%, respectively), but the cyclopenta[*b*]pyrans **4c**-Me and **4c**-*c*Pr, respectively, were obtained as the main products.

Table 3. Reactions of **2ca** with propyne, 1-pentyne, and cyclopropylethyne.



R^2	**4c**-R^2 (%)	**6**-R^2 (%)
Me	18	7
*n*Pr	21	38
*c*Pr	20	14

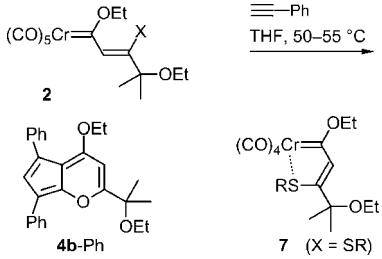
Cyclopenta[*b*]pyrans **4** were not only obtained from 2-dialkylaminoethenylcarbenechromium complexes, but also from 2-alkoxyethenyl-substituted analogues. Thus, **2bg** reacted with phenylethyne to give **4b**-Ph in 27% yield. Hence a series of 2-organyloxyethenyl- and of 2-organylthioethenyl-substituted complexes of type **2b** was tested for the reaction with phenylethyne.

All of them except **2bm** did indeed provide the cyclopenta[*b*]pyran **4b**-Ph, albeit in low yields (18–37%) (Table 4). With the *p*-fluorophenyloxy substituent in **2bk** constituting a better leaving group at a later stage, the yield of the cyclopenta[*b*]pyran **4b**-Ph was highest (37%).

The phenylthio- **2bl** and ethylthio-substituted complex **2bn** also gave the cyclopenta[*b*]pyran **4b**-Ph in 23 and 27% yield, respectively, whereas the *p*-nitrophenylthio-substituted complex **2bm** yielded only decomposition products. In the reaction of **2bl** and **2bn**, the chelated complexes **7l** and **7n** were obtained as major products (Table 4). In principle, these chelates would be expected to undergo cocyclizations with alkynes as well, as had been demonstrated for the dialkylamino-substituted analogues in the synthesis of 5-dialkylamino-3-ethoxycyclopentadienes.[18]

It is also noteworthy that (3-trialkylsilyloxy)butenylcarbenechromium complexes of type **2** upon reaction with alkynes not only gave the 5,7-disubstituted cyclopenta[*b*]pyrans **4c**,**f**,**g**,**h**-R^2, but also the 5,6-disubstituted regioisomers **8c**,**f**,**g**,**h**-R^2 in low yields (see Table 5). It is remarkable that complex **2fb** gave a total of 96% of the two isomers **4f**-Ph and **8f**-Ph in its reaction with phenylethyne in contrast to its dimethylamino counterpart **2fa** providing a total yield of only 41%. This indicates once more that dibenzylamino-substituted complexes **2** usually give the highest yields of cyclopenta[*b*]pyrans. Likewise, these results confirm that ethenylcarbene complexes **2** with bulky substituents in the 2-position like the *tert*-butyldiphenylsilyloxy-substituted ones consistently give higher yields than those with the less bulky substituents like the *tert*-butyldimethylsilyloxy-substituted complexes. The trimethylsilyloxy-substituted complex **2hb** did not afford any of the normal product **4h**-Ph, but only **8h**-Ph. Whereas pentacarbonyl[(2*Z*)-3-dibenzylamino-1-ethoxy-3-(2′-methyldioxolan-2′-yl)propenylidene]chromium (**2ib**) gave a high total yield (81%) of both regioisomeric cyclopenta[*b*]pyrans **4i**-Ph and **8i**-Ph, **2ia** afforded only **4i**-Ph in 56% yield (Table 5).

Table 4. Reactions of **2b**-X with phenylethyne.



Starting material	X	Yield of **4b**-Ph (%)	Second product	Yield of **7** (%)
2bg	OEt	27	–	–
2bh	OPh	28	–	–
2bi	OBn	18	–	–
2bk	OC_6H_4-4-F	37	–	–
2bl	SPh	23	**7l**	69
2bm	SC_6H_4-4-NO_2	0	**7m**	0
2bn	SEt	27	**7n**	55[a]

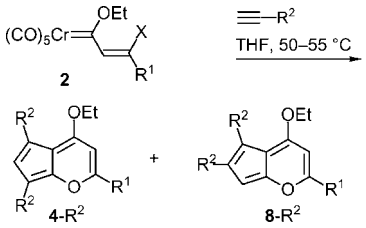
[a] In addition to **4b**-Ph and **7n**, ethyl 4-ethoxy-3-ethylthio-4-methylpentenoate was isolated in 9% yield.

Crystals of the regioisomer **4i**-Ph, suitable for X-ray diffraction, were grown and subjected to a structure analysis in order to prove the regiochemistry, as both isomers had rather similar spectroscopic data. The structure analysis of **4i**-Ph (Figure 2) disclosed virtually planar rings (0.3 pm deviation from planarity for the five-membered ring, and 0.6 pm deviation for the six-membered ring). The interplanar angle between the two rings was found to be 1.9°.

Finally, the influence of the nature of the donor group in the 1-position of the starting complexes was examined. Instead of alkoxy(2-aminoethenyl)carbene complexes **2**, dimethylamino(2-dibenzylaminoethenyl)carbene complexes **9b**[14b] and **9c** were cocyclized with phenylethyne. The starting materials were synthesized by 1,2-addition of dimethylamine (Scheme 1) to the 3-dibenzylaminoallenylidenechromium complexes **3bb** and **3cb**, respectively, in excellent yields in close analogy to protocols by Fischer et al. and Berke

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 5. Cocyclizations of **2c**, **f**–**i**-X with phenylethyne and 1-propyne.



Starting material	R^1	X	R^2	Product	Yield (%)	Product	Yield (%)
2cb	CMe_2OSiMe_3	NBn_2	*n*Pr	**4c**-*n*Pr	0	**8c**-*n*Pr	16[a]
2fa	$CHMe(OSitBuPh_2)$	NMe_2	Ph	**4f**-Ph	39	**8f**-Ph	2
2fb	$CHMe(OSitBuPh_2)$	NBn_2	Ph	**4f**-Ph	74	**8f**-Ph	22
2fa	$CHMe(OSitBuPh_2)$	NMe_2	*n*Pr	**4f**-*n*Pr	13	**8f**-*n*Pr	0
2fb	$CHMe(OSitBuPh_2)$	NBn_2	*n*Pr	**4f**-*n*Pr	23	**8f**-*n*Pr	0
2ga	$CHMe(OSitBuMe_2)$	NMe_2	Ph	**4g**-Ph	27	**8g**-Ph	14
2gb	$CHMe(OSitBuMe_2)$	NBn_2	Ph	**4g**-Ph	41	**8g**-Ph	23
2gb	$CHMe(OSitBuMe_2)$	NBn_2	*n*Pr	**4g**-*n*Pr	11	**8g**-*n*Pr	0
2hb	$CHMe(OSiMe_3)$	NBn_2	Ph	**4h**-Ph	0	**8h**-Ph	21
2ia		NMe_2	Ph	**4i**-Ph	56	**8i**-Ph	0
2ib		NBn_2	Ph	**4i**-Ph	44	**8i**-Ph	37

[a] In addition to **8c**-*n*Pr, 6-dibenzylamino-4-ethoxy-7-oxa-1-oxo-2-*n*-propyl-6-[1′-methyl-1′-(trimethylsilyloxy)ethyl-2,4-cycloheptadiene was isolated in 9% yield.

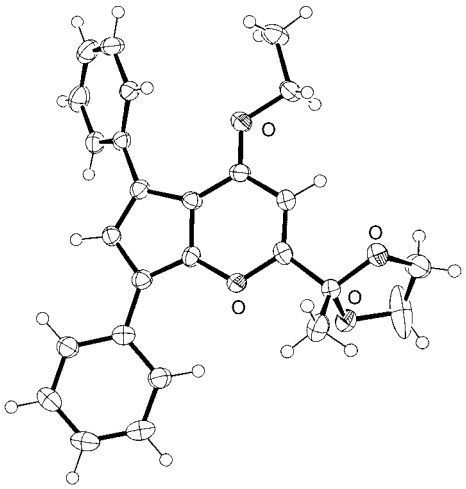
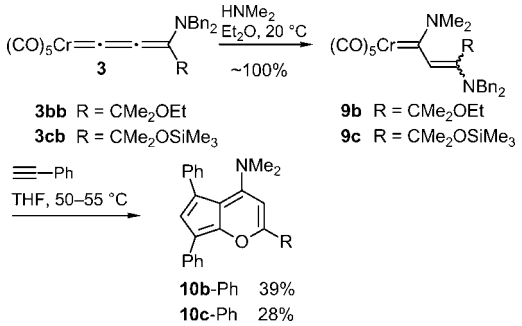


Figure 2. Structure of **4i**-Ph in the crystal.[15]

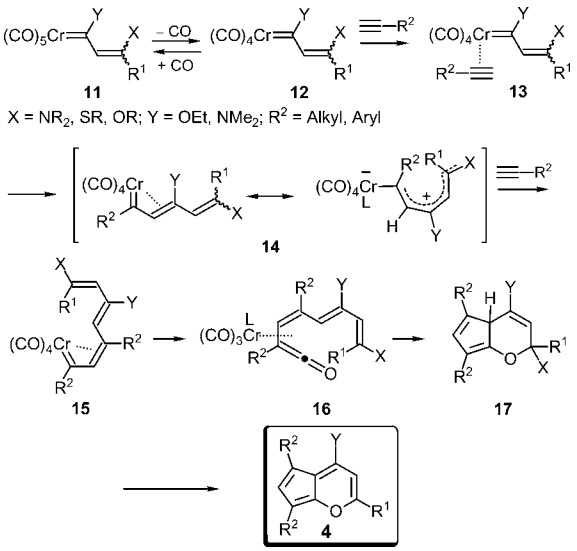


Scheme 1.

et al.[19] These α,β-unsaturated complexes **9b**,**c** were identified as mixtures of (*E*)- and (*Z*)-diastereomers with the (*E*)-isomers predominating.

The reaction of dimethylamino(2-dibenzylaminoethenyl)carbene complexes **9b** and **9c** with phenylethyne afforded the 4-dimethylaminocyclopenta[*b*]pyrans **10b**-Ph and **10c**-Ph in moderate yields. Surprisingly, even from the trimethylsilyloxyisopropyl-substituted complex **9c** the 5,7-disubstituted cyclopenta[*b*]pyran **10c**-Ph was isolated exclusively (28%).

As for the mechanism of the cyclopenta[*b*]pyran formation, the reaction certainly starts with the loss of a carbonyl ligand to form **12**, followed by alkyne insertion, which in this case must lead to the (*Z*)-configured complex **14**, since with the (*E*)-configuration subsequent 6π-electrocyclization (with[20] or without CO insertion) would take place. A second alkyne insertion apparently follows which presumably gives a 1-chroma-(2*Z*,4*Z*)-octatetraene **15**. Insertion of CO must ensue to form the dienyl-substituted alkenylketene complex **16** which, by subsequent intramolecular [4+2] cycloaddition, can give the dihydrocyclopenta[*b*]pyran **17**. The cyclopenta[*b*]pyran **4** finally results by 1,4-elimination of HX ($HNMe_2$ in the case of the leaving group NMe_2) (Scheme 2).

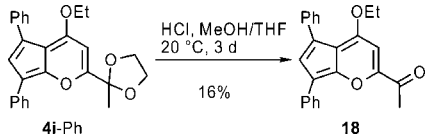


Scheme 2. Proposed mechanism for the formation of cyclopenta[*b*]pyrans **4** (for the definition of R^1 see Table 2).

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

This rationalization does not include the formation of the regioisomeric cyclopenta[*b*]pyrans **8**-R. However, the phenomenon of an apparently "wrong" insertion of an alkyne into the chromium–carbene double bond has been observed lately,[16b,21] and has been attributed to steric factors. The bulky substituent on the alkyne would be too close to the *cis*-positioned CO ligand on chromium. According to this hypothesis, the first alkyne would insert with the "normal" regiochemistry in all cases. The cyclization products, resulting from an inverse insertion of the second alkyne, were isolated even as major products in some cases, which has never been observed for single insertions. This is understandable, as the second alkyne does not insert into a Fischer-type, but into a Schrock-type carbene complex which has completely different electronic features. This and a different steric environment may explain the formation of the observed regioisomers. However, it is not at all understood, why both regioisomers were isolated only for some examples and not for all of them.

In order to be able to widen the spectrum of accessible cyclopenta[*b*]pyrans with respect to types of substituents, the possibility of liberating the ethylene acetal-protected ketone moiety in **4i**-Ph was examined. It turned out that the **4i**-Ph is extraordinarily stable under a variety of conditions that usually lead to clean acetal cleavage. Eventually, the acetyl-substituted cyclopenta[*b*]pyran **18** was obtained in 16% yield after treatment of **4i**-Ph with 5% hydrochloric acid in methanol/tetrahydrofuran for 3 d. Obviously, the stability of the acetal in **4i**-Ph stems from the fact that the positive charge in the protonated species is delocalized over the cyclopenta[*b*]pyran moiety. It is conceivable that a dimethyl acetal corresponding to **4i**-Ph would be hydrolyzed to **18** more readily and with better yields.



Conclusion

This new three-step synthesis of cyclopenta[*b*]pyrans from easily prepared starting materials is superior to previously developed accesses to such so-called pseudoazulenes. Further studies, examining the recently found fluorescence anomaly as well as dual fluorescence of this type of compounds are in progress and will be published separately.

Experimental Section

General methods: All operations were performed under nitrogen. Solvents were dried by distillation from sodium or potassium/benzophenone. ^{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: Finnigan MAT 95, MAT 731. HRMS: Finnigan MAT 731. Melting points: Büchi 510 melting point apparatus, values are uncorrected. Elemental analysis: Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen. Molecular composition and bulk purity were determined by microanalysis for representative examples of new compounds, for all others molecular masses were confirmed by high-resolution mass spectrometry with preselected ion peak matching at $R \approx 10000$ to be within 2 ppm of the exact masses.

General procedure for the preparation of pentacarbonyl[3′-(dialkylamino)-, [3′-(aryloxy)-, [3′-(benzyloxy)-, [3′-(arylthio)-, and [3′-(alkylthio)-propenyl]carbenechromium complexes (2) from pentacarbonyl(1-ethoxy-2-alkynylidene)chromium complexes (1) (GP 1): To a stirred solution of complex **1** (10 mmol) in Et_2O (50 mL) was added dropwise (liquid amines) or by bubbling (gaseous amines) at 20 °C the respective amine until the starting material could not be detected any more by thin-layer chromatography (TLC). When phenols, thiophenols or thiols were used as nucleophiles, 10 mmol of the complex **1** was dissolved in 50 mL of Et_2O/ethanol (1:1). After the nucleophile (20 mmol) had been added dropwise to this solution, the mixture was added to 5 mol% of a solution of the corresponding sodium phenolate or thiolate in Et_2O/ethanol (1:1), respectively. The reaction mixture was stirred at ambient temperature until the starting material could not be detected any more by TLC. It was then neutralized by addition of a saturated ammonium chloride solution, and the aqueous phase was extracted with Et_2O (3×25 mL). The solvents were removed under reduced pressure, and the residue was purified by chromatography on silica gel to afford the pure complex.

General procedure for the preparation of cyclopenta[*b*]pyrans (4) (GP 2): A 25 mL thick-walled Pyrex bottle with a screw cap equipped with a magnetic stirring bar was charged with a solution of an ethenylcarbenechromium complex **2** or **9** (1.00 mmol) and an alkyne (8.00 mmol) in THF (20 mL). The mixture was then heated at 55 °C until no complex **2** or **9** could be detected by TLC. After cooling to ambient temperature, the reaction mixture was filtered. The solvents were removed under reduced pressure, and the residue was purified by chromatography on silica gel.

Pentacarbonyl[1-ethoxy-3-(1′-chlorocyclopropyl)-2-propyn-1-ylidene]-chromium (1e): *Variant A*: To 1-chloro-1-(trichloroethenyl)cyclopropane[22] (4.12 g, 20.0 mmol) in Et_2O (100 mL) was added at −78 °C methyllithium (25.0 mL, 1.60 N in Et_2O, 40.0 mmol), and the solution was stirred at the same temperature for 30 min and at 20 °C for an additional 1 h. Then, hexacarbonylchromium (4.40 g, 20.0 mmol) was added to the solution at 0 °C, and the mixture was stirred at the same temperature for 1 h. It was diluted with THF (15 mL) and stirred at 0 °C for 13 h and at 20 °C for 3 h. Triethyloxonium tetrafluoroborate (4.75 g, 25.0 mmol) was added to the orange solution. After stirring at 0 °C for an additional 30 min and at 20 °C for 3 h, the dark-red solution was filtered over Celite, and the solvent was removed under reduced pressure. The residue was purified by chromatography [150 g silica gel, elution with pentane] to give **1e** ($R_f=0.44$) as a dark-red oil (1.60 g, 23%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=1.52$ (t, $^3J=7.0$ Hz, 3H, OCH_2CH_3), 1.71–1.80 (m, 4H, *c*Pr-H), 4.63 (q, $^3J=7.0$ Hz, 2H, OCH_2CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): $\delta=14.9$ (+, OCH_2CH_3), 23.7 (−, *c*Pr-C), 28.0 (C_{quat}, *c*Pr-C), 76.5 (−, OCH_2CH_3), 85.6 (C_{quat}, C-2), 140.1 (C_{quat}, C-3), 216.0, 224.9 (C_{quat}, C=O), 312.6 (C_{quat}, C-1); IR (film): $\tilde{\nu}=2980$, 2940, 2144 (C≡C), 2058 (C=O), 1945 (C=O), 1420, 1368 cm^{-1}; MS (70 eV): *m*/*z* (%): 350/348 (17/37) [M^+], 294/292 (9/23) [M^+-2CO], 266/264 (4/20) [M^+-3CO], 238/236 (2/8) [M^+-4CO], 210/208 (38/100) [M^+-5CO], 182/180 (11/25) [M^+-5CO$-C_2H_4$], 144 (70), 115 (43), 86 (19), 80 (15), 52 (79) [Cr^+]; HRMS (EI): *m*/*z*: calcd for $C_{13}H_9ClCrO_6$: 347.9492 (correct HRMS).

Pentacarbonyl[4-(*tert*-butyldiphenylsiloxy)-1-ethoxy-2-pentyn-1-ylidene]-chromium (1f): Complex **1f** was prepared according to a previously published protocol[14a,b] from 3-(*tert*-butyldiphenylsilyloxy)-1-butyne[23] (3.08 g, 10.0 mmol) in Et_2O (50 mL), *n*-butyllithium (4.24 mL, 2.36 N in hexane, 10.0 mmol), hexacarbonylchromium (2.20 g, 10.0 mmol), THF (20 mL) and triethyloxonium tetrafluoroborate (2.18 g, 11.5 mmol). After

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

chromatography [200 g silica gel, elution with pentane], **1f** (R_f = 0.58) was obtained as a black-red oil (4.61 g, 83%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10 [s, 9H, SiC(CH_3)$_3$], 1.39 (t, ^3J = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.62 (d, ^3J = 7.2 Hz, 3H, CHC*H*$_3$), 4.32 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 5.40 (q, ^3J = 7.2 Hz, 1H, C*H*CH$_3$), 7.32–7.49 (m, 6H, Ph-H), 7.62–7.73 (m, 4H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.8 (+, OCH$_2$*C*H$_3$), 19.1 [C_{quat}, Si*C*(CH_3)$_3$], 24.3 (+, CH*C*H$_3$), 27.7 [+, SiC(*C*H$_3$)$_3$], 60.8 (+, *C*HCH$_3$), 76.1 (−, O*C*H$_2$CH$_3$), 86.9 (C_{quat}, C-2), 127.5, 127.6, 130.1 (+, Ph-C), 132.9, 133.1 (C_{quat}, Ph-C), 135.7, 135.8 (+, Ph-C), 139.0 (C_{quat}, C-3), 216.0, 225.4 (C_{quat}, C=O), 316.3 (C_{quat}, C-1); IR (film): $\tilde{\nu}$ = 3074, 2932, 2160 (C≡C), 2060 (C=O), 1991 (C=O), 1948 (C=O), 1429, 1368 cm^{-1}; MS (70 eV): *m*/*z* (%): 251 (42), 207 (100), 181 (14), 147 (27), 129 (4), 105 (11) [SiC$_6$H$_5^+$], 77 (17) [C$_6$H$_5^+$], 52 (6) [Cr$^+$], 45 (10).

Pentacarbonyl[4-(*tert*-butyldimethylsiloxy)-1-ethoxy-2-pentyn-1-ylidene]-chromium (1g): Complex **1g** was prepared according to a previously published protocol[14a,b] from 3-(*tert*-butyldimethylsilyloxy)-1-butyne[24] (1.84 g, 10.0 mmol) in Et_2O (50 mL), *n*-butyllithium (4.24 mL, 2.36 N in hexane, 10.0 mmol), hexacarbonylchromium (2.20 g, 10.0 mmol), THF (20 mL) and triethyloxonium tetrafluoroborate (2.18 g, 11.5 mmol). After chromatography [200 g silica gel, elution with pentane], **1g** (R_f = 0.53) was obtained as a black-red oil (2.72 g, 63%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12 (s, 3H, SiCH$_3$), 0.13 (s, 3H, SiCH$_3$), 0.91 [s, 9H, SiC(CH_3)$_3$], 1.52 (t, ^3J = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.58 (d, ^3J = 7.2 Hz, 3H, CHC*H*$_3$), 4.67 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 5.08 (q, ^3J = 7.2 Hz, 1H, C*H*CH$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.1, −4.9 (+, SiCH$_3$), 14.9 (+, OCH$_2$*C*H$_3$), 18.1 [C_{quat}, Si*C*(CH_3)$_3$], 24.4 (+, CH*C*H$_3$), 25.6 [+, SiC(*C*H$_3$)$_3$], 59.9 (+, *C*HCH$_3$), 76.1 (−, O*C*H$_2$CH$_3$), 86.4 (C_{quat}, C-2), 138.5 (C_{quat}, C-3), 216.1, 225.4 (C_{quat}, C=O), 316.8 (C_{quat}, C-1); IR (film): $\tilde{\nu}$ = 2975, 2925, 2059 (C=O), 1951 (C=O), 1460, 1382, 1361 cm^{-1}; MS (70 eV): *m*/*z* (%): 432 (6) [*M*$^+$], 376 (5) [*M*$^+$−2CO], 320 (8) [*M*$^+$−4CO], 292 (19) [*M*$^+$−5CO], 211 (8), 199 (44), 171 (30), 155 (78), 147 (57), 126 (25), 111 (58), 103 (53), 75 (100), 52 (18) [Cr$^+$]; HRMS (EI): *m*/*z*: calcd for $C_{18}H_{24}CrO_7Si$: 432.0696 (correct HRMS).

Pentacarbonyl[1-ethoxy-4-(trimethylsilyloxy)-2-pentyn-1-ylidene]chromium (1h): Complex **1h** was prepared according to a previously published protocol[14a,b] from 3-(trimethylsiyloxy)-1-butyne[25] (1.42 g, 10.0 mmol) in Et_2O (50 mL), *n*-butyllithium (4.24 mL, 2.36 N in hexane, 10.0 mmol), hexacarbonylchromium (2.20 g, 10.0 mmol), THF (20 mL) and triethyloxonium tetrafluoroborate (2.18 g, 11.5 mmol). After chromatography [200 g silica gel, elution with pentane], **1h** (R_f = 0.62) was obtained as a black-red oil (3.08 g, 79%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.16 (s, 9H, SiCH$_3$), 1.52 (t, ^3J = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.59 (d, ^3J = 7.2 Hz, 3H, CHC*H*$_3$), 4.64 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 5.06 (q, ^3J = 7.2 Hz, 1H, C*H*CH$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −0.2 [+, Si(CH_3)$_3$], 14.9 (+, OCH$_2$*C*H$_3$), 24.4 (+, CH*C*H$_3$), 59.3 (+, *C*HCH$_3$), 76.2 (−, O*C*H$_2$CH$_3$), 85.3 (C_{quat}, C-2), 139.0 (C_{quat}, C-3), 216.0, 225.4 (C_{quat}, C=O), 316.8 (C_{quat}, C-1); IR (film): $\tilde{\nu}$ = 2961, 2165 (C≡C), 2063 (C=O), 1940 (C=O), 1712, 1444 cm^{-1}; MS (70 eV): *m*/*z* (%): 390 (2) [*M*$^+$], 334 (9) [*M*$^+$−2CO], 278 (19) [*M*$^+$−4CO], 250 (7) [*M*$^+$−5CO], 235 (5), 206 (4), 191 (20), 126 (100), 75 (17), 52 (21) [Cr$^+$]; HRMS (EI): *m*/*z*: calcd for $C_{15}H_{18}CrO_7Si$: 390.0226 (correct HRMS).

Pentacarbonyl[1-ethoxy-3-(2′-methyldioxolan-2′-yl)-2-pentyn-1-ylidene]-chromium (1i): Complex **1i** was prepared according to a previously published protocol[14a,b] from 2-ethynyl-2-methyldioxolane (2.24 g, 20.0 mmol) in Et_2O (100 mL), *n*-butyllithium (12.5 mL, 2.36 N in hexane, 20.0 mmol), hexacarbonylchromium (4.40 g, 20.0 mmol), THF (40 mL) and triethyloxonium tetrafluoroborate (4.37 g, 23.0 mmol). After chromatography [300 g silica gel, elution with pentane], **1i** (R_f = 0.45) was obtained as a black-red oil (6.71 g, 93%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.52 (t, ^3J = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.81 (s, 3H, CH$_3$), 4.11 (s, 4H, OC*H*$_2$CH$_2$O), 4.68 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.6 (+, OCH$_2$*C*H$_3$), 25.4 (+, CH$_3$), 64.4 (−, O*C*H$_2$CH$_2$O), 76.2 (−, O*C*H$_2$CH$_3$), 83.7 (C_{quat}, C-2), 101.5 [C_{quat}, *C*(OCH)$_2$], 130.8 (C_{quat}, C-3), 215.7, 225.2 (C_{quat}, C=O), 316.6 (C_{quat}, C-1); IR (film): $\tilde{\nu}$ = 2985, 2170 (C≡C), 2064 (C=O), 1936 (C=O), 1442, 1376 cm^{-1}; MS (70 eV): *m*/*z* (%): 360 (2) [*M*$^+$], 304 (2) [*M*$^+$−2CO], 220 (16) [*M*$^+$−5CO], 154 (32), 108 (50), 80 (82), 52 (100) [Cr$^+$], 41 (29); HRMS (EI): *m*/*z*: calcd for $C_{14}H_{12}CrO_8$: 359.9937 (correct HRMS).

(2*E*)- and (2*Z*)-Pentacarbonyl[3-benzyloxy-1,4-diethoxy-4-methyl-2-penten-1-ylidene]chromium [(*E*/*Z*)-2bi]: According to GP 1, a solution of complex **1b** (681 mg, 1.89 mmol), and benzyl alcohol (409 mg, 3.78 mmol) in Et_2O/ethanol (1:1, 20 mL) was treated at 20 °C with a 1 N solution (0.19 mL) of sodium benzylate in Et_2O/ethanol (1:1). After chromatography [50 g silica gel, elution with pentane/Et_2O (10:1)], (*E*/*Z*)-**2bi** (R_f = 0.35; *E*/*Z* 5:1) was obtained as orange crystals (876 mg, 99%). M.p. 96 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02–1.20 (m, 3H, OCH$_2$C*H*$_3$), 1.27 and 1.32 [s, 6H, C(CH_3)$_2$], 1.40–1.62 (m, 3H, OCH$_2$C*H*$_3$), 3.33–3.56 (m, 2H, OC*H*$_2$CH$_3$), 4.56 and 4.68 (br s, 2H, OC*H*$_2$Ph), 4.74–4.92 (m, 2H, OC*H*$_2$CH$_3$), 5.56 and 5.79 (s, 1H, 2-H), 7.18–7.41 (m, 5H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): (*E*/*Z*)-**2bi**: δ = 14.0, 14.6, 15.5, 15.6 (+, OCH$_2$*C*H$_3$), 22.3, 25.7 [+, C(*C*H$_3$)$_2$], 57.8, 57.9 (−, O*C*H$_2$CH$_3$), 65.4, 70.6 [C_{quat}, *C*(CH_3)$_2$], 76.3, 76.5 (−, O*C*H$_2$CH$_3$), 77.5, 82.0 (−, O*C*H$_2$Ph), 120.1, 120.4 (+, C-2), 127.1, 127.3, 127.5, 127.8, 128.2, 128.4 (+, C-Ph), 134.5, 136.3 (C_{quat}, C-Ph), 157.9, 158.7 (C_{quat}, C-3), 217.0, 217.2, 224.0 (C_{quat}, C=O), 334.3, 334.7 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 3024, 2941, 2870, 2042 (C=O), 1977 (C=O), 1930 (C=O), 1500, 1451 cm^{-1}; MS (70 eV): *m*/*z* (%): 468 (<1) [*M*$^+$], 412 (9) [*M*$^+$−2CO], 384 (30) [*M*$^+$−3CO], 356 (<1) [*M*$^+$−4CO], 328 (26) [*M*$^+$−5CO], 238 (100), 91 (38) [PhCH$_2^+$], 52 (16) [Cr$^+$].

Pentacarbonyl[(2*Z*)-1,4-diethoxy-3-(1-fluorophenoxy)-4-methyl-2-penten-1-ylidene]chromium [(*Z*)-2bk]: According to GP 1, a solution of complex **1b** (400 mg, 1.11 mmol) and 4-fluorophenol (249 mg, 2.22 mmol) in Et_2O/ethanol (1:1, 10 mL) was treated at 20 °C with a 1 N solution (0.11 mL) of sodium 4-fluorophenolate in Et_2O/ethanol (1:1). After chromatography [30 g silica gel, elution with pentane/Et_2O (10:1)], (*Z*)-**2bk** (R_f = 0.18) was obtained as orange crystals (513 mg, 98%). M.p. 108 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.12–1.33 (m, 6H, OCH$_2$C*H*$_3$), 1.42 [s, 6H, C(CH_3)$_2$], 3.52 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 4.49 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 6.72–6.86 (m, 2H, Ph-H), 6.90–7.11 (m, 2H, Ph-H), 7.40 (s, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.8 (+, OCH$_2$*C*H$_3$), 15.7 (+, OCH$_2$*C*H$_3$), 25.6 [+, C(*C*H$_3$)$_2$], 58.9 (−, O*C*H$_2$CH$_3$), 65.9 [C_{quat}, *C*(CH_3)$_2$], 77.1 (−, O*C*H$_2$CH$_3$), 116.54 (+, d, $^2J_{C\text{-}F}$ = 17.2 Hz, Ph-C), 117.03 (+, C-2), 123.1 (+, d, $^3J_{C\text{-}F}$ = 9.2 Hz, Ph-C), 151.1 (C_{quat}, C-3), 153.1 (C_{quat}, d, $^4J_{C\text{-}F}$ = 3.0 Hz, Ph-C), 158.2 (C_{quat}, d, $^1J_{C\text{-}F}$ = 266.1 Hz, Ph-C), 216.5, 223.8 (C_{quat}, C=O), 333.0 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 3055, 2987, 2880, 2050 (C=O), 1980 (C=O), 1930 (C=O), 1585, 1500, 1462 cm^{-1}; MS (70 eV): *m*/*z* (%): 472 (4) [*M*$^+$], 388 (6) [*M*$^+$−3CO], 360 (2) [*M*$^+$−4CO], 332 (17) [*M*$^+$−5CO], 252 (10), 209 (79), 191 (19), 163 (18), 113 (20), 87 (78), 59 (100), 52 (40) [Cr$^+$]; HRMS (EI): *m*/*z*: calcd for $C_{21}H_{21}CrFO_8$: 472.0626 (correct HRMS).

Pentacarbonyl[(2*Z*)-1,4-diethoxy-4-methyl-3-(4′-nitrophenylthio)-2-penten-1-ylidene]chromium [(*Z*)-2bm] and tetracarbonyl[(1,4-diethoxy-4-methyl-2-pentyn-1-ylidene)-4-nitrothiophenol-*S*]chromium: According to GP 1, a solution of complex **1b** (313 mg, 0.87 mmol) and 4-nitrothiophenol (260 mg, 1.68 mmol) in 10 mL of Et_2O/ethanol (1:1) was treated at 20 °C with a 0.5 N solution of 4-nitrothiophenolate (0.18 mL) in Et_2O/ethanol (1:1), and the mixture was stirred for 10 min. After chromatography [30 g silica gel, elution with pentane/Et_2O (10:1)], 75 mg (17%) of (*Z*)-**2bm** (R_f = 0.11) and tetracarbonyl[(1,4-diethoxy-4-methyl-2-pentyn-1-ylidene)-4-nitrothiophenol-*S*]chromium (R_f = 0.02) were obtained as an orange oil and a red oil, respectively (total 31 mg, 7%). (*Z*)-**2bm**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.71 (t, ^3J = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.18 (t, ^3J = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.52 [s, 6H, C(CH_3)$_2$], 3.41 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 4.38 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 6.67 (s, 1H, 2-H), 7.62 (d, ^3J = 8.4 Hz, 2H, Ph-H), 8.16 (d, ^3J = 8.4 Hz, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.3, 15.7 (+, OCH$_2$*C*H$_3$), 26.2 [+, C(*C*H$_3$)$_2$], 59.1, 74.8 (−, O*C*H$_2$CH$_3$), 77.8 [C_{quat}, *C*(CH_3)$_2$], 117.1 (+, C-2), 120.7, 124.1 (+, C-Ph), 130.8 (C_{quat}, C-Ph), 145.9, 146.5 (C_{quat}, C-Ph, C-3), 218.0, 224.0 (C_{quat}, C=O), 309.5 (C_{quat}, C-1); IR (film): $\tilde{\nu}$ = 2980, 2961, 2033 (C=O), 1882 (C=O), 1480, 1129 cm^{-1}.

Tetracarbonyl[(1,4-diethoxy-4-methyl-2-pentyn-1-ylidene)-4-nitrothiophenol-*S*]chromium: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.33 (t, ^3J = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.64 [s, 6H, C(CH_3)$_2$], 3.48 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 3.62 (q, ^3J = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 7.53 (d, ^3J = 8.1 Hz, 2H, Ph-H), 8.03 (d, ^3J = 8.4 Hz, 2H, Ph-H), 10.10 (s, 1H, SH); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ =

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

15.2, 15.9 (+, OCH_2CH_3), 25.6 [+, $C(CH_3)_2$], 59.5, 65.8 (−, OCH_2CH_3), 81.1 [C_{quat}, $C(CH_3)_2$], 120.9 (C_{quat}, C-2), 124.4, 126.5 (+, C-Ph), 136.1, 144.1, 152.3 (C_{quat}, C-Ph, C-3), 216.7, 218.1, 224.0 (C_{quat}, C=O), 251.2 (C_{quat}, C-1); IR (film): $\tilde{\nu}$ = 2984, 2920, 1965 (C=O), 1903 (C=O), 1570, 1500, 1451 cm^{-1}; MS (70 eV): *m/z* (%): 220 (38) [$M^+ - C_6H_5NO_2S - 4CO$], 170 (8), 108 (42), 86 (100), 59 (43).

Pentacarbonyl[(2*Z*)-1,4-diethoxy-3-ethylthio-4-methyl-2-penten-1-ylidene]chromium [(*Z*)-2bn]: According to GP 1, a solution of complex **1b** (440 mg, 1.22 mmol) and ethanethiol (152 mg, 2.45 mmol) in Et_2O/ethanol (1:1, 12 mL) was at 20 °C treated with a 0.5 N solution (0.24 mL) of sodium ethanethiolate in Et_2O/ethanol (1:1). After chromatography [30 g silica gel, elution with pentane/Et_2O (10:1)], (*Z*)-**2bn** (R_f = 0.39) was obtained as a red oil (479 mg, 93 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 1.24 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 1.49 [s, 6H, $C(CH_3)_2$], 1.65 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 2.80 (q, ^3J = 7.0 Hz, 2H, SCH_2CH_3), 3.41 (q, ^3J = 7.0 Hz, 2H, CH_2CH_3), 4.86 (q, ^3J = 7.0 Hz, 2H, CH_2CH_3), 7.29 (s, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.2, 15.0, 15.5 (+, CH_2CH_3), 27.2 [+, $C(CH_3)_2$], 29.5 (−, SCH_2CH_3), 58.6, 76.3 (−, CH_2CH_3), 79.6 [C_{quat}, $C(CH_3)_2$], 139.9 (+, C-2), 140.7 (C_{quat}, C-3), 216.9, 224.1 (C_{quat}, C=O), 292.2 (C_{quat}, C-1); IR (film): $\tilde{\nu}$ = 2972, 2920, 2054 (C=O), 1981 (C=O), 1930 (C=O), 1440, 1361 cm^{-1}; MS (70 eV): *m/z* (%): 422 (1) [M^+], 394 (6) [$M^+ - CO$], 338 (9) [$M^+ - 3CO$], 310 (2) [$M^+ - 4CO$], 282 (23) [$M^+ - 5CO$], 246 (8), 238 (7), 202 (3), 179 (6), 156 (19), 87 (100), 59 (61), 52 (5) [Cr^+]; HRMS (EI): *m/z*: calcd for $C_{17}H_{22}CrO_7S$: 422.0491 (correct HRMS).

Pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-4-methyl-4-(trimethylsilyloxy)-2-penten-1-yliden]chromium [(*Z*)-2ca] and pentacarbonyl[3-dimethylamino-4-(trimethylsilyloxy)-4-methyl-1,2-pentadienylidene]chromium (3ca): According to GP 1, complex **1c** (500 mg, 1.24 mmol) in Et_2O (14 mL) was at 20 °C treated with dimethylamine. After chromatography [50 g silica gel, elution with pentane/Et_2O (5:1)], (*Z*)-**2ca** (R_f = 0.26) and **3ca** (R_f = 0.04) were obtained as yellow (486 mg, 87 %) and orange crystals (58 mg, 12 %). The spectral data have previously been reported.[14a]

Pentacarbonyl[(2*Z*)-3-dibenzylamino-1-ethoxy-4-methyl-4-(trimethylsilyloxy)-2-penten-1-ylidene]chromium [(*Z*)-2cb] and pentacarbonyl[3-dibenzylamino-4-methyl-4-(trimethylsilyloxy)-1,2-pentadienylidene]chromium (3cb): According to GP 1, complex **1c** (983 mg, 2.43 mmol) in Et_2O (12 mL) was treated at 20 °C with dibenzylamine (594 mg, 3.01 mmol). After chromatography [50 g silica gel, elution with pentane/Et_2O (5:1)], (*Z*)-**2cb** (R_f = 0.42) and **3cb** (R_f = 0.24) were obtained as a yellow oil (596 mg, 41 %) and red crystals (794 mg, 59 %), m.p. 79 °C. (*Z*)-**2cb**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11 [s, 9H, $Si(CH_3)_3$], 1.12 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.76 [s, 6H, $C(CH_3)_2$], 4.43 [brs, 4H, $N(CH_2)_2$], 4.71 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 6.68 (s, 1H, 2-H), 7.08–7.12 (m, 4H, Ph-H), 7.31–7.40 (m, 6H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 2.3 [+, $Si(CH_3)_3$], 15.9 (+, OCH_2CH_3), 31.8 [+, $C(CH_3)_2$], 57.9 [−, $N(CH_2)_2$], 74.4 (−, OCH_2CH_3), 77.8 [C_{quat}, $C(CH_3)_2$], 115.5 (+, C-2), 128.2, 128.3, 128.7 (+, C-Ph), 136.2 (C_{quat}, C-Ph), 164.3 (C_{quat}, C-3), 219.1, 223.4 (C_{quat}, C=O), 286.9 (C_{quat}, C-1); IR (film): $\tilde{\nu}$ = 3073, 2980, 2012 (C=O), 1936 (C=O), 1896 (C=O), 1590, 1520, 1494, 1353, 1345 cm^{-1}; MS (70 eV): *m/z* (%): 363 (9) [$M^+ - Cr(CO)_5 - C_2H_5OH$], 348 (41), 273 (42), 258 (12), 230 (76), 192 (23), 117 (5), 108 (45), 91 (7) [$C_7H_7^+$], 77 (13) [$C_6H_5^+$], 44 (100); elemental analysis calcd (%) for $C_{30}H_{35}CrNO_7Si$ (601.7): C 59.89, H 5.86, N 2.33; found C 59.95, H 5.87, N 2.43.

Compound 3cb: ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.03 [s, 9H, $Si(CH_3)_3$], 1.81 [s, 6H, $C(CH_3)_2$], 5.08 (s, 2H, NCH_2), 5.22 (s, 2H, NCH_2), 7.15–7.21 (m, 2H, Ph-H), 7.32–7.49 (m, 8H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 1.9 [+, $Si(CH_3)_3$], 31.2 [+, $C(CH_3)_2$], 53.6, 58.2 [−, $N(CH_2)_2$], 78.2 [C_{quat}, $C(CH_3)_2$], 122.6 (C_{quat}, C-2), 127.2, 128.1, 128.4, 128.8, 129.1, 129.2 (+, C-Ph), 134.0, 134.1 (C_{quat}, C-Ph), 161.0 (C_{quat}, C-3), 217.3, 223.8 (C_{quat}, C=O), 233.3 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 3048, 2960, 2933, 2060, 1999, 1930 (C=O), 1521 cm^{-1}; MS (70 eV): *m/z* (%): 555 (5) [M^+], 471 (<1) [$M^+ - 3CO$], 443 (13) [$M^+ - 4CO$], 415 (10) [$M^+ - 5CO$], 400 (39) [$M^+ - 5CO - CH_3$], 325 (4), 275 (4), 234 (3), 219 (22), 184 (47), 142 (12), 107 (25), 91 (100) [$C_7H_7^+$], 73 (65) [$C_3H_9Si^+$], 52 (73) [Cr^+]; HRMS (EI): *m/z*: calcd for $C_{28}H_{29}CrNO_6Si$: 555.1169 (correct HRMS).

The same experiment, when carried out at −78 °C, gave (*Z*)-**2cb** (1.32 g, 91 %) and **3cb** (53.8 mg, 4 %).

Pentacarbonyl[(2*Z*)-3-diethylamino-1-ethoxy-4-methyl-4-(trimethylsilyloxy)-2-penten-1-ylidene]chromium [(*Z*)-2cf] and pentacarbonyl[3-diethylamino-4-methyl-4-(trimethylsilyloxy)-1,2-pentadienylidene]chromium (3cf): According to GP 1, complex **1c** (776 mg, 1.92 mmol) in Et_2O (15 mL) was treated at 20 °C with diethylamine (174 mg, 2.38 mmol). After chromatography [40 g silica gel, elution with pentane/Et_2O (5:1)], (*Z*)-**2cf** (R_f = 0.48) and **3cf** (R_f = 0.16) were obtained as yellow crystals (313 mg, 38 %), m.p. 103 °C and a red oil (313 mg, 38 %), respectively. (*Z*)-**2cf**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12 [s, 9H, $Si(CH_3)_3$], 1.19 [t, ^3J = 7.0 Hz, 6H, $N(CH_2CH_3)_2$], 1.41 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.60 [s, 6H, $C(CH_3)_2$], 3.72 [q, ^3J = 7.0 Hz, 4H, $N(CH_2CH_3)_2$], 4.62 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 6.29 (s, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 2.1 [+, $Si(CH_3)_3$], 13.7 [+, $N(CH_2CH_3)_2$], 15.9 (+, OCH_2CH_3), 30.9 [+, $C(CH_3)_2$], 47.4 [−, $N(CH_2CH_3)_2$], 72.8 (−, OCH_2CH_3), 77.0 [C_{quat}, $C(CH_3)_2$], 114.4 (+, C-2), 166.4 (C_{quat}, C-3), 219.7, 224.4 (C_{quat}, C=O), 274.8 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 2981, 2950, 2062 (C=O), 1976 (C=O), 1920 (C=O), 1530, 1455, 1445 cm^{-1}; MS (70 eV): *m/z* (%): 477 (4) [M^+], 421 (1) [$M^+ - 2CO$], 393 (9) [$M^+ - 3CO$], 337 (24) [$M^+ - 5CO$], 291 (26) [$M^+ - 5CO - C_2H_6O$], 242 (19), 224 (61), 196 (60), 170 (36), 152 (53), 131 (65), 110 (13), 75 (100) [$C_2H_7OSi^+$], 59 (72), 52 (11) [Cr^+], 45 (92); HRMS (EI): *m/z*: calcd for $C_{20}H_{31}CrNO_7Si$: 477.1274 (correct HRMS).

Compound 3cf: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.19 [s, 9H, $Si(CH_3)_3$], 1.35 (t, ^3J = 7.0 Hz, 3H, NCH_2CH_3), 1.41 (t, ^3J = 7.0 Hz, 3H, NCH_2CH_3), 1.70 [s, 6H, $C(CH_3)_2$], 3.92 (q, ^3J = 7.0 Hz, 2H, NCH_2CH_3), 4.18 (q, ^3J = 7.0 Hz, 2H, NCH_2CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 2.1 [+, $Si(CH_3)_3$], 11.8, 13.9 [+, $N(CH_2CH_3)_2$], 31.0 [+, $C(CH_3)_2$], 46.6, 51.2 [−, $N(CH_2CH_3)_2$], 77.4 [C_{quat}, $C(CH_3)_2$], 119.9 (C_{quat}, C-2), 160.1 (C_{quat}, C-3), 217.6, 223.9 (C_{quat}, C=O), 225.7 (C_{quat}, C-1); IR (Film): $\tilde{\nu}$ = 2980, 2957, 2040 (C=O), 1914 (C=O), 1872 (C=O), 1520 cm^{-1}; MS (70 eV): *m/z* (%): 431 (23) [M^+], 375 (1) [$M^+ - 2CO$], 347 (2) [$M^+ - 3CO$], 319 (43) [$M^+ - 4CO$], 291 (100) [$M^+ - 5CO$], 276 (38) [$M^+ - 5CO - CH_3$], 247 (5), 201 (26), 170 (5), 150 (24), 131 (30), 102 (4), 73 (31) [$C_3H_9Si^+$], 52 (12) [Cr^+]; HRMS (EI): *m/z*: calcd for $C_{18}H_{25}CrNO_6Si$: 431.0856 (correct HRMS).

Pentacarbonyl[(2*Z*)-3-(1′-chlorocyclopropyl)-3-dimethylamino-1-ethoxypropen-1-ylidene]chromium [(*Z*)-2ea]: According to GP 1, complex **1e** (711 mg, 2.04 mmol) in Et_2O (23 mL) was treated with dimethylamine at 20 °C. After chromatography [60 g silica gel, elution with pentane/Et_2O (5:1)], (*Z*)-**2ea** (R_f = 0.26) was obtained as yellow crystals (780 mg, 97 %). M.p. 104 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.13 (m, 2H, *c*Pr-H), 1.44 (m, 2H, *c*Pr-H), 1.62 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 3.21 [brs, 6H, $N(CH_3)_2$], 4.80 (brs, 2H, OCH_2CH_3), 6.12 (s, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 15.6 (+, OCH_2CH_3), 20.6 (−, *c*Pr-C), 37.9 (C_{quat}, *c*Pr-C), 41.8 [+, $N(CH_3)_2$], 74.6 (−, OCH_2CH_3), 117.2 (+, C-2), 155.0 (C_{quat}, C-3), 219.0, 224.5 (C_{quat}, C=O), 296.7 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 2928, 2041 (C=O), 1900 (C=O), 1518, 1472 cm^{-1}; MS (70 eV): *m/z* (%): 395/393 (4/11) [M^+], 367/365 (<1/1) [$M^+ - CO$], 339/337 (<1/1) [$M^+ - 2CO$], 311/309 (<1/2) [$M^+ - 3CO$], 283/281 (<1/1) [$M^+ - 4CO$], 255/253 (1/7) [$M^+ - 5CO$], 227/225 (8/23) [$M^+ - 5CO - C_2H_4$], 166 (100), 138 (19), 111 (52), 84 (90), 69 (21), 52 (16) [Cr^+], 44 (69); HRMS (EI): *m/z*: calcd for $C_{15}H_{16}ClCrNO_6$: 393.0071 (correct HRMS).

Pentacarbonyl[(2*E*)-4-(*tert*-butyldiphenylsilyloxy)-3-dimethylamino-1-ethoxypenten-1-ylidene]chromium [(*E*)-2fa] and pentacarbonyl[4-(*tert*-butyldiphenylsilyloxy)-3-dimethylamino-1,2-pentadienylidene]chromium (3fa): According to GP 1, complex **1f** (2.78 g, 5.00 mmol) in Et_2O (25 mL) was treated at 20 °C with dimethylamine. After chromatography [100 g silica gel, elution with pentane/Et_2O (5:1)], (*E*)-**2fa** (R_f = 0.36) and **3fa** (R_f = 0.07) were obtained as yellow crystals (2.85 g, 95 %), m.p. 131 °C, and a red oil (83 mg, 3 %), respectively. (*E*)-**2fa**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.07 [s, 9H, $SiC(CH_3)_3$], 1.39 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 3.23 [brs, 6H, $N(CH_3)_2$], 4.07 (m, 1H, OCH_2CH_3), 4.50 (m, 1H, OCH_2CH_3), 5.68 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.16 (s, 1H, 2-H), 7.32–7.47 (m, 6H, Ph-H), 7.53–7.65 (m, 4H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.8 (+, OCH_2CH_3), 19.2 [C_{quat}, $SiC(CH_3)_3$], 21.2 (+, $CHCH_3$), 26.9 [+, SiC-

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

(CH_3)$_3$], 42.8 [+, N(CH_3)$_2$], 68.1 (+, $CHCH_3$), 73.6 (−, OCH_2CH_3), 117.1 (+, C-2), 127.7, 127.8, 130.0, 130.2 (+, C-Ph), 132.4, 133.2 (C_{quat}, C-Ph), 135.58, 135.62 (+, C-Ph), 159.28 (C_{quat}, C-3), 219.1, 224.3 (C_{quat}, C=O), 290.0 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 3061, 3002, 2039 (C≡O), 1964 (C=O), 1919 (C=O), 1533, 1475 cm^{-1}; MS (70 eV): *m*/*z* (%): 601 (1) [M^+], 573 (3) [M^+−CO], 545 (1) [M^+−2CO], 517 (3) [M^+−3CO], 489 (6) [M^+−4CO], 461 (100) [M^+−5CO], 415 (23), 359 (7), 308 (6), 251 (18), 199 (98), 186 (17), 154 (9), 110 (24), 52 (9) [Cr^+].

Compound 3 fa: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10 [s, 9H, SiC(CH_3)$_3$], 1.51 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 3.08 (s, 3H, NCH_3), 3.32 (s, 3H, NCH_3), 4.70 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 7.38–7.50 (m, 6H, Ph-H), 7.62–7.75 (m, 4H, Ph-H); IR (Film): $\tilde{\nu}$ = 3069, 2958, 2080 (C=C=C), 2001 (C=O), 1992 (C=O), 1930 (C=O), 1570, 1427, 1408 cm^{-1}; MS (70 eV): *m*/*z* (%): 555 (7) [M^+], 471 (18) [M^+−3CO], 415 (4) [M^+−5CO], 363 (2) [M^+−5CO−Cr], 199 (100), 52 (29) [Cr^+]; HRMS (EI): *m*/*z*: calcd for $C_{28}H_{29}CrNO_6Si$: 555.1169 (correct HRMS).

Pentacarbonyl[(2*E*)-4-(*tert*-butyldiphenylsilyloxy)-3-dibenzylamino-1-ethoxy]-2-penten-1-ylidene]chromium [(*E*)-2 fb] and pentacarbonyl[4-(*tert*-butyldiphenylsilyloxy)-3-dibenzylamino-1,2-pentadienylidene]chromium (3 fb): According to GP 1, complex **1 f** (2.78 g, 5.00 mmol) in Et_2O (25 mL) was treated at 20 °C with dibenzylamine (1.28 g, 6.49 mmol). After chromatography [100 g silica gel, elution with pentane/Et_2O (5:1)], (*E*)-**2 fb** (R_f = 0.37) and **3 fb** (R_f = 0.13) were obtained as yellow crystals (2.71 g, 72%), m.p. 115 °C, and a purple oil (492 mg, 14%), respectively. (*E*)-**2 fb**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.98 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.13 [s, 9H, SiC(CH_3)$_3$], 1.30 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 4.11 (m, 1H, OCH_2CH_3), 4.52 (m, 3H, OCH_2CH_3, NCH_2), 5.73 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.11 (br s, 2H, NCH_2), 6.53 (s, 1H, 2-H), 7.12–7.25 (m, 4H, Ph-H), 7.28–7.51 (m, 12H, Ph-H), 7.59–7.70 (m, 4H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.8 (+, OCH_2CH_3), 19.2 [C_{quat}, SiC(CH_3)$_3$], 22.0 (+, $CHCH_3$), 27.0 [+, SiC(CH_3)$_3$], 55.5 [−, N-(CH_2-)$_2$], 68.4 (+, $CHCH_3$), 73.9 (−, OCH_2CH_3), 118.3 (+, C-2), 127.9, 129.0, 130.1, 130.2 (+, C-Ph), 132.3, 135.7 (C_{quat}, C-Ph), 135.7, 135.8 (+, C-Ph), 158.3 (C_{quat}, C-3), 218.5, 224.2 (C_{quat}, C=O), 296.3 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 3064, 3020, 2041 (C=O), 1966 (C=O), 1923 (C=O), 1510, 1480 cm^{-1}; MS (70 eV): *m*/*z* (%): 753 (0.3) [M^+], 697 (2) [M^+−2CO], 641 (0.8) [M^+−4CO], 613 (17) [M^+−5CO], 561 (8) [M^+−5CO−Cr^+], 515 (22), 458 (26), 352 (89), 260 (100), 199 (58), 135 (24), 91 (23) [$C_7H_7^+$], 52 (11) [Cr^+]; elemental analysis calcd for $C_{42}H_{43}CrNO_7Si$ (753.9): C 66.92, H 5.75, N 1.86; found C 66.85, H 5.77, N 1.93.

Compound 3 fb: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.04 [s, 9H, SiC(CH_3)$_3$], 1.39 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 4.18 (d, ^2J = 21.2 Hz, 1H, NCH_2), 4.50 (d, ^2J = 21.2 Hz, 1H, NCH_2), 4.66 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 4.96 (d, ^2J = 21.2 Hz, 1H, NCH_2), 5.19 (d, ^2J = 21.2 Hz, 1H, NCH_2), 6.78–6.90 (m, 2H, Ph-H), 7.24–7.47 (m, 14H, Ph-H), 7.55–7.69 (m, 4H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 19.1 [C_{quat}, SiC(CH_3)$_3$], 22.7 (+, $CHCH_3$), 26.6 [+, SiC(CH_3)$_3$], 52.3 (−, NCH_2), 58.1 (−, NCH_2), 69.2 (+, $CHCH_3$), 122.6 (C_{quat}, C-2), 126.8, 127.1, 127.5, 127.8, 127.9, 128.0, 128.2, 128.5, 128.9, 129.0 (+, C-Ph), 132.3, 132.7, 133.1, 133.5 (C_{quat}, C-Ph), 135.6, 135.7 (+, C-Ph), 157.7 (C_{quat}, C-3), 217.3, 223.8 (C_{quat}, C=O), 234.7 (C_{quat}, C-1); IR (Film): $\tilde{\nu}$ = 3080, 3057, 2851, 1984 (C=O), 1932 (C=O), 1538, 1492, 1450 cm^{-1}; MS (70 eV): *m*/*z* (%): 256 (5), 205 (23), 199 (100), 52 (2) [Cr^+].

Pentacarbonyl[(2*E*)-4-(*tert*-butyldimethylsilyloxy)-3-dimethylamino-1-ethoxy-2-penten-1-ylidene]chromium [(*E*)-2 ga]: According to GP 1, complex **1 g** (2.16 g, 5.00 mmol) in Et_2O (25 mL) was treated at 20 °C with dimethylamine. After chromatography [100 g silica gel, elution with pentane/Et_2O (5:1)], (*E*)-**2 ga** (R_f = 0.28) was obtained as orange crystals (2.29 g, 96%). M.p. 109 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 (s, 3H, $SiCH_3$), 0.14 (s, 3H, $SiCH_3$), 0.96 [s, 9H, SiC(CH_3)$_3$], 1.49 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 1.58 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 3.31 [br s, 6H, N-(CH_3)$_2$], 4.80 (m, 2H, OCH_2CH_3), 5.23 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.29 (s, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.3, −5.1 (+, $SiCH_3$), 15.5 (+, OCH_2CH_3), 18.0 [C_{quat}, SiC(CH_3)$_3$], 21.3 (+, $CHCH_3$), 25.7 [+, SiC(CH_3)$_3$], 42.8 [+, N(CH_3)$_2$], 67.1 (+, $CHCH_3$), 73.7 (−, OCH_2CH_3), 117.4 (+, C-2), 160.3 (C_{quat}, C-3), 219.2, 224.4 (C_{quat}, C=O), 289.7 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 2956, 2935, 2046 (C=O), 1960 (C=O), 1939 (C=O), 1911 (C=O), 1885 (C=O), 1537 cm^{-1}; MS (70 eV): *m*/*z* (%): 477 (4) [M^+], 449 (2) [M^+−CO], 421 (1) [M^+−2CO], 393 (8) [M^+−3CO], 365 (3) [M^+−4CO], 337 (46) [M^+−5CO], 293 (22), 256 (18), 218 (10), 150 (41), 126 (38), 110 (56), 85 (46), 75 (93), 69 (100), 57 (61) [$C_4H_9^+$], 41 (99); HRMS (EI): *m*/*z*: calcd for $C_{20}H_{31}CrNO_7Si$: 477.1274 (correct HRMS).

Pentacarbonyl[(2*E*)-4-(*tert*-butyldimethylsilyloxy)-3-dibenzylamino-1-ethoxy-2-penten-1-ylidene]chromium [(*E*)-2 gb] and pentacarbonyl[4-(*tert*-butyldimethylsilyloxy)-3-dibenzylamino-1,2-pentadienylidene]chromium (3 gb): According to GP 1, complex **1 g** (2.16 g, 5.00 mmol) in Et_2O (25 mL) was treated at 20 °C with dibenzylamine (1.28 g, 6.50 mmol). After chromatography [100 g silica gel, elution with pentane/Et_2O (5:1)], (*E*)-**2 gb** (R_f = 0.33) and **3 gb** (R_f = 0.09) were obtained as yellow crystals (2.58 g, 82%), m.p. 95 °C, and orange crystals (379 mg, 13%), m.p. 78 °C, respectively. (*E*)-**2 gb**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11 (s, 3H, $SiCH_3$), 0.14 (s, 3H, $SiCH_3$), 0.94 [s, 9H, SiC(CH_3)$_3$], 1.50 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 1.58 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 4.52 [br s, 4H, N(CH_2)$_2$], 4.83 (m, 2H, OCH_2CH_3), 5.78 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.53 (s, 1H, 2-H), 7.12–7.22 (m, 4H, Ph-H), 7.30–7.46 (m, 6H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.1, −4.8 (+, $SiCH_3$), 15.6 (+, OCH_2CH_3), 18.1 [C_{quat}, SiC(CH_3)$_3$], 22.4 (+, $CHCH_3$), 25.7 [+, SiC-(CH_3)$_3$], 55.1 [−, N(CH_2-)$_2$], 67.3 (+, $CHCH_3$), 74.0 (−, OCH_2CH_3), 118.4 (+, C-2), 126.6, 127.7, 129.0 (+, C-Ph), 136.7 (C_{quat}, C-Ph), 159.2 (C_{quat}, C-3), 218.5, 224.2 (C_{quat}, C=O), 296.6 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 3080, 3048, 3018, 2032 (C=O), 1960 (C=O), 1905 (C=O), 1500, 1459 cm^{-1}; MS (70 eV): *m*/*z* (%): 629 (0.1) [M^+], 573 (0.4) [M^+−2CO], 545 (2) [M^+−3CO], 517 (0.3) [M^+−4CO], 489 (19) [M^+−5CO], 391 (11), 376 (27), 334 (18), 260 (46), 228 (16), 159 (14), 91 (100) [$PhCH_2^+$], 73 (58), 65 (17), 52 (10) [Cr^+]; HRMS (EI): *m*/*z*: calcd for $C_{32}H_{39}CrNO_7Si$: 629.1900 (correct HRMS).

Compound 3 gb: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.10 (s, 3H, $SiCH_3$), 0.12 (s, 3H, $SiCH_3$), 0.63 [s, 9H, SiC(CH_3)$_3$], 1.60 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 4.91–5.19 [m, 5H, $CHCH_3$, N(CH_2-)$_2$], 7.12–7.23 (m, 4H, Ph-H), 7.30–7.50 (m, 6H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −4.6, −4.5 (+, $SiCH_3$), 18.1 [C_{quat}, SiC(CH_3)$_3$], 22.5 (+, $CHCH_3$), 25.6 [+, SiC(CH_3)$_3$], 52.5 (−, NCH_2), 57.5 (−, NCH_2), 71.6 (+, $CHCH_3$), 123.8 (C_{quat}, C-2), 127.0, 128.7, 128.9, 129.0, 129.1, 129.5 (+, C-Ph), 133.5, 133.7 (C_{quat}, C-Ph), 157.5 (C_{quat}, C-3), 217.3, 223.3 (C_{quat}, C=O), 235.4 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 3048, 3021, 2840, 1974 (C=O), 1933 (C=O), 1522 cm^{-1}; MS (70 eV): *m*/*z* (%): 583 (3) [M^+], 471 (11) [M^+−4CO], 443 (3) [M^+−5CO], 428 (22) [M^+−5CO−CH_3], 386 (13) [M^+−5CO−C_4H_9], 337 (32), 309 (64), 291 (78), 149 (35), 91 (59) [$PhCH_2^+$], 75 (100), 52 (21) [Cr^+]; elemental analysis calcd for $C_{30}H_{33}CrNO_6Si$ (583.7): C 61.73, H 5.70, N 2.40; found C 62.26, H 6.01, N 2.47; calcd 583.1537 (correct HRMS).

Pentacarbonyl[(2*E*)-3-dimethylamino-1-ethoxy-4-(trimethylsilyloxy)-2-penten-1-ylidene]chromium [(*E*)-2 ha]: According to GP 1, complex **1 h** (1.95 g, 5.00 mmol) in Et_2O (25 mL) was treated at 20 °C with dimethylamine. After chromatography [100 g silica gel, elution with pentane/Et_2O (5:1)], (*E*)-**2 ha** (R_f = 0.32) was obtained as yellow crystals (2.13 g, 98%). M.p. 134 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 9H, Si(CH_3)$_3$], 1.41 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 1.51 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 3.22 [br s, 6H, N(CH_3)$_2$], 4.72 (m, 2H, OCH_2CH_3), 5.68 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.22 (s, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −0.4 [+, Si(CH_3)$_3$], 15.6 (+, OCH_2CH_3), 21.4 (+, $CHCH_3$), 42.8 [+, N(CH_3)$_2$], 66.7 (+, $CHCH_3$), 77.0 (−, OCH_2CH_3), 117.3 (+, C-2), 160.2 (C_{quat}, C-3), 219.2, 224.3 (C_{quat}, C=O), 298.9 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$ = 2961, 2045 (C=O), 1957 (C=O), 1937 (C=O), 1905 (C=O), 1630, 1537, 1479 cm^{-1}; MS (70 eV): *m*/*z* (%): 435 (12) [M^+], 407 (5) [M^+−CO], 379 (2) [M^+−2CO], 351 (15) [M^+−3CO], 323 (11) [M^+−4CO], 295 (63) [M^+−5CO], 251 (39) [M^+−5CO−N(CH_3)$_2$], 205 (6), 154 (75), 126 (51), 110 (100), 95 (11), 84 (19), 72 (21), 52 (6) [Cr^+], 44 (20) [N(CH_3)$_2^+$]; HRMS (EI): *m*/*z*: calcd for $C_{17}H_{25}CrNO_7Si$: 435.0805 (correct HRMS).

Pentacarbonyl[(2*E*)-3-dibenzylamino-1-ethoxy-4-(trimethylsilyloxy)-2-penten-1-ylidene]chromium [(*E*)-2 hb] and pentacarbonyl[3-dibenzylamino-4-(trimethylsilyloxy)-1,2-pentadienylidene]chromium (3 hb): According to GP 1, complex **1 h** (1.95 g, 5.00 mmol) in Et_2O (25 mL) was treated at 20 °C with dibenzylamine (1.28 g, 6.50 mmol). After chromatography [100 g silica gel, elution with pentane/Et_2O (5:1)], (*E*)-**2 hb** (R_f = 0.27)

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

and **3hb** (R_f=0.11) were obtained as yellow crystals (2.32 g, 79%), m.p. 122°C, and a red oil (460 mg, 17%), respectively. (*E*)-**2hb**: ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.02 [s, 9H, $Si(CH_3)_3$], 1.51 (d, ^3J=7.2 Hz, 3H, $CHCH_3$), 1.57 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 4.35–5.12 [m, 6H, OCH_2CH_3, $N(CH_2\text{-})_2$], 5.86 (q, ^3J=7.2 Hz, 1H, $CHCH_3$), 6.50 (s, 1H, 2-H), 7.11–7.19 (m, 4H, Ph-H), 7.31–7.42 (m, 6H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=−0.4 [+, $Si(CH_3)_3$], 15.6 (+, OCH_2CH_3), 22.6 (+, $CHCH_3$), 55.2 [−, $N(CH_2\text{-})_2$], 66.8 (+, $CHCH_3$), 74.1 (−, OCH_2CH_3), 118.0 (+, C-2), 126.5, 127.6, 128.8 (+, C-Ph), 135.1 (C_{quat}, C-Ph), 159.2 (C_{quat}, C-3), 218.6, 224.5 (C_{quat}, C=O), 295.3 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$=3033, 2963, 2047 (C=O), 1924 (C=O), 1684 cm^{-1}; MS (70 eV): *m*/*z* (%): 587 (5) [M^+], 503 (6) [M^+−3CO], 445 (11), 395 (11), 334 (12), 320 (38), 304 (22), 261 (9), 147 (13), 117 (12), 91 (100) [$PhCH_2^+$], 73 (82) [$Si(CH_3)_3^+$], 57 (20), 52 (19) [Cr^+], 43 (24); HRMS (EI): *m*/*z*: calcd for $C_{29}H_{33}CrNO_7Si$: 587.1431 (correct HRMS).

Compound 3hb: ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.09 [s, 9H, $Si(CH_3)_3$], 1.62 (d, ^3J=7.2 Hz, 3H, $CHCH_3$), 4.75–5.22 [m, 5H, $CHCH_3$, $N(CH_2\text{-})_2$], 7.08–7.53 (m, 10H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=0.1 [+, $Si(CH_3)_3$], 22.6 (+, $CHCH_3$), 52.6, 57.4 [−, $N(CH_2\text{-})$], 71.1 (+, $CHCH_3$), 123.4 (C_{quat}, C-2), 127.1, 128.6, 128.8, 129.0, 129.1, 129.3 (+, C-Ph), 133.5, 133.7 (C_{quat}, C-Ph), 157.5 (C_{quat}, C-3), 217.2, 223.8 (C_{quat}, C=O), 235.7 (C_{quat}, C-1); IR (film): $\tilde{\nu}$=3071, 3033, 2155 (C≡C≡C), 2076 (C=O), 1984 (C=O), 1938 (C=O), 1652 cm^{-1}; MS (70 eV): *m*/*z* (%): 541 (14) [M^+], 485 (0.3) [M^+−2CO], 429 (39) [M^+−4CO], 401 (25) [M^+−5CO], 386 (100) [M^+−5CO−CH_3], 310 (6), 295 (16), 126 (19), 91 (61) [$C_7H_7^+$], 73 (14) [$Si(CH_3)_3^+$], 53 (21); HRMS (EI): *m*/*z*: calcd for $C_{27}H_{27}CrNO_6Si$: 541.1012 (correct HRMS).

The same experiment, when carried out at −78°C, gave (*E*)-**2hb** (2.67 g, 91%) and **3hb** (108.2 mg, 4%).

Pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-3-(2′-methyldioxolan-2′-yl)-2-propen-1-ylidene]chromium [(*Z*)-2ia]: According to GP 1, complex **1i** (500 mg, 1.39 mmol) in Et_2O (14 mL) was treated at 20°C with dimethylamine. After chromatography [50 g silica gel, elution with pentane/Et_2O (5:1)], (*Z*)-**2ia** (R_f=0.19) was obtained as yellow crystals (519 mg, 92%). M.p. 134°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.48 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.61 (s, 3H, CH_3), 3.11 [s, 6H, $N(CH_3)_2$], 3.92 (m, 4H, OCH_2CH_2O), 4.71 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.64 (s, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=15.8 (+, OCH_2CH_3), 25.0 (+, CH_3), 45.5 [+, $N(CH_3)_2$], 64.7 (−, OCH_2CH_2O), 73.3 (−, OCH_2CH_3), 107.6 [C_{quat}, $C(OCH_2)_2$], 114.5 (+, C-2), 158.0 (C_{quat}, C-3), 219.2, 224.5 (C_{quat}, C=O), 288.8 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$=2994, 2049 (C=O), 1977 (C=O), 1935 (C=O), 1659 cm^{-1}; MS (70 eV): *m*/*z* (%): 405 (16) [M^+], 377 (5) [M^+−CO], 349 (4) [M^+−2CO], 321 (7) [M^+−3CO], 293 (12) [M^+−4CO], 265 (40) [M^+−5CO], 235 (41), 205 (100), 191 (11), 161 (11), 121 (15), 96 (27), 87 (84) [$C_4H_7O_2^+$], 73 (19), 52 (24) [Cr^+], 43 (45); HRMS (EI): *m*/*z*: calcd for $C_{16}H_{19}CrNO_8$: 405.0515 (correct HRMS).

Pentacarbonyl[(2*Z*)-3-dibenzylamino-1-ethoxy-3-(2′-methyldioxolan-2′-yl)-2-propen-1-ylidene]chromium [(*Z*)-2ib]: According to GP 1, complex **1i** (500 mg, 1.39 mmol) in Et_2O (14 mL) was treated at −115°C with dibenzylamine (335 mg, 1.70 mmol). After chromatography [50 g silica gel, elution with pentane/Et_2O (5:1)], (*Z*)-**2ib** (R_f=0.43) was obtained as an orange oil (680 mg, 88%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.23 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.68 (s, 3H, CH_3), 4.02 (brs, 4H, OCH_2CH_2O), 4.35 [brs, 4H, $N(CH_2\text{-})_2$], 4.79 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 7.10 (brs, 5H, 2-H, Ph-H), 7.35 (brs, 6H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=15.6 (+, OCH_2CH_3), 26.3 (+, CH_3), 57.1 [−, $N(CH_2\text{-})_2$], 65.1 (−, OCH_2CH_2O), 74.6 (−, OCH_2CH_3), 108.1 [C_{quat}, $C(OCH_2)_2$], 115.9 (+, C-2), 128.2, 128.8 (+, C-Ph), 136.2 (C_{quat}, C-Ph), 155.0 (C_{quat}, C-3), 218.7, 224.4 (C_{quat}, C=O), 298.0 (C_{quat}, C-1); IR (film): $\tilde{\nu}$=3064, 3026, 2982, 2049 (C=O), 1973 (C=O), 1919 (C=O), 1638 cm^{-1}; MS (70 eV): *m*/*z* (%): 557 (2) [M^+], 529 (3) [M^+−CO], 501 (1) [M^+−2CO], 445 (<1) [M^+−4CO], 417 (1) [M^+−5CO], 365 (3) [M^+−$Cr(CO)_5$], 319 (45), 304 (100), 115 (6), 108 (35), 91 (84) [$C_7H_7^+$], 52 (43) [Cr^+]; HRMS (EI): *m*/*z*: calcd for $C_{28}H_{27}CrNO_8$: 557.1141 (correct HRMS).

Pentacarbonyl[(2*Z*)-3-adamantyl-3-dimethylamino-1-ethoxy-2-propen-1-ylidene]chromium [(*Z*)-2ja]: According to the one-pot procedure as previously reported,[16] complex (*Z*)-**2ja** was prepared from adamantylethyne (624 mg, 3.89 mmol) in THF (40 mL), *n*-butyllithium (1.60 mL, 2.36 M in *n*-hexane, 3.78 mmol), hexacarbonyl-chromium (880 mg, 4.00 mmol), triethyloxonium tetrafluoroborate (855 mg, 4.50 mmol) and then gaseous dimethylamine. After chromatography [50 g silica gel, elution with pentane/Et_2O (3:1)], (*Z*)-**2ja** (R_f=0.55, Et_2O) was obtained as yellow crystals (1.59 g, 90%). M.p. 102°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.40 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.72 (brs, 6H, 4′-H), 2.02 (brs, 6H, 2′-H), 2.09 (brs, 3H, 3′-H), 3.19 [brs, 6H, $N(CH_3)_2$], 4.58 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.21 (s, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=15.9 (+, OCH_2CH_3), 28.4 (+, C-3′), 36.2 (−, C-4′), 39.4 (−, C-2′), 41.3 (C_{quat}, C-1′), 46.4 [+, $N(CH_3)_2$], 72.2 (−, OCH_2CH_3), 116.6 (+, C-2), 170.6 (C_{quat}, C-3), 219.8, 224.6 (C_{quat}, C=O), 283.3 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$=2909, 2044 (C=O), 1961 (C=O), 1878 (C=O), 1540 cm^{-1}; MS (70 eV): *m*/*z* (%): 453 (2) [M^+], 425 (4) [M^+−CO], 397 (6) [M^+−2CO], 369 (10) [M^+−3CO], 341 (13) [M^+−4CO], 313 (100) [M^+−5CO], 267 (25), 256 (50), 215 (40), 185 (10), 158 (49), 135 (17), 95 (19), 79 (23), 52 (71) [Cr^+]; elemental analysis calcd for $C_{22}H_{27}CrNO_6$ (453.5): C 58.27, H 6.00; found C 58.42, H 6.14.

Pentacarbonyl[(2*Z*)-3-adamantyl-3-dibenzylamino-1-ethoxy-2-propen-1-ylidene]chromium [(*Z*)-2jb]: According to the one-pot procedure as previously reported,[16] complex (*Z*)-**2jb** was prepared from adamantylethyne (416 mg, 2.61 mmol) in THF (40 mL), *n*-butyllithium (1.1 mL, 2.36 M in *n*-hexane, 2.6 mmol), hexacarbonyl-chromium (572 mg, 2.60 mmol), triethyloxonium tetrafluoroborate (570 mg, 3.00 mmol) and dibenzylamine (985 mg, 5.00 mmol). After chromatography [50 g silica gel, elution with pentane/Et_2O (3:1)], (*Z*)-**2jb** (R_f=0.58, Et_2O) was obtained as yellow crystals (1.15 g, 72%). M.p. 126°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.05 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.76 (brs, 6H, 4′-H), 2.12 (brs, 3H, 3′-H), 2.20 (brs, 6H, 2′-H), 4.31 [brs, 4H, $N(CH_2\text{-})_2$], 4.68 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.70 (s, 1H, 2-H), 7.10–7.20 (m, 4H, Ph-H), 7.35–7.48 (m, 6H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=15.8 (+, OCH_2CH_3), 28.6 (+, C-3′), 36.2 (−, C-4′), 41.2 (−, C-2′), 41.7 (C_{quat}, C-1′), 57.8 [−, $N(CH_2\text{-})_2$], 74.3 (−, OCH_2CH_3), 118.3 (+, C-2), 128.3, 128.7 (+, C-Ph), 136.1 (C_{quat}, C-Ph), 166.6 (C_{quat}, C-3), 219.0, 224.4 (C_{quat}, C=O), 283.4 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$=2901, 2046 (C=O), 1928 (C=O), 1894 (C=O), 1479, 1453 cm^{-1}.

Pentacarbonyl[(2*E*)- and (2*Z*)-3-dibenzylamino-1-dimethylamino-4-methyl-4-(trimethylsilyloxy)-2-penten-1-ylidene]chromium [(*E*/*Z*)-9c]: According to GP 1, complex **3cb** (400 mg, 0.72 mmol) in Et_2O (6 mL) was treated at 20°C with dimethylamine. After filtration on silica gel (3 g) and washing with Et_2O, (*E*/*Z*)-**9c** (R_f=0.43; *E*/*Z* 2:1) was obtained as yellow crystals (432 mg, 100%). ^{1}H NMR (250 MHz, $CDCl_3$): (*E*)-**9c**: δ=0.18 [s, 9H, $Si(CH_3)_3$], 1.12 [s, 3H, CCH_3], 1.59 [s, 3H, CCH_3], 3.09 (s, 3H, NCH_3), 3.73 (d, ^2J=14.1 Hz, 2H, NCH_2), 3.78 (s, 3H, NCH_3), 4.38 (d, ^2J=14.1 Hz, 2H, NCH_2), 6.22 (s, 1H, 2-H), 7.23–7.44 (m, 10H, Ph-H); (*Z*)-**9c**: δ=0.30 [s, 9H, $Si(CH_3)_3$], 1.88 [s, 3H, CCH_3], 1.90 [s, 3H, CCH_3], 2.79 (s, 3H, NCH_3), 3.62 (d, ^2J=14.4 Hz, 2H, NCH_2), 3.66 (s, 3H, NCH_3), 4.70 (d, ^2J=14.4 Hz, 2H, NCH_2), 5.96 (s, 1H, 2-H), 7.23–7.44 (m, 10H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): (*E*)-**9c**: δ=2.8 [+, $Si(CH_3)_3$], 27.7, 28.7 [+, $C(CH_3)_2$], 45.8, 50.8 (+, NCH_3), 59.7 [−, $N(CH_2\text{-})_2$], 78.1 [C_{quat}, $C(CH_3)_2$], 116.3 (+, C-2), 127.1, 128.1, 130.1 (+, C-Ph), 138.8 (C_{quat} C-Ph), 139.7 (C_{quat}, C-3), 217.9, 223.0 (C_{quat}, C=O), 264.6 (C_{quat}, C-1); (*Z*)-**9c**: δ=3.3 [+, $Si(CH_3)_3$], 32.2, 32.7 [+, $C(CH_3)_2$], 45.4, 50.1 (+, NCH_3), 52.8 [−, $N(CH_2\text{-})_2$], 78.2 [C_{quat}, $C(CH_3)_2$], 116.3 (+, C-2), 127.3, 128.2, 131.0 (+, C-Ph), 138.8 (C_{quat} C-Ph), 143.6 (C_{quat}, C-3), 217.8, 223.6 (C_{quat}, C=O), 267.7 (C_{quat}, C-1); IR (KBr): $\tilde{\nu}$=3044, 3010, 2981, 2942, 2020 (C=O), 1966 (C=O), 1921 (C=O), 1540, 1490, 1448 cm^{-1}; MS (70 eV): *m*/*z* (%): 600 (3) [M^+], 572 (3) [M^+−CO], 544 (1) [M^+−2CO], 516 (7) [M^+−3CO], 488 (10) [M^+−4CO], 460 (37) [M^+−5CO], 406 (43), 391 (13), 363 (19), 348 (52), 319 (51), 131 (19), 106 (24), 91 (58) [$C_7H_7^+$], 86 (65), 84 (100), 75 (38), 52 (12) [Cr^+]; HRMS (EI): *m*/*z*: calcd for $C_{30}H_{36}CrN_2O_6Si$: 600.1747 (correct HRMS).

4-Ethoxy-2,5,7-triphenylcyclopenta[*b*]pyran (4a-Ph): *Variant A*: According to GP 2, complex (*E*)-**2aa** (437 mg, 1.10 mmol) in THF (22 mL) was treated with phenylethyne (900 mg, 8.81 mmol), and the mixture was heated for 16 h. After chromatography [50 g silica gel, elution with hexane/chloroform (2:1)], **4a**-Ph (R_f=0.49) was obtained as red crystals (103 mg, 24%). M.p. 179°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.35 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 4.28 (q, ^3J=7.0 Hz, 2H, OCH_2), 6.72 (s, 1H, 6-

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

H), 7.06–7.20 (m, 3H, Ph-H, 3-H), 7.22–7.48 (m, 7H, Ph-H), 7.59 (d, ^3J= 7.1 Hz, 2H, Ph-H), 7.81–7.93 (m, 4H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.5 (+, OCH_2CH_3), 65.0 (−, OCH_2), 91.8 (+, C-6), 108.0, 109.7, 117.3 (C_{quat}, C-4a,5,7), 124.3, 124.9, 125.6, 126.0, 127.4, 128.6, 129.16, 129.19, 130.7 (+, C-3, C-Ph), 132.7, 135.7, 138.3 (C_{quat}, C-Ph), 148.3, 159.5, 160.3 (C_{quat}, C-2,4,7a); IR (KBr): $\tilde{\nu}$=3015, 2980, 1622, 1600, 1490, 1428 cm^{-1}; MS (70 eV): *m*/*z* (%): 390 (100) [M^+], 362 (62) [$M^+-C_2H_4$], 259 (31), 181 (24), 129 (22); elemental analysis calcd for $C_{28}H_{22}O_2$ (390.5): C 86.13, H 5.68; found C 86.06, H 5.60.

Variant B: According to GP 2, complex (*E*)-**2ab** (400 mg, 0.73 mmol) in THF (15 mL) was treated with phenylethyne (596 mg, 5.84 mmol) and the mixture was heated for 14 h. **4a**-Ph (137 mg, 48%) was obtained after chromatography on silica gel (50 g).

Variant C: According to GP 2, complex (*E*)-**2ac** (190 mg, 0.42 mmol) in THF (8.5 mL) was treated with phenylethyne (343 mg, 3.36 mmol) and the mixture was heated for 15 h. **4a**-Ph (71 mg, 43%) was obtained after chromatography on silica gel (50 g).

Variant D: According to GP 2, complex (*E*)-**2ad** (459 mg, 1.09 mmol) in THF (22 mL) was treated with phenylethyne (891 mg, 8.72 mmol) and the mixture was heated for 3 d. Compound **4a**-Ph (21 mg, 5%) was obtained after chromatography on silica gel (15 g).

Variant E: According to GP 2, complex (*E*)-**2ae** (100 mg, 0.22 mmol) in THF (5 mL) was treated with phenylethyne (180 mg, 1.76 mmol) and the mixture was heated for 3 d. Compound **4a**-Ph (15 mg, 17%) was obtained after chromatography on silica gel (10 g).

4-Ethoxy-2-phenyl-5,7-dipropylcyclopenta[*b*]pyran (4a-*n*Pr): *Variant A*: According to GP 2, complex (*E*)-**2aa** (416 mg, 1.05 mmol) in THF (20 mL) was treated with 1-pentyne (690 mg, 10.1 mmol), and the mixture was heated for 37 h. After chromatography [50 g silica gel, elution with pentane/Et_2O (10:1)], **4a**-*n*Pr (R_f=0.44) was obtained as a red oil (67 mg, 19%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.00 (t, ^3J=7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.04 (t, ^3J=7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.54 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.70 (tq, ^3J=7.4, ^3J=7.4 Hz, 2H, $CH_2CH_2CH_3$), 1.77 (tq, ^3J=7.4, ^3J=7.4 Hz, 2H, $CH_2CH_2CH_3$), 2.72 (t, ^3J=7.4 Hz, 2H, $CH_2CH_2CH_3$), 2.81 (t, ^3J=7.4 Hz, 2H, $CH_2CH_2CH_3$), 4.37 (q, ^3J=7.0 Hz, 2H, OCH_2), 6.58 [s, 1H, 6-H(3-H)], 6.65 [s, 1H, 3-H(6-H)], 7.46–7.57 (m, 3H, Ph-H), 7.89–7.94 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.2, 14.4, 14.7 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 23.8, 25.1 (−, $CH_2CH_2CH_3$), 27.5, 31.6 (−, $CH_2CH_2CH_3$), 64.2 (−, OCH_2), 90.3 (+, C-6), 105.3, 109.7, 115.2 (C_{quat}, C-4a,5,7), 125.7, 126.0, 128.8, 129.9 (+, C-3, C-Ph), 133.6 (C_{quat}, C-Ph), 145.3, 158.0, 174.1 (C_{quat}, C-2,4,7a); IR (film): $\tilde{\nu}$=3015, 2980, 1622, 1600 cm^{-1}; MS (70 eV): *m*/*z* (%): 322 (8) [M^+], 301 (43), 257 (100), 217 (10), 182 (17), 166 (29), 137 (32), 105 (54), 77 (36), 43 (54); HRMS (EI): *m*/*z*: calcd for $C_{22}H_{26}O_2$: 322.1932 (correct HRMS).

Variant B: According to GP 2, complex (*E*)-**2ae** (100 mg, 0.22 mmol) in THF (5 mL) was treated with 1-pentyne (120 mg, 1.76 mmol) and the mixture was heated for 3 d. **4a**-*n*Pr (8 mg, 11%) was obtained after chromatography on silica gel (10 g).

4-Ethoxy-2-(1′-ethoxy-1′-methylethyl)-5,7-diphenylcyclopenta[*b*]pyran (4b-Ph): *Variant A*: According to GP 2, complex (*Z*)-**2ba** (304 mg, 0.75 mmol) in THF (15 mL) was treated with phenylethyne (613 mL, 6.00 mmol), and the mixture was heated for 31 h. After chromatography [50 g silica gel, elution with pentane/Et_2O (1:1)], **4b**-Ph (R_f=0.62) was obtained as red crystals (151 mg, 51%). M.p. 127°C; IR (KBr): $\tilde{\nu}$=3070, 3047, 1939, 1639 (C=C), 1609 (C=C), 1510, 1072, 954, 765, 702, 680, 663 cm^{-1}. The other spectral data have previously been reported.[9]

Variant B: According to GP 2, complex (*Z*)-**2bb** (164 mg, 0.29 mmol) in THF (6 mL) was treated with phenylethyne (237 mg, 2.32 mmol) and the mixture was heated for 3 d. Compound **4b**-Ph (79 mg, 68%) was obtained after chromatography on silica gel (10 g).

Variant C: According to GP 2, complex (*Z*)-**2bc** (247 mg, 0.54 mmol) in THF (11 mL) was treated with phenylethyne (441 mg, 4.32 mmol) and the mixture was heated for 3 d. **4b**-Ph (91 mg, 42%) was obtained after chromatography on silica gel (15 g).

Variant D: According to GP 2, complex (*Z*)-**2bd** (384 mg, 0.89 mmol) in THF (18 mL) was treated with phenylethyne (727 mg, 7.12 mmol) and the mixture was heated for 3 d., **4b**-Ph (25 mg, 7%) was obtained after chromatography on silica gel (20 g).

4-Ethoxy-2-(1′-ethoxy-1′-methylethyl)-5,7-dipropylcyclopenta[*b*]pyran (4b-*n*Pr): *Variant A*: According to GP 2, complex (*Z*)-**2ba** (304 mg, 0.75 mmol) in THF (15 mL) was treated with 1-pentyne (409 mg, 6.00 mmol), and the mixture was heated for 165 h. After chromatography [50 g silica gel, elution with pentane/Et_2O (1:1)], **4b**-*n*Pr (R_f=0.51) was obtained as red crystals (148 mg, 59%). M.p. 132°C; ^{1}H NMR (250 MHz, C_6D_6): δ=0.72 (t, ^3J=7.0 Hz, 3H, $CH_2CH_2CH_3$), 0.79 (t, ^3J=7.0 Hz, 3H, $CH_2CH_2CH_3$), 1.10 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.39 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.46 [s, 6H, $C(CH_3)_2$], 1.51–1.57 (m, 4H, $CH_2CH_2CH_3$), 2.53 (t, ^3J=7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.66 (t, ^3J=7.0 Hz, 2H, $CH_2CH_2CH_3$), 3.39 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 4.18 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.26 (s, 1H, 6-H), 6.49 (s, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.0, 14.2, 14.3, 14.9 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 23.9, 25.1 (−, $CH_2CH_2CH_3$), 26.1 [+, $C(CH_3)_2$], 27.6, 31.7 (−, $CH_2CH_2CH_3$), 64.1 (−, OCH_2CH_3), 68.2 (−, OCH_2CH_3), 76.7 [C_{quat}, $C(CH_3)_2$], 89.8 (+, C-6), 105.2, 115.0, 125.2 (C_{quat}, C-4a,5,7), 128.8 (+, C-3), 134.7 (C_{quat}, C-7a), 158.2, 166.2 (C_{quat}, C-2,4); IR (KBr): $\tilde{\nu}$=2974, 2949, 2882, 1780, 1647 (C=C), 1470, 1385, 1303 cm^{-1}; MS (70 eV): *m*/*z* (%): 332 (41) [M^+], 303 (100) [$M^+-C_2H_5$], 287 (6), 276 (8), 257 (9), 245 (4), 231 (4), 201 (5), 139 (4), 122 (5), 87 (19), 82 (3), 67 (4), 55 (4); HRMS (EI): *m*/*z*: calcd for $C_{21}H_{32}O_3$: 332.2351 (correct HRMS).

Variant B: According to GP 2, complex (*Z*)-**2bb** (500 mg, 0.90 mmol) in THF (18 mL) was treated with 1-pentyne (490 mg, 7.20 mmol), and the mixture heated for 2 d. After chromatography [40 g silica gel, elution with pentane/Et_2O (1:1)], along with **4b**-*n*Pr (69 mg, 23%), 2-dibenzylamino-5-(1′-ethoxy-1′-methylethyl)furan (**5**) (R_f=0.03) was obtained as a colorless oil (157 mg, 50%). **5**: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.01 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.52 (s, 6H, $C(CH_3)_2$], 3.28 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 5.61 (s, 2H, NCH_2), 6.21 (d, ^3J=3.5 Hz, 1H, =CH), 6.24 (d, ^3J=3.5 Hz, 1H, =CH), 6.68 (s, 1H, NCH), 6.76 (s, 1H, NCH), 7.09–7.32 (m, 10H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=15.7 (+, OCH_2CH_3), 28.3 [+, $C(CH_3)_2$], 48.2 [−, $N(CH_2\text{-})_2$], 58.2 (−, OCH_2CH_3), 74.2 [C_{quat}, $C(CH_3)_2$], 107.9 (+, =CH), 108.5 (+, =CH), 125.5, 126.3, 126.9, 128.0, 128.1, 129.3 (+, C-Ph), 133.7, 136.7 (C_{quat}, C-Ph), 136.8 (C_{quat}, C-2), 140.2 (C_{quat}, C-5); IR (film): $\tilde{\nu}$=3100, 3078, 2962, 1600, 1598, 1575, 1565 cm^{-1}; MS (70 eV): *m*/*z* (%): 319 (25) [M^+-OCH_2], 304 (32), 274 (31), 210 (21), 182 (10), 91 (100) [$PhCH_2^+$], 59 (58), 43 (67).

4-Ethoxy-2-[1′-methyl-1′-(trimethylsilyloxy)ethyl]-5,7-diphenylcyclopenta[*b*]pyran (4c-Ph): *Variant A*: According to GP 2, complex (*Z*)-**2ca** (200 mg, 0.44 mmol) in THF (9 mL) was treated with phenylethyne (364 mg, 3.56 mmol) for 2 d. After chromatography [15 g silica gel, elution with pentane/Et_2O (5:1)], **4c**-Ph (R_f=0.49) was obtained as red crystals (177 mg, 90%). M.p. 129°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.21 [s, 9H, $Si(CH_3)_3$], 1.41 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.72 [s, 6H, $C(CH_3)_2$], 4.33 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.62 (s, 1H, 6-H), 7.08–7.21 (m, 2H, *p*-Ph-H), 7.32 (s, 1H, 3-H), 7.33–7.42 (m, 4H, *m*-Ph-H), 7.61 (m, 2H, *o*-Ph-H), 7.85 (m, 2H, *o*-Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=2.4 [+, $Si(CH_3)_3$], 14.5 (+, OCH_2CH_3), 29.9 [+, $C(CH_3)_2$], 64.8 (−, OCH_2CH_3), 74.9 [C_{quat}, $C(CH_3)_2$], 90.5 (+, C-6), 107.3, 117.0 (C_{quat}, C-5,7), 124.1, 124.4, 124.8, 125.3, 127.4, 128.5, 129.1 (+, C-Ph, C-3), 135.7, 135.7 (C_{quat}, C-Ph), 138.4, 148.3, 160.9, 170.3 (C_{quat}, C-2,4,4a,7a); IR (KBr): $\tilde{\nu}$=3075, 3044, 3010, 2980, 1723, 1629, 1598, 1575 cm^{-1}; UV (MeCN): λ_{max} (lg ε)=204 (4.532), 228 (4.443), 310 (4.517), 483 nm (2.986); MS (70 eV): *m*/*z* (%): 444 (4) [M^+], 158 (100), 131 (24), 115 (17), 73 (19); elemental analysis calcd for $C_{28}H_{32}O_3Si$ (444.6): C 75.63, H 7.25; found C 75.31, H 7.27; HRMS (EI): *m*/*z*: calcd for $C_{28}H_{32}O_3Si$: 444.2121 (correct HRMS).

Variant B: According to GP 2, complex (*Z*)-**2cb** (120 mg, 0.20 mmol) in THF (2 mL) was treated with phenylethyne (163 mg, 1.60 mmol) for 3 d. Compound **4c**-Ph (69 mg, 78%) was obtained after chromatography on silica gel (5 g).

Variant C: According to GP 2, complex (*Z*)-**2cf** (248 mg, 0.52 mmol) in THF (10 mL) was treated with phenylethyne (425 mg, 4.16 mmol) for 3 d.

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Compound **4c**-Ph (201 mg, 87%) was obtained after chromatography on silica gel (20 g).

4-Ethoxy-2-[1′-methyl-1′-(trimethylsilyloxy)ethyl]-5,7-di-*n*-propylcyclopenta[*b*]pyran (4c-*n*Pr): According to GP 2, complex (*Z*)-**2cf** (248 mg, 0.52 mmol) in THF (10 mL) was treated with 1-pentyne (283 mg, 4.16 mmol), and the mixture was heated for 6 d. After chromatography [20 g silica gel, elution with pentane/Et_2O (5:1)], **4c**-*n*Pr (R_f=0.41) was obtained as red crystals (48 mg, 25%). M.p. 122°C; ^{1}H and ^{13}C NMR data of the title compound have previously been reported.[18] IR (KBr): $\tilde{\nu}$=2977, 2948, 1651, 1607, 1548 cm^{-1}; UV (MeCN): λ_{max} (lg ε)=216 (4.222), 263 (4.007), 334 (3.813), 460 nm (2.528); MS (70 eV): *m*/*z* (%): 376 (13) [M^+], 347 (42), 322 (3), 290 (31), 244 (5), 196 (100), 131 (73), 122 (23), 73 (51); HRMS (EI): *m*/*z*: calcd for $C_{22}H_{36}O_3Si$: 376.2433 (correct HRMS).

4-Ethoxy-2-(1′-ethoxycyclopropyl)-5,7-diphenylcyclopenta[*b*]pyran (4d-Ph): *Variant A*: According to GP 2, complex (*Z*)-**2da** (300 mg, 0.74 mmol) in THF (15 mL) was treated with phenylethyne (600 mg, 5.87 mmol), and the mixture was heated for 50 h. After chromatography [30 g silica gel, elution with pentane/Et_2O (1:1)], **4d**-Ph (R_f=0.42) was obtained as red crystals (120 mg, 41%). M.p. 135°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.30 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.46 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.54–1.60 (m, 4H, *c*Pr-H), 3.68 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 4.38 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.70 (s, 1H, 6-H), 7.13 (tt, ^3J=7.1, ^4J=1.2 Hz, 1H, Ph-H), 7.19 (tt, ^3J=7.1, ^4J=1.2 Hz, 1H, Ph-H), 7.28 (s, 1H, 3-H), 7.33 (ddd, ^3J=7.1, ^4J=1.2, ^5J=0.4 Hz, 2H, Ph-H), 7.37 (ddd, ^3J=7.1, ^4J=1.2, ^5J=0.4 Hz, 2H, Ph-H), 7.64 (ddd, ^3J=7.1, ^4J=1.2, ^5J=0.4 Hz, 2H, Ph-H), 7.72 (ddd, ^3J=7.1, ^4J=1.2, ^5J=0.4 Hz, 2H, Ph-H); ^{13}C NMR (125.7 MHz, $CDCl_3$, plus APT): δ=14.9 (+, OCH_2CH_3), 16.0 (+, OCH_2CH_3), 16.8 (−, *c*Pr-CH_2), 62.0 (−, *c*Pr-C), 63.0 (−, OCH_2CH_3), 63.1 (−, OCH_2CH_3), 92.0 (+, C-6), 107.3, 108.3, 117.3 (−, C-4a,5,7), 124.0, 124.5, 124.8, 125.3, 125.5, 127.5, 129.5, 129.6 (+, C-Ph, C-3), 136.0, 138.8 (−, C-Ph), 148.0 (−, C-7a), 160.6, 163.2 (−, C-2,4); IR (KBr): $\tilde{\nu}$=3071, 3042, 1637, 1604, 1502 cm^{-1}; MS (70 eV): *m*/*z* (%): 398 (100) [M^+], 370 (35) [$M^+-C_2H_4$], 342 (7), 325 (7), 313 (5), 259 (10); elemental analysis calcd for $C_{27}H_{26}O_3$ (398.5): C 81.38, H 6.58; found C 81.40, H 6.59.

Variant B: According to GP 2, complex (*Z*)-**2 db** (128 mg, 0.23 mmol) in THF (5 mL) was treated with phenylethyne (188 mg, 1.84 mmol), and the mixture was heated for 26 h. Compound **4d**-Ph (43 mg, 47%) was obtained after chromatography on silica gel (10 g).

4-Ethoxy-2-(1′-ethoxycyclopropyl)-5,7-di-*n*-propylcyclopenta[*b*]pyran (4d-*n*Pr): According to GP complex (*Z*)-**2da** (240 mg, 0.60 mmol) in THF (15 mL) was treated with 1-pentyne (326 mg, 4.79 mmol), and the mixture was heated for 100 h. After chromatography [30 g silica gel, elution with pentane/Et_2O (1:1)], **4d**-*n*Pr (R_f=0.53) was obtained as red crystals (65 mg, 33%). M.p. 123°C; ^{1}H NMR (250 MHz, C_6D_6): δ =0.96–1.29 (m, 16H, OCH_2CH_3, $CH_2CH_2CH_3$, *c*Pr-H), 1.84–1.93 (m, 4H, $CH_2CH_2CH_3$), 2.81 (t, ^3J=7.0 Hz, 2H, $CH_2CH_2CH_3$), 3.14 (t, ^3J=7.0 Hz, 2H, $CH_2CH_2CH_3$), 3.28 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.26 (s, 1H, 6-H), 6.77 (s, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus APT): δ=14.4, 14.4, 14.7, 15.6, 15.7 (+, $CH_2CH_2CH_3$, OCH_2CH_3, *c*Pr-C), 16.5, 25.7 (−, $CH_2CH_2CH_3$), 28.1, 32.5 (−, $CH_2CH_2CH_3$), 61.8 (−, C-1′), 63.8 (−, OCH_2CH_3), 90.6 (+, C-6), 105.3, 110.2 (−, C-5,7), 115.7 (−, C-4a), 125.9 (+, C-3), 145.9, 157.5, 161.9 (−, C-2,4,7a); IR (KBr): $\tilde{\nu}$=2975, 2948, 2881, 1780, 1704, 1651, 1559, 1480 cm^{-1}; MS (70 eV): *m*/*z* (%): 330 (29) [M^+], 301 (100) [$M^+-C_2H_5$], 273 (14), 257 (20), 245 (11); HRMS (EI): *m*/*z*: calcd for $C_{21}H_{30}O_3$: 330.2195 (correct HRMS).

2-(1′-Chlorocyclopropyl)-4-ethoxy-5,7-di-*n*-propylcyclopenta[*b*]pyran (4e-*n*Pr): According to GP 2, complex (*Z*)-**2ea** (299 mg, 0.76 mmol) in THF (15 mL) was treated with 1-pentyne (414 mg, 6.08 mmol), and the mixture was heated for 36 h. After chromatography [30 g silica gel, elution with pentane/Et_2O (5:1)], **4e**-*n*Pr (R_f=0.62) was obtained as a red oil (11 mg, 5%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.91 (m, 4H, *c*Pr-H), 1.41–1.71 (m, 9H, $CH_2CH_2CH_3$, OCH_2CH_3), 2.20–2.32 (m, 2H, $CH_2CH_2CH_3$), 2.32–2.42 (m, 2H, $CH_2CH_2CH_3$), 2.51 (t, ^3J=6.9 Hz, 2H, $CH_2CH_2CH_3$), 2.71 (t, ^3J=7.0 Hz, 2H, $CH_2CH_2CH_3$), 4.31 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.42 (s, 1H, 6-H), 6.58 (s, 1H, 3-H); IR (film): $\tilde{\nu}$=2959, 2930, 2888, 1640, 1455 cm^{-1}.

2-(1′-Chlorocyclopropyl)-4-ethoxy-5,7-phenylcyclopenta[*b*]pyran (4e-Ph): According to GP 2, complex (*Z*)-**2ea** (209 mg, 0.53 mmol) in THF (11 mL) was treated with phenylethyne (433 mg, 4.24 mmol), and the mixture was heated for 12 h. After chromatography [20 g silica gel, elution with pentane/Et_2O (5:1)], **4e**-Ph (R_f=0.33) was obtained as a red oil (173 mg, 84%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.42 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.69 (m, 2H, *c*-Pr-H), 1.82 (m, 2H, *c*-Pr-H), 4.38 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.80 (s, 1H, 6-H), 7.14–7.25 (m, 2H, Ph-H), 7.30–7.42 (m, 5H, Ph-H, 3-H), 7.61–7.70 (m, 2H, Ph-H), 7.71–7.80 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.4 (+, OCH_2CH_3), 19.6 (−, *c*Pr-C), 39.63 (C_{quat}, *c*Pr-C), 65.1 (−, OCH_2CH_3), 93.8 (+, C-6), 107.6, 109.0, 117.5 (C_{quat}, C-4a,5,7), 124.4, 125.0, 125.1, 125.2, 127.4, 128.6, 129.1 (+, C-Ph, C-3), 135.3, 138.1 (C_{quat}, C-Ph), 147.6 (C_{quat}, C-7a), 159.9, 161.6 (C_{quat}, C-2,4); IR (film): $\tilde{\nu}$=3048, 3025, 2980, 2929, 1629, 1599, 1492, 1444 cm^{-1}; MS (70 eV): *m*/*z* (%): 388 (100) [M^+], 360 (35) [$M^+-C_2H_4$], 326 (7), 259 (31), 232 (16), 202 (19), 149 (3), 129 (22), 102 (11), 57 (17); HRMS (EI): *m*/*z*: calcd for $C_{25}H_{21}ClO_2$: 388.1230 (correct HRMS).

2-Adamantyl-4-ethoxy-5,7-diphenylcyclopenta[*b*]pyran (4j-Ph): *Variant A*: According to GP 2, complex (*Z*)-**2ja** (455 mg, 1.00 mmol) in THF (20 mL) was treated with phenylethyne (817 mg, 8.00 mmol), and the mixture was heated for 15 h. After chromatography [20 g silica gel, elution with pentane/Et_2O (5:1)], **4j**-Ph (R_f=0.38) was obtained as red crystals (253 mg, 56%). M.p. 210°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.43 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.86 (brs, 6H, 4′-H), 2.12 (brs, 6H, 2′-H), 2.20 (brs, 3H, 3′-H), 4.32 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.24 (s, 1H, 6-H), 7.14–7.47 (m, 7H, 3-H, Ph-H), 7.67 (dd, ^3J=8.4, ^4J=1.1 Hz, 2H, Ph-H), 7.93 (dd, ^3J=8.4, ^4J=1.1 Hz, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.5 (+, OCH_2CH_3), 28.1 (+, C-3′), 36.49 (−, C-4′), 38.7 (C_{quat}, C-1′), 40.6 (−, C-2′), 64.7 (−, OCH_2CH_3), 90.0 (+, C-6), 107.2, 108.5, 116.6 (C_{quat}, C-4a,5,7), 123.95, 124.03, 124.6, 125.4, 127.4, 128.5, 129.1 (+, C-3, C-Ph), 135.8, 138.5 (C_{quat}, C-Ph), 148.7, 161.1, 172.3 (C_{quat}, C-2,4,7a); IR (KBr): $\tilde{\nu}$=2911, 2848, 1630, 1599, 1540, 1499 cm^{-1}; MS (70 eV): *m*/*z* (%): 448 (100) [M^+], 420 (22) [$M^+-C_2H_4$], 259 (13); HRMS (EI): *m*/*z*: calcd for $C_{32}H_{32}O_2$: 448.2402 (correct HRMS).

Variant B: According to GP 2, complex (*Z*)-**2jb** (400 mg, 0.66 mmol) in THF (20 mL) was treated with phenylethyne (539 mg, 5.28 mmol), and the mixture was heated for 6 h. Compound **4j**-Ph (140 mg, 47%) was obtained after chromatography on silica gel (20 g).

4-Ethoxy-2-[1′-methyl-1′-(trimethylsilyloxy)ethyl]-5,6-di-*n*-propylcyclopenta[*b*]pyran (8c-*n*Pr) and 6-dibenzylamino-4-ethoxy-7-oxa-1-oxo-2-*n*-propyl-6-[1′-methyl-1′-(trimethylsilyloxy)ethyl]-2,4-cycloheptadiene: According to GP 2, complex (*Z*)-**2cb** (253 mg, 0.42 mmol) in THF (8 mL) was treated with 1-pentyne (229 mg, 3.36 mmol), and the mixture was heated for 2 d. After chromatography [20 g silica gel, elution with pentane/Et_2O (5:1)], **8c**-*n*Pr (R_f=0.66) and the cycloheptadiene derivative (R_f=0.14) were obtained as a red (25 mg, 16%) and a yellow oil (20 mg, 9%), respectively. **8c**-*n*Pr: ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.23 [s, 9H, $Si(CH_3)_3$], 1.01 (t, ^3J=6.9 Hz, 6H, $CH_2CH_2CH_3$), 1.50 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.62 [s, 6H, $C(CH_3)_2$], 1.63–1.69 (m, 4H, $CH_2CH_2CH_3$), 2.63 (t, ^3J=6.9 Hz, 2H, $CH_2CH_2CH_3$), 2.79 (t, ^3J=7.0 Hz, 2H, $CH_2CH_2CH_3$), 4.30 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.44 (s, 1H, 7-H), 6.50 (s, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=2.4 [+, $Si(CH_3)_3$], 14.2, 14.3, 14.9 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 23.7, 25.1 (−, $CH_2CH_2CH_3$), 27.6, 29.8 (−, $CH_2CH_2CH_3$), 31.7 [+, $C(CH_3)_2$], 63.9 (−, OCH_2CH_3), 74.8 [C_{quat}, $C(CH_3)_2$], 88.7 (+, C-7), 104.7, 108.8 (C_{quat}, C-5,6), 114.9 (C_{quat}, C-4a), 124.7 (+, C-3), 145.4, 158.7, 168.6 (C_{quat}, C-2,4,7a).

6-Dibenzylamino-4-ethoxy-7-oxa-1-oxo-2-*n*-propyl-6-[1′-methyl-1′-(trimethylsilyloxy)ethyl-2,4-cycloheptadiene: ^{1}H NMR (250 MHz, $CDCl_3$): δ= 0.14 [s, 9H, $Si(CH_3)_3$], 0.86–1.00 (m, 6H, $CH_2CH_2CH_3$, OCH_2CH_3), 1.42–1.56 (m, 2H, $CH_2CH_2CH_3$), 1.62 [s, 6H, $C(CH_3)_2$], 2.28 (t, ^3J=6.9 Hz, 2H, $CH_2CH_2CH_3$), 4.24 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 4.51 [s, 4H, N-$(CH_2)_2$], 5.43 (s, 1H, 3-H), 6.13 (s, 1H, 5-H), 7.16–7.34 (m, 10H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=2.4 [+, $Si(CH_3)_3$], 14.1 (+, $CH_2CH_2CH_3$), 15.3 (+, OCH_2CH_3), 20.8 (−, $CH_2CH_2CH_3$), 31.8 [+, C-$(CH_3)_2$], 36.4 (−, $CH_2CH_2CH_3$), 57.4 [−, $N(CH_2)_2$], 65.8 (−, OCH_2CH_3), 77.2 [C_{quat}, $C(CH_3)_2$], 95.0 (C_{quat}, C-6), 99.0 (+, C-3), 127.1, 127.9, 128.3 (+, C-Ph), 131.9 (+, C-5), 137.7 (C_{quat}, C-Ph), 142.8 (C_{quat}, C-2), 170.7

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

(C_{quat}, C-4), 182.8 (C_{quat}, C-1); IR (film): $\tilde{\nu}$ = 3063, 1708 (C=O), 1646, 1613, 1456, 1383 cm^{-1}; MS (70 eV): *m/z* (%): 521 (9) [M^+], 476 (4) [$M^+ - C_2H_5O$], 430 (100) [$M^+ - C_7H_7$], 340 (37), 179 (5), 169 (18), 141 (25), 131 (66), 91 (99) [$C_7H_7^+$], 73 (49) [$C_3H_9Si^+$], 43 (5) [$C_3H_7^+$]; HRMS (EI): *m/z*: calcd for $C_{31}H_{43}NO_4Si$: 521.2961 (correct HRMS).

2-[1′-(*tert*-Butyldiphenylsilyloxy)ethyl]-4-ethoxy-5,7-diphenylcyclopenta[*b*]pyran (4 f-Ph) and 2-[1′-(*tert*-butyldiphenylsilyloxy)ethyl]-4-ethoxy-5,6-diphenylcyclopenta[*b*]pyran (8 f-Ph): *Variant A*: Following GP 2, complex (*E*)-**2 fa** (411 mg, 0.68 mmol) in THF (14 mL) was treated with phenylethyne (556 mg, 5.44 mmol), and the mixture was heated for 39 h. After chromatography [30 g silica gel, elution with pentane/Et_2O (5:1)], **8 f**-Ph (8 mg, 2%; R_f = 0.62) and **4 f**-Ph (160 mg, 39%; R_f = 0.39) were obtained as red oils. **8 f**-Ph: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 1.07 [s, 9H, $SiC(CH_3)_3$], 1.56 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 4.42 (m, 2H, OCH_2CH_3), 5.31 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.27 (s, 1H, 7-H), 6.98–7.50 (m, 19H, 3-H, Ph-H), 7.79–7.84 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.5 (+, OCH_2CH_3), 19.1 [C_{quat}, $SiC(CH_3)_3$], 25.1 (+, $CHCH_3$), 26.9 [+, $SiC(CH_3)_3$], 65.6 (−, OCH_2CH_3), 66.7 (+, $CHCH_3$), 80.5 (+, C-7), 107.5, 119.2 (C_{quat}, C-5,6), 124.5, 125.4, 125.8, 126.1, 126.7, 127.5, 127.6, 127.7, 128.1, 128.5, 128.7, 129.6, 129.7 (+, C-3, C-Ph), 133.7, 135.0, 135.6, 135.6 (C_{quat}, C-Ph), 139.3, 142.6, 156.4, 162.6 (C_{quat}, C-2,4,4a,7a).

Compound 4 f-Ph: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15 [s, 9H, $SiC(CH_3)_3$], 1.32 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.57 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 4.11 (m, 2H, OCH_2CH_3), 4.94 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.52 (s, 1H, 6-H), 7.04–7.43 (m, 13H, 3-H, Ph-H), 7.53–7.68 (m, 4H, Ph-H), 7.70–7.76 (m, 2H, Ph-H), 7.79–7.85 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.4 (+, OCH_2CH_3), 19.2 [C_{quat}, $SiC(CH_3)_3$], 23.4 (+, $CHCH_3$), 26.9 [+, $SiC(CH_3)_3$], 64.7 (−, OCH_2CH_3), 69.3 (+, $CHCH_3$), 91.7 (+, C-6), 107.5, 117.0 (C_{quat}, C-5,7), 124.1, 124.5, 124.8, 125.4, 127.4, 127.7, 127.8, 128.2, 128.4, 128.6, 129.1, 129.9, 130.1 (+, C-3, C-Ph), 132.8, 133.0, 135.5, 135.7 (C_{quat}, C-Ph), 138.3, 148.2, 160.3, 166.7 (C_{quat}, C-2,4,4a,7a); IR (film): $\tilde{\nu}$ = 3032, 2926, 2842, 1631, 1599, 1500 cm^{-1}; MS (70 eV): *m/z* (%): 596 (100) [M^+], 539 (1) [$M^+ - C_4H_9$], 199 (22), 111 (17), 97 (23), 85 (26), 71 (38), 57 (68) [$C_4H_9^+$]; HRMS (EI): *m/z*: calcd for $C_{40}H_{40}O_3Si$: 596.2746 (correct HRMS).

Variant B: According to GP 2, complex (*E*)-**2 fb** (280 mg, 0.37 mmol) in THF (8 mL) was treated with phenylethyne (302 mg, 2.96 mmol), and the mixture was heated for 16 h. **8 f**-Ph (49 mg, 22%) and **4 f**-Ph (163 mg, 74%) were obtained after chromatography on silica gel (15 g).

2-[1′-(*tert*-Butyldiphenylsilyloxy)ethyl]-4-ethoxy-5,7-di-*n*-propylcyclopenta[*b*]pyran (4 f-*n*Pr): *Variant A*: According to GP 2, complex (*E*)-**2 fa** (300 mg, 0.50 mmol) in THF (10 mL) was treated with 1-pentyne (272 mg, 4.00 mmol), and the mixture was heated for 2 d. After chromatography [30 g silica gel, elution with pentane/Et_2O (10:1)], **4 f**-*n*Pr (R_f = 0.51) was obtained as red crystals (33 mg, 13%). M.p. 134 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.1 Hz, 3H, $CH_2CH_2CH_3$), 0.96 (t, ^3J = 7.1 Hz, 3H, $CH_2CH_2CH_3$), 1.22 [s, 9H, $SiC(CH_3)_3$], 1.41 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.45 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 1.51–1.54 (m, 4H, $CH_2CH_2CH_3$), 2.51 (t, ^3J = 7.1 Hz, 2H, $CH_2CH_2CH_3$), 2.55 (t, ^3J = 7.1 Hz, 2H, $CH_2CH_2CH_3$), 4.30 (m, 2H, OCH_2CH_3), 4.75 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.32 (s, 1H, 6-H), 6.44 (s, 1H, 3-H), 7.25–7.50 (m, 6H, Ph-H), 7.55–7.64 (m, 2H, Ph-H), 7.66–7.75 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.2, 14.3, 14.9 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 19.3 [C_{quat}, $SiC(CH_3)_3$], 23.3 (+, $CHCH_3$), 24.3, 25.1 (−, $CH_2CH_2CH_3$), 26.9 [+, $SiC(CH_3)_3$], 27.4, 31.7 (−, $CH_2CH_2CH_3$), 64.0 (−, OCH_2CH_3), 69.3 (+, $CHCH_3$), 89.9 (+, C-6), 105.0, 109.2, 115.1 (C_{quat}, C-4a,5,7), 124.7 (+, C-3), 125.4 (C_{quat}, C-7a), 127.7, 127.8, 129.8, 129.9 (+, C-Ph), 133.1, 133.5 (C_{quat}, C-Ph), 135.7, 135.8 (+, C-Ph), 158.2, 165.6 (C_{quat}, C-2,4); IR (KBr): $\tilde{\nu}$ = 3064, 3041, 2954, 2925, 1642, 1606 cm^{-1}; MS (70 eV): *m/z* (%): 528 (18) [M^+], 499 (24) [$M^+ - C_2H_5$], 327 (16), 306 (5), 256 (17), 206 (100), 199 (54); HRMS (EI): *m/z*: calcd for $C_{34}H_{44}O_3Si$: 528.3059 (correct HRMS).

Variant B: According to GP 2, complex (*E*)-**2 fb** (233 mg, 0.31 mmol) in THF (6 mL) was treated with 1-pentyne (169 mg, 2.48 mmol), and the mixture was heated for 35 h. Compound **4 f**-*n*Pr (38 mg, 23%) was obtained after chromatography on silica gel (20 g).

2-[1′-(*tert*-Butyldimethylsilyloxy)ethyl]-4-ethoxy-5,7-diphenylcyclopenta[*b*]pyran (4 g-Ph) and 2-[1′-(*tert*-butyldimethylsilyloxy)ethyl]-4-ethoxy-5,6-diphenylcyclopenta[*b*]-pyran (8 g-Ph): *Variant A*: Following GP 2, complex (*E*)-**2 ga** (180 mg, 0.38 mmol) in THF (8 mL) was treated with phenylethyne (311 mg, 3.04 mmol) and the mixture was heated for 37 h. After chromatography [20 g silica gel, elution with pentane/Et_2O (5:1)] **8 g**-Ph (R_f = 0.45) and **4 g**-Ph (R_f = 0.39) were obtained as a red oil (25 mg, 14%) and as red crystals (48 mg, 27%), m.p. 138 °C. **8 g**-Ph: ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.10 [s, 6H, $Si(CH_3)_2$], 0.81 [s, 9H, $SiC(CH_3)_3$], 1.18 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 1.58 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 4.44 (m, 2H, OCH_2CH_3), 5.20 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.07 (s, 1H, 7-H), 7.14 (s, 1H, 3-H), 7.30–7.47 (m, 8H, Ph-H), 7.80–7.88 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.0, −4.9 (+, $SiCH_3$), 14.5 (+, OCH_2CH_3), 18.1 [C_{quat}, $SiC(CH_3)_3$], 25.4 (+, $CHCH_3$), 25.8 [+, $SiC(CH_3)_3$], 65.6 (+, $CHCH_3$), 65.7 (−, OCH_2CH_3), 80.6 (+, C-7), 107.5, 117.5, 119.0 (C_{quat}, C-4a,5,6), 124.6, 125.5, 126.2, 126.4, 127.9, 128.6, 130.2 (+, C-Ph, C-3), 135.0, 139.8×2, 157.1, 162.6 (C_{quat}, C-Ph, C-2,4,7a); IR (film): $\tilde{\nu}$ = 3064, 3050, 2980, 1625, 1593, 1530, 1490, 1448 cm^{-1}; MS (70 eV): *m/z* (%): 472 (100) [M^+], 73 (26); HRMS (EI): *m/z*: calcd for $C_{30}H_{36}O_3Si$: calcd for 472.2433 (correct HRMS).

Compound 4 g-Ph: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.15 (s, 3H, $SiCH_3$), 0.20 (s, 3H, $SiCH_3$), 0.98 [s, 9H, $SiC(CH_3)_3$], 1.44 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.63 (d, ^3J = 7.2 Hz, 3H, $CHCH_3$), 4.32 (m, 2H, OCH_2CH_3), 4.95 (q, ^3J = 7.2 Hz, 1H, $CHCH_3$), 6.63 (s, 1H, 6-H), 7.11–7.25 (m, 2H, Ph-H), 7.31 (s, 1H, 3-H), 7.33–7.42 (m, 4H, Ph-H), 7.62–7.70 (m, 2H, Ph-H), 7.83–7.91 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −5.0, −4.8 (+, $SiCH_3$), 14.5 (+, OCH_2CH_3), 18.1 [C_{quat}, $SiC(CH_3)_3$], 23.9 (+, $CHCH_3$), 25.7 [+, $SiC(CH_3)_3$], 64.9 (−, OCH_2CH_3), 68.2 (+, $CHCH_3$), 91.0 (+, C-6), 107.5, 117.2, 117.4 (C_{quat}, C-4a,5,7), 124.2, 124.5, 124.8, 125.5, 127.4, 128.5, 129.2 (+, C-Ph, C-3), 135.6, 138.4 (C_{quat}, C-Ph), 147.3, 160.7, 168.0 (C_{quat}, C-2,4,7a); IR (KBr): $\tilde{\nu}$ = 3060, 3039, 3007, 2837, 1622, 1590, 1560, 1491 cm^{-1}; MS (70 eV): *m/z* (%): 472 (59) [M^+], 453 (11), 408 (4), 396 (7), 362 (53), 316 (8), 259 (5), 230 (10), 202 (11), 156 (9), 111 (11), 97 (17), 91 (100), 73 (70), 57 (46) [$C_4H_9^+$], 43 (47); HRMS (EI): *m/z*: calcd for $C_{30}H_{36}O_3Si$: 472.2433 (correct HRMS).

Variant B: According to GP 2, complex [(*E*)-**2 gb**] (85 mg, 0.14 mmol) in THF (3 mL) was treated with phenylethyne (114 mg, 1.12 mmol), and the mixture was heated for 26 h. Compounds **8 g**-Ph (15 mg, 23%) and **4 g**-Ph (27 mg, 41%) were obtained after chromatography on silica gel (10 g).

2-[1′-(*tert*-Butyldimethylsilyloxy)ethyl]-4-ethoxy-5,7-di-*n*-propylcyclopenta[*b*]pyran (4 g-*n*Pr): According to GP 2, complex (*E*)-**2 gb** (85 mg, 0.14 mmol) in THF (3 mL) was treated with 1-pentyne (76 mg, 1.12 mmol), and the mixture was heated for 4 d. After column chromatography [10 g silica gel, elution with pentane/Et_2O (10:1)], **4 g**-*n*Pr (R_f = 0.51) was obtained as a red oil (6 mg, 11%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.09 (s, 3H, $SiCH_3$), 0.13 (s, 3H, $SiCH_3$), 0.72–1.04 (m, 9H, OCH_2CH_3, $CH_2CH_2CH_3$), 1.28 [s, 9H, $SiC(CH_3)_3$], 1.49 (d, ^3J = 7.1 Hz, 3H, $CHCH_3$), 1.52–1.74 (m, 4H, $CH_2CH_2CH_3$), 2.58 (t, ^3J = 7.2 Hz, 2H, $CH_2CH_2CH_3$), 2.74 (t, ^3J = 7.2 Hz, 2H, $CH_2CH_2CH_3$), 4.28 (m, 2H, OCH_2CH_3), 4.79 (q, ^3J = 7.1 Hz, 1H, $CHCH_3$), 6.37 (s, 1H, 6-H), 6.42 (s, 1H, 3-H); IR (film): $\tilde{\nu}$ = 2938, 2904, 2839, 1635, 1598, 1523, 1450, 1364 cm^{-1}; MS (70 eV): *m/z* (%): 404 (20) [M^+], 375 (37) [$M^+ - C_2H_5$], 206 (21), 108 (19), 80 (39), 52 (100); HRMS (EI): *m/z*: calcd for $C_{24}H_{40}O_3Si$: 404.2746 (correct HRMS).

4-Ethoxy-5,6-diphenyl-2-[1′-(trimethylsilyloxy)ethyl]cyclopenta[*b*]pyran (8 h-Ph): According to GP 2, complex (*E*)-**2 hb** (1.50 g, 2.55 mmol) in THF (50 mL) was treated with phenylethyne (2.08 g, 20.4 mmol), and the mixture was heated for 12 h. After chromatography [150 g silica gel, elution with pentane/Et_2O (10:1)], **8 h**-Ph (R_f = 0.44) was obtained as a red oil (230 mg, 21%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.03 [s, 9H, $Si(CH_3)_3$], 1.19 (d, ^3J = 7.0 Hz, 3H, $CHCH_3$), 1.56 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 4.42 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 5.20 (q, ^3J = 7.0 Hz, 1H, $CHCH_3$), 6.01 (s, 1H, 7-H), 7.18 (s, 1H, 3-H), 7.31–7.46 (m, 8H, Ph-H), 7.80–7.88 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = −0.2 [+, $Si(CH_3)_3$], 14.5 (+, OCH_2CH_3), 25.2 (+, $CHCH_3$), 65.1 (+, $CHCH_3$), 65.7 (−, OCH_2CH_3), 80.6 (+, C-7), 107.6, 117.6, 119.0 (C_{quat}, C-4a,5,6), 124.6, 125.5, 126.2, 126.3, 127.8, 128.5, 130.1 (+, C-3, C-Ph), 135.0, 139.8 (C_{quat}, C-Ph), 143.2, 156.7, 162.6 (C_{quat}, C-2,4,7a); IR (film):

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

$\tilde{\nu}$=3058, 3025, 2976, 2899, 1635, 1601, 1538 cm^{-1}; MS (70 eV): *m*/*z* (%): 430 (2) [M^+], 210 (29), 117 (18), 105 (36), 91 (100), 73 (51), 57 (21), 44 (32).

4-Ethoxy-2-(2′-methyldioxolan-2′-yl)-5,7-diphenylcyclopenta[*b*]pyran (4i-Ph): *Variant A*: According to GP 2, complex (*Z*)-**2ia** (400 mg, 0.99 mmol) in THF (20 mL) was treated with phenylethyne (809 mg, 7.92 mmol), and the mixture was heated for 3 d. After chromatography [20 g silica gel, elution with pentane/Et_2O (5:1)], **4i**-Ph (R_f=0.09) was obtained as a red oil (222 mg, 56%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.43 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.90 (s, 3H, CH_3), 4.08 (m, 4H, OCH_2CH_2O), 4.36 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.71 (s, 1H, 6-H), 7.13–7.70 (m, 7H, 3-H, Ph-H), 7.64–7.82 (m, 2H, Ph-H), 7.92–8.00 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.4 (+, OCH_2CH_3), 24.3 (+, CH_3), 65.1 (−, OCH_2CH_3), 65.4 (−, OCH_2CH_2O), 91.9 (+, C-6), 106.1 [C_{quat}, *C*-$(OCH_2)_2$], 107.8, 109.9, 117.3 (C_{quat}, C-4a,5,7), 124.3, 124.9, 125.4, 125.5, 127.4, 128.6, 129.1 (+, C-3, C-Ph), 135.3, 138.2 (C_{quat}, C-Ph), 148.3, 159.7, 161.8 (C_{quat}, C-2,4,7a); IR (film): $\tilde{\nu}$=3047, 3026, 2895, 1631, 1596, 1578, 1499 cm^{-1}; MS (70 eV): *m*/*z* (%): 400 (59) [M^+], 372 (2) [$M^+-C_2H_4$], 286 (9), 267 (12), 255 (31), 197 (9), 146 (19), 106 (41), 91 (100), 87 (84) [$C_4H_7O_2^+$], 71 (14), 43 (53); HRMS (EI): *m*/*z*: calcd for $C_{26}H_{24}O_4$: 400.1674 (correct HRMS).

Variant B: According to GP 2, complex (*Z*)-**2ib** (450 mg, 0.81 mmol) in THF (26 mL) was treated with phenylethyne (662 mg, 6.48 mmol), and the mixture was heated for 3 h. After chromatography [20 g silica gel, elution with pentane/Et_2O (5:1)], 4-ethoxy-2-(2′-methyldioxolan-2′-yl)-5,6-diphenylcyclopenta[*b*]pyran (**8i**-Ph) (R_f=0.18; 120 mg, 37%) and **4i**-Ph (143 mg, 44%) were obtained as red oils. **8i**-Ph: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.56 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.68 (s, 3H, CH_3), 3.71 (m, 4H, OCH_2CH_2O), 4.48 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 5.98 (s, 1H, 7-H), 7.16–7.52 (m, 9H, 3-H, Ph-H), 7.83–7.90 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.5 (+, OCH_2CH_3), 26.1 (+, CH_3), 63.9 (−, OCH_2CH_2O), 65.8 (−, OCH_2CH_3), 82.1 (+, C-7), 106.8 [C_{quat}, *C*-$(OCH_2)_2$], 107.5, 107.8, 119.8 (C_{quat}, C-4a,5,6), 124.8, 125.6, 125.7, 126.7, 128.5, 129.0, 130.3 (+, C-3, C-Ph), 134.7, 138.2 (C_{quat}, C-Ph), 141.5, 152.5, 161.7 (C_{quat}, C-2,4,7a); IR (film): $\tilde{\nu}$=3055, 2936, 2889, 1656, 1630, 1591, 1535, 1454 cm^{-1}; MS (70 eV): *m*/*z* (%): 400 (8) [M^+], 372 (4) [$M^+-C_2H_4$], 286 (10), 267 (14), 255 (31), 197 (11), 106 (43), 91 (79), 87 (100) [$C_4H_7O_2^+$], 77 (7), 65 (18), 62 (25), 49 (17); HRMS (EI): *m*/*z*: calcd for $C_{26}H_{24}O_4$: 400.1674 (correct HRMS).

2-(1′,1′-Dimethylethyl)-4-ethoxy-5,7-diphenylcyclopenta[*b*]pyran (4k-Ph): According to GP 2, complex (*Z*)-**2ka** (750 mg, 2.00 mmol) in THF (40 mL) was treated with phenylethyne (1.63 g, 16.0 mmol), and the mixture was heated for 4 d. After chromatography [80 g silica gel, elution with pentane/Et_2O (5:1)], **4k**-Ph (R_f=0.24) was obtained as red crystals (385 mg, 52%). M.p. 141 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.38 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.46 [s, 9H, $C(CH_3)_3$], 4.23 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.22 (s, 1H, 6-H), 7.08–7.23 (m, 2H, Ph-H), 7.28–7.47 (m, 5H, 3-H, Ph-H), 7.62 (d, ^3J=8.2 Hz, 2H, Ph-H), 7.89 (d, ^3J=8.2 Hz, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.4 (+, OCH_2CH_3), 28.8 [+, $C(CH_3)_3$], 37.0 [C_{quat}, $C(CH_3)_3$], 64.8. (−, OCH_2CH_3), 90.2 (+, C-6), 107.4, 116.9, 123.9 (C_{quat}, C-4a,5,7), 124.0, 124.2, 124.7, 125.3, 127.4, 128.5, 129.1 (+, C-Ph, C-3), 135.8, 138.5 (C_{quat}, C-Ph), 148.7, 160.7, 172.2 (C_{quat}, C-2,4,7a); IR (KBr): $\tilde{\nu}$=2940, 1595, 1485, 1380, 1290, 1240, 1135 cm^{-1}; MS (70 eV): *m*/*z* (%): 370 (42) [M^+], 111 (41), 97 (59), 71 (61), 57 (100) [$C_4H_9^+$].

2-(1′,1′-Dimethylethyl)-4-ethoxy-5,7-di-*n*-propylcyclopenta[*b*]pyran (4k-*n*Pr): According to GP 2, complex (*E*)-**2ka** (275 mg, 0.73 mmol) in THF (15 mL) was treated with 1-pentyne (400 mg, 5.88 mmol), and the mixture was heated for 4 d. After chromatography [35 g silica gel, elution with pentane/Et_2O (10:1)], **4k**-*n*Pr (R_f=0.51) was obtained as a red oil (95 mg, 43%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.95 (t, ^3J=7.3 Hz, 3H, $CH_2CH_2CH_3$), 0.98 (t, ^3J=7.3 Hz, 3H, $CH_2CH_2CH_3$), 1.32 [s, 9H, $C(CH_3)_3$], 1.45 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.63 (tq, ^3J=7.3, ^3J=7.3 Hz, 2H, $CH_2CH_2CH_3$), 1.68 (tq, ^3J=7.3, ^3J=7.3 Hz, 2H, $CH_2CH_2CH_3$), 2.61 (t, ^3J=7.3 Hz, 2H, $CH_2CH_2CH_3$), 2.74 (t, ^3J=7.3 Hz, 2H, $CH_2CH_2CH_3$), 4.27 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 6.02 (s, 1H, 6-H), 6.47 (s, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.4, 14.4, 14.9 (+, $CH_2CH_2CH_3$, OCH_2CH_3), 23.7, 25.2 (−, $CH_2CH_2CH_3$), 27.6 (−, $CH_2CH_2CH_3$), 28.6 [+, $C(CH_3)_3$], 31.7 (−, $CH_2CH_2CH_3$), 36.7 [C_{quat}, *C*-$(CH_3)_3$], 63.9 (−, OCH_2CH_3), 88.3 (+, C-6), 104.6, 108.5, 114.7 (C_{quat}, C-4a,5,7), 124.6 (+, C-3), 145.7, 158.6, 170.6 (C_{quat}, C-2,4,7a); IR (film): $\tilde{\nu}$=2959, 2927, 1643, 1547, 1463, 1381 cm^{-1}; MS (70 eV): *m*/*z* (%): 302 (23) [M^+], 273 (100) [$M^+-C_2H_5$], 245 (22) [$M^+-C_4H_9^+$], 57 (23) [$C_4H_9^+$].

Cycloadditions of the [(*Z*)-3-(aryloxy)-, (benzyloxy)-, (arylthio)- and (alkylthio)ethenyl]carbene complexes and alkynes

4-Ethoxy-2-(1′-ethoxy-1′-methylethyl)-5,7-diphenylcyclopenta[*b*]pyran (4b-Ph): *Variant A*: According to GP 2, complex (*E*/*Z*)-**2bg** (177 mg, 0.44 mmol) in THF (9 mL) was treated with phenylethyne (360 mg, 3.52 mmol), and the mixture was heated for 3 d. After chromatography [15 g silica gel, elution with pentane/Et_2O (10:1)], **4b**-Ph (R_f=0.15) was obtained as red crystals (46 mg, 27%). M.p. 127 °C; the spectral data have previously been reported.[9]

Variant B: According to GP 2, complex (*Z*)-**2bh** (232 mg, 0.51 mmol) in THF (10 mL) was treated with phenylethyne (417 mg, 4.08 mmol), and the mixture was heated for 2 d. Compound **4b**-Ph (57 mg, 28%) was obtained after chromatography on silica gel (15 g).

Variant C: According to GP 2, complex [(*E*/*Z*)-**2bi**] (169 mg, 0.36 mmol) in THF (7 mL) was treated with phenylethyne (294 mg, 2.88 mmol), and the mixture was heated for 2 d. Compound **4b**-Ph (26 mg, 18%) was obtained after chromatography on silica gel (10 g).

Variant D: According to GP 2, complex (*Z*)-**2bk** (170 mg, 0.36 mmol) in THF (7 mL) was treated with phenylethyne (294 mg, 2.88 mmol), and the mixture was heated for 2 d. **4b**-Ph (53 mg, 37%) was obtained after chromatography on silica gel (10 g).

Tetracarbonyl[(2*Z*)-1,4-diethoxy-4-methyl-3-phenylthio-2-penten-1-ylidene-*C*^{1},*S*]chromium [(*Z*)-7l] and 4-ethoxy-2-(1′-ethoxy-1′-methylethyl)-5,7-diphenylcyclopenta[*b*]pyran (4b-Ph): According to GP 2, complex (*Z*)-**2bl** (442 mg, 0.94 mmol) in THF (19 mL) was treated with phenylethyne (768 mg, 7.52 mmol), and the mixture was heated for 16 d. After chromatography [40 g silica gel, elution with pentane/Et_2O (5:1)], besides **4b**-Ph (88 mg, 23%), (*Z*)-**7l** (R_f=0.38) was obtained as a red oil (287 mg, 69%). (*Z*)-**7l**: ^{1}H NMR (250 MHz, C_6H_6): δ=0.92 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.10 [s, 6H, $C(CH_3)_2$], 1.28 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 2.99 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 5.03 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 7.14–7.28 (m, 6H, 2-H, Ph-H); ^{13}C NMR (62.9 MHz, C_6H_6, plus DEPT): δ=15.0, 15.8 (+, OCH_2CH_3), 27.6 [+, $C(CH_3)_2$], 58.4, 77.5 (−, OCH_2CH_3), 78.7 [C_{quat}, $C(CH_3)_2$], 129.4, 129.5, 130.3 (+, C-Ph), 136.3 (C_{quat}, C-Ph), 148.7 (+, C-2), 172.2 (C_{quat}, C-3), 217.3, 231.1, 234.0 (C_{quat}, C=O), 338.9 (C_{quat}, C-1); IR (film): $\tilde{\nu}$=3070, 3045, 2895, 2859, 2000 (C=O), 1915 (C=O), 1868 (C=O), 1578 cm^{-1}; MS (70 eV): *m*/*z* (%): 442 (1) [M^+], 386 (2) [M^+-2CO], 358 (0.2) [M^+-3CO], 330 (7) [M^+-4CO], 294 (38), 250 (43), 208 (61), 203 (20), 87 (100), 59 (77), 52 (3) [Cr^+]; HRMS (EI): *m*/*z*: calcd for $C_{20}H_{22}CrO_6S$: 442.0542 (correct HRMS).

Tetracarbonyl[(2*Z*)-1,4-diethoxy-3-ethylthio-4-methyl-2-penten-1-ylidene-*C*^{1},*S*]chromium [(*Z*)-7n] and 4-ethoxy-2-(1′-ethoxy-1′-methylethyl)-5,7-diphenylcyclopenta[*b*]pyran (4b-Ph): According to GP 2, complex (*Z*)-**2bn** (329 mg, 0.78 mmol) in THF (16 mL) was treated with phenylethyne (637 mg, 6.24 mmol), and the mixture was heated for 3 d. After chromatography [30 g silica gel, elution with pentane/Et_2O (5:1)], besides **4b**-Ph (84 mg, 27%), ethyl 4-ethoxy-3-ethylthio-4-methylpentenoate ((17 mg, 9%; R_f=0.43) and (*Z*)-**7n** (169 mg, 55%; R_f=0.37) were obtained as a colorless and a red oil, respectively. Ethyl 4-ethoxy-3-ethylthio-4-methylpentenoate: ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.93 (t, ^3J=7.0 Hz, 3H, CH_2CH_3), 1.32 (t, ^3J=7.0 Hz, 3H, CH_2CH_3), 1.42 (t, ^3J=7.0 Hz, 3H, CH_2CH_3), 1.49 [s, 6H, $C(CH_3)_2$], 2.98 (q, ^3J=7.0 Hz, 2H, SCH_2CH_3), 3.35 (q, ^3J=7.0 Hz, 2H, CH_2CH_3), 4.20 (q, ^3J=7.0 Hz, 2H, CH_2CH_3), 6.28 (s, 1H, 2-H).

Complex (*Z*)-7n: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.22 (t, ^3J=7.0 Hz, 3H, CH_2CH_3), 1.42 (t, ^3J=7.0 Hz, 3H, CH_2CH_3), 1.54 [s, 6H, $C(CH_3)_2$], 1.66 (t, ^3J=7.0 Hz, 3H, CH_2CH_3), 3.28 (q, ^3J=7.0 Hz, 2H, CH_2CH_3), 3.40 (q, ^3J=7.0 Hz, 2H, CH_2CH_3), 5.09 (q, ^3J=7.0 Hz, 2H, CH_2CH_3), 6.68 (s, 1H, 2-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ=14.3, 15.2, 15.6 (+, CH_2CH_3), 27.9 [+, $C(CH_3)_2$], 37.0 (−, SCH_2CH_3), 58.8, 76.7 (−, OCH_2CH_3), 78.2 [C_{quat}, $C(CH_3)_2$], 145.9 (+, C-2), 173.5 (C_{quat}, C-3), 216.5, 230.1, 233.1 (C_{quat}, C=O), 336.4 (C_{quat}, C-1); IR (film): $\tilde{\nu}$=2985,

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2882, 2009 (C=O), 1971 (C=O), 1912 (C=O), 1860 (C=O), 1594 cm^{-1}; MS (70 eV): *m/z* (%): 394 (22) [M^+], 338 (8) [M^+-2CO], 310 (5) [M^+-3CO], 282 (75) [M^+-4CO], 238 (39), 209 (23), 194 (31), 156 (100), 131 (22), 115 (24), 87 (79), 59 (52), 52 (53) [Cr^+]; HRMS (EI): *m/z*: calcd for $C_{16}H_{22}CrO_6S$: 394.0542 (correct HRMS).

4-Dimethylamino-2-[1′-ethoxy-1′-methylethyl]-5,7-diphenylcyclopenta[*b*]pyran (10b-Ph): According to GP 2, complex (*E*/*Z*)-**9b**[14b] (267 mg, 0.48 mmol) in THF (10 mL) was treated with phenylethyne (392 mg, 3.84 mmol), and the mixture was heated for 5 d. After chromatography [15 g silica gel, elution with pentane/Et_2O (5:1)], **10b**-Ph (R_f = 0.11) was obtained as a red oil (74 mg, 39%). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.61 [s, 6H, $C(CH_3)_2$], 2.86 [s, 6H, $N(CH_3)_2$], 3.41 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 6.39 (s, 1H, 6-H), 6.99–7.12 (m, 3H, Ph-H, 3-H), 7.21–7.38 (m, 6H, Ph-H), 7.73–7.81 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 16.0 (+, OCH_2CH_3), 26.3 [+, $C(CH_3)_2$], 43.0 [+, $N(CH_3)_2$], 59.0 (−, OCH_2CH_3), 76.6 [C_{quat}, $C(CH_3)_2$], 94.3 (+, C-6), 107.1, 116.5 (C_{quat}, C-5,7), 121.7, 123.6, 124.4, 125.3, 128.1, 128.4, 131.4 (+, C-Ph, C-3), 136.4 (C_{quat}, C-Ph), 141.4, 147.5 (C_{quat}, C-4a,7a), 154.0, 164.6 (C_{quat}, C-2,4); IR (film): $\tilde{\nu}$ = 3057, 2977, 2803, 1625, 1598 cm^{-1}; MS (70 eV): *m/z* (%): 399 (100) [M^+], 384 (22) [M^+-CH_3], 362 (71), 317 (62), 271 (11), 242 (11), 225 (93), 200 (18), 150 (5), 115 (4), 91 (44) [$C_7H_7^+$], 87 (95), 77 (8), 65 (6), 59 (37), 43 (12); HRMS (EI): *m/z*: calcd for $C_{27}H_{29}NO_2$: 399.2198 (correct HRMS).

4-Dimethylamino-2-[1′-methyl-1′-(trimethylsilyloxy)ethyl]-5,7-diphenylcyclopenta[*b*]pyran (10c-Ph): According to GP 2, complex (*E*/*Z*)-**9c** (402 mg, 0.67 mmol) in THF (13 mL) was treated with phenylethyne (547 mg, 5.36 mmol), and the mixture was heated for 3 d. After chromatography [20 g silica gel, elution with pentane/Et_2O (5:1)], **10c**-Ph (R_f = 0.49) was obtained as a red oil (84 mg, 28%). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.16 [s, 9H, $Si(CH_3)_3$], 1.63 [s, 6H, $C(CH_3)_2$], 2.84 [s, 6H, $N(CH_3)_2$], 6.49 (s, 1H, 6-H), 7.02 (s, 1H, 3-H), 7.04–7.40 (m, 8H, Ph-H), 7.72–7.80 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 2.4 [+, $Si(CH_3)_3$], 29.9 [+, $C(CH_3)_2$], 42.9 [+, $N(CH_3)_2$], 74.8 [C_{quat}, $C(CH_3)_2$], 93.3 (+, C-6), 107.0, 116.7 (C_{quat}, C-5,7), 123.5, 123.5, 124.3, 125.2, 128.0, 128.1, 128.3 (+, C-Ph, C-3), 136.4 (C_{quat}, C-Ph), 141.3, 147.3 (C_{quat}, C-4a,7a), 154.4, 166.9 (C_{quat}, C-2,4); IR (film): $\tilde{\nu}$ = 3050, 2951, 2899, 1620, 1598 cm^{-1}; MS (70 eV): *m/z* (%): 443 (2) [M^+], 428 (<1) [M^+-CH_3], 120 (53), 91 (100) [$C_7H_7^+$], 77 (25) [$C_6H_5^+$]; HRMS (EI): *m/z*: calcd for $C_{28}H_{33}NO_2Si$: 443.2280 (correct HRMS).

4-Ethoxy-2-[1′-methyl-1′-(trimethylsilyloxy)ethyl]-5,7-di-*n*-propylcyclopenta[*b*]pyran (4c-*n*Pr) and tricarbonyl(6,6-dimethyl-1-dimethylamino-3-ethoxy-2-*n*-propylfulvene)chromium (6-*n*Pr): According to GP 2, complex (*Z*)-**2ca** (325 mg, 0.72 mmol) in THF (14 mL) was treated with 1-pentyne (392 mg, 5.76 mmol), and the mixture was heated for 36 h. After chromatography [30 g silica gel, elution with pentane/Et_2O (10:1)], along with **4c**-*n*Pr (57 mg, 21%), **6**-*n*Pr (R_f = 0.32) was obtained as orange crystals (102 mg, 38%). M.p. 133 °C; ^1H and ^{13}C NMR data of the title compound have been reported previously;[17] IR (KBr): $\tilde{\nu}$ = 2975, 2952, 2921, 2860, 1950 (C=O), 1865 (C=O), 1511, 1450 cm^{-1}; MS (70 eV): *m/z* (%): 371 (9) [M^+], 315 (5) [M^+-2CO], 287 (7) [M^+-3CO], 257 (22), 244 (100), 81 (11), 54 (18), 41 (12); HRMS (EI): *m/z*: calcd for $C_{18}H_{25}CrNO_4$: 371.1189 (correct HRMS).

4-Ethoxy-5,7-dimethyl-2-[1′-methyl-1′-(trimethylsilyloxy)ethyl]cyclopenta[*b*]pyran (4c-Me) and tricarbonyl(1-dimethylamino-3-ethoxy-6,6-dimethyl-2-methylfulvene)chromium (6-Me): According to GP 2, complex (*Z*)-**2ca** (400 mg, 0.89 mmol) in THF (18 mL) was treated with propyne (285 mg, 7.12 mmol), and the mixture was heated for 3 d. After chromatography [40 g silica gel, elution with pentane/Et_2O (5:1)], 50 mg (18%) of **4c**-Me (R_f = 0.61) and 21 mg (7%) of **6**-Me (R_f = 0.50) were obtained as a red and an orange oil, respectively. **4c**-Me: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.22 [s, 9H, $Si(CH_3)_3$], 1.50 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.66 [s, 6H, $C(CH_3)_2$], 2.23 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.30 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 6.42 (br s, 2H, 3-H, 6-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 2.4 [+, $Si(CH_3)_3$], 9.8, 14.5, 14.9 (+, OCH_2CH_3, CH_3), 29.7 [+, $C(CH_3)_2$], 64.0 (−, OCH_2CH_3), 74.8 [C_{quat}, $C(CH_3)_2$], 88.7 (+, C-6), 99.1, 109.4, 118.0 (C_{quat}, C-4a,5,7), 126.1 (+, C-3), 145.5 (C_{quat}, C-7a), 159.0, 168.8 (C_{quat}, C-2,4); IR (film): $\tilde{\nu}$ = 2964, 2944, 2850, 1600, 1548, 1472, 1375, 1352 cm^{-1}; MS (70 eV): *m/z* (%): 320 (100) [M^+], 305 (5) [M^+-CH_3], 277 (4), 249 (2), 234 (43), 201 (19), 188 (25), 174 (21), 152 (20), 131 (37), 119 (16), 91 (18), 73 (77) [$Si(CH_3)_3^+$], 41 (17); HRMS (EI): *m/z*: calcd for $C_{18}H_{28}O_3Si$: 320.1807 (correct HRMS).

Compound 6-Me: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.42 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.92 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.73 [s, 6H, $N(CH_3)_2$], 3.39 (m, 1H, OCH_2CH_3), 3.69 (s, 1H, 4-H), 3.75 (m, 1H, OCH_2CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 9.5 (+, CH_3), 14.5 (+, OCH_2CH_3), 23.0, 26.9 [+, $C(CH_3)_2$], 39.6, 44.5 (+, NCH_3), 60.5 (+, C-4), 65.8 (−, OCH_2CH_3), 85.5, 97.8, 117.5, 131.0, 140.3 (C_{quat}, C-1,2,3,5,6), 238.7 (C_{quat}, C=O); IR (film): $\tilde{\nu}$ = 2980, 2941, 2891, 1943 (C=O), 1882 (C=O), 1848 (C=O), 1500, 1381 cm^{-1}; MS (70 eV): *m/z* (%): 343 (46) [M^+], 315 (4) [M^+-CO], 287 (12) [M^+-2CO], 259 (100) [M^+-3CO], 229 (21), 216 (17), 190 (13), 95 (10), 73 (15) [$Si(CH_3)_3^+$], 52 (14) [Cr^+]; HRMS (EI): *m/z*: calcd for $C_{16}H_{21}CrNO_4$: 343.0875 (correct HRMS).

5,7-Dicyclopropyl-4-ethoxy-2-[1′-methyl-1′-(trimethylsilyloxy)ethyl]cyclopenta[*b*]pyran (4c-*c*Pr) and tricarbonyl(2-cyclopropyl-1-dimethylamino-3-ethoxy-6,6-dimethylfulven)chromium (6-*c*Pr): According to GP 2, complex (*Z*)-**2ca** (400 mg, 0.89 mmol) in THF (18 mL) was treated with cyclopropylethyne (471 mg, 7.12 mmol), and the mixture was heated for 3 d. After chromatography [40 g silica gel, elution with pentane/Et_2O (5:1)], **4c**-*c*Pr (R_f = 0.64) and **6**-*c*Pr (R_f = 0.57) were obtained as a red (67 mg, 20%) and an orange oil (47 mg, 14%), respectively. **4c**-*c*Pr: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.25 [s, 9H, $Si(CH_3)_3$], 0.59 (m, 2H, *c*Pr-H), 0.71 (m, 2H, *c*Pr-H), 0.81 (m, 4H, *c*Pr-H), 1.51 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.63 [s, 6H, $C(CH_3)_2$], 1.90 (m, 1H, *c*Pr-H), 2.22 (m, 1H, *c*Pr-H), 4.32 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 6.18 (s, 1H, 6-H), 6.43 (s, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 2.4 [+, $Si(CH_3)_3$], 6.4 (−, *c*Pr-C), 6.9 (+, *c*Pr-C), 7.9 (−, *c*Pr-C), 9.7 (+, *c*Pr-C), 14.9 (+, OCH_2CH_3), 29.8 [+, $C(CH_3)_2$], 64.2 (−, OCH_2CH_3), 74.8 [C_{quat}, $C(CH_3)_2$], 89.0 (+, C-6), 106.0, 109.6 (C_{quat}, C-5,7), 116.5 (C_{quat}, C-4a), 118.8 (+, C-3), 145.3 (C_{quat}, C-7a), 159.3, 169.0 (C_{quat}, C-2,4); IR (film): $\tilde{\nu}$ = 2979, 2875, 1599, 1460 cm^{-1}; MS (70 eV): *m/z* (%): 372 (2) [M^+], 293 (100), 278 (33), 263 (32), 240 (17), 218 (79), 189 (10), 131 (37), 91 (16), 73 (45) [$Si(CH_3)_3^+$]; HRMS (EI): *m/z*: calcd for $C_{22}H_{32}O_3Si$: 372.2120 (correct HRMS).

Compound 6-*c*Pr: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.78–0.99 (m, 4H, *c*Pr-H), 1.31 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.57–1.66 (m, 1H, *c*Pr-H), 1.92 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.81 [s, 6H, $N(CH_3)_2$], 3.35 (m, 1H, OCH_2CH_3), 3.61 (s, 1H, 4-H), 3.70 (m, 1H, OCH_2CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 6.0, 7.6 (−, *c*Pr-C), 9.5 (+, *c*Pr-C), 14.6 (+, OCH_2CH_3), 23.2, 26.8 [+, $C(CH_3)_2$], 44.6 [+, $N(CH_3)_2$], 60.1 (+, C-4), 65.7 (−, OCH_2CH_3), 91.6, 97.7, 117.4, 132.3, 140.7 (C_{quat}, C-1,2,3,5,6), 238.8 (C_{quat}, C=O); IR (film): $\tilde{\nu}$ = 2956, 1912 (C=O), 1880 (C=O), 1846 (C=O), 1700, 1653, 1617 cm^{-1}; MS (70 eV): *m/z* (%): 369 (39) [M^+], 341 (<1) [M^+-CO], 313 (6) [M^+-2CO], 285 (22) [M^+-3CO], 257 (100) [$M^+-3CO-C_2H_4$], 240 (36) [$M^+-3CO-C_2H_5O$], 228 (25), 214 (17), 176 (10), 160 (5), 131 (13), 73 (18), 52 (39) [Cr^+]; HRMS (EI): *m/z*: calcd for $C_{18}H_{23}CrNO_4$: 369.1032 (correct HRMS).

2-Acetyl-4-ethoxy-5,7-diphenylcyclopenta[*b*]pyran (18): A solution of 66 mg (0.16 mmol) of 4-ethoxy-2-(2′-methyldioxolan-2′-yl)-5,7-diphenylcyclopenta[*b*]pyran (**4i**-Ph) in methanol (3 mL) and tetrahydrofuran (3 mL) was stirred with 5% aqueous HCl (3 mL) at ambient temperature for 3 d. After the usual work-up, column chromatography on 5 g silica gel (column 6×1 cm), eluting with pentane/diethyl ether 5:3 gave: Fraction I (R_f = 0.33): **18** as a green-yellow oil (9 mg, 16%); a solution of which exhibited a weak green fluorescence. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.37 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 2.72 (s, 3H, CH_3), 4.30 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 7.08–7.41 (m, 8H, 6-H, 3-H, Ph-H), 7.51–7.58 (m, 2H, Ph-H), 7.79–7.86 (m, 2H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ = 14.4 (+, OCH_2CH_3), 26.0 (+, CH_3), 65.6 (−, OCH_2CH_3), 96.2 (+, C-6), 108.4, 111.2, 118.1 (C_{quat}, C-4a,5,7), 125.0, 125.4, 125.7, 127.5, 128.8, 129.3, 130.2 (+, C-3, C-Ph), 134.8, 137.5 (C_{quat}, C-Ph), 146.3, 153.0, 158.3 (C_{quat}, C-2,4,7a), 191.8 (C_{quat}, C=O); IR (film): $\tilde{\nu}$ = 3078, 3049, 2963, 2930, 2854, 1720, 1600, 1531, 1493, 1389, 1308, 1261, 1094, 1017, 912, 868, 802, 731, 689, 548, 480, 448 cm^{-1}; UV (CH_2Cl_2): λ_{max} (lg ε) = 252 (4.090), 282 (4.038), 393 (3.453), 590 nm (1.957); MS (70 eV): *m/z* (%): 356 (49) [M^+], 328 (26) [$M^+-C_2H_4$], 256 (4), 205 (16), 170 (79), 149

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

(25), 141 (65), 131 (19), 105 (23), 91 (10), 77 (100) [$C_6H_5^+$], 58 (26), 44 (19); HRMS (EI): m/z: calcd for $C_{24}H_{20}O_3$: 356.1412 (correct HRMS).

Fraction II: **4i**-Ph (33 mg; $R_f = 0.16$).

Fraction III: 11 mg ($R_f = 0.04$) of an unidentified compound as a yellow oil.

X-ray Crystal structure analysis of pentacarbonyl[(2*Z*)-3-dimethylamino-1-ethoxy-4-methyl-4-(trimethylsilyloxy)-2-penten-1-ylidene]chromium (2ca):[15] Formula $C_{18}H_{27}CrNO_7Si$, M_w 449.50, triclinic, space group $P1$, $Z = 2$, $a = 968.1(2)$, $b = 1014.7(2)$, $c = 1281.4(2)$ pm, $\alpha = 70.210(10)$, $\beta = 71.420(10)$, $\gamma = 81.150(10)°$, $V = 1.1212(4)$ nm^3, $\rho_{calcd} = 1.331$ Mg m^{-3}, crystal dimensions $1.00 \times 0.70 \times 0.70$ mm, 2907 unique reflections were measured with a Stoe-Siemens four-circle diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm) at 153(2) K, 2Θ range: 3.51–22.48°. The structure was solved by direct methods (SHELXL-97[26]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-97[27]). All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were included in calculated positions and refined by using a riding model. R values: $R_1 = 0.0476$ [for $F > 4\sigma(F)$], $wR_2 = 0.1447$ (for all data) with 261 parameters and 0 restraints, $P = (F_o^2 + 2F_c^2)/3$, maximum and minimum residual electron density 613 and -778 e$^-$ nm^{-3}.

X-ray Crystal structure analysis of 4-ethoxy-2-(2′-methyldioxolan-2′-yl)-5,7-diphenylcyclopenta[*b*]pyran (4i-Ph):[15] Formula $C_{26}H_{24}O_4$, M_w 400.45, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 1117.2(2)$, $b = 1018.40(10)$, $c = 1835.5(2)$ pm, $\alpha = 90$, $\beta = 101.720(10)$, $\gamma = 90°$, $V = 2.0448(5)$ nm^3, $\rho_{calcd} = 1.301$ Mg m^{-3}, crystal dimensions $0.60 \times 0.60 \times 0.20$ mm, 2666 unique reflections were measured with a Stoe-Siemens four-circle diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm) at 153(2) K, 2Θ range: 3.53–22.55°. The structure was solved by direct methods (SHELXL-97[26]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-97[27]). All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were included in calculated positions and refined by using a riding model. R values: $R_1 = 0.0614$ [for $F > 4\sigma(F)$], $wR_2 = 0.1945$ (for all data) with 271 parameters and 0 restraints, $P = (F_o^2 + 2F_c^2)/3$, maximum and minimum residual electron density 382 and -481 e$^-$ nm^{-3}.

Acknowledgements

This work was supported by the Volkswagen-Stiftung and the Fonds der Chemischen Industrie. Generous gifts of chemicals by the Hoechst AG, Hüls AG and Chemetall GmbH are gratefully acknowledged. M.D. is indebted to the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Kinetik und Selektivität chemischer Prozesse in verdichteter fluider Phase") for a graduate fellowship. The authors are indebted to Mr. S. Beußhausen for his technical support.

[1] For reviews see: a) K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, VCH, Weinheim, **1983**; b) K. H. Dötz, *Angew. Chem.* **1984**, *96*, 573–594; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587–608; c) K. H. Dötz in *Organometallics in Organic Synthesis. Aspects of a Modern Interdisciplinary Field* (Eds.: A. de Meijere, H. tom Dieck), Springer, Berlin, **1988**; d) W. D. Wulff, *Adv. Met.-Org. Chem.* **1989**, *1*, 209–393; e) W. D. Wulff in *Comprehensive Organic Synthesis*, *Vol. 5* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 1065–1113; f) H. Rudler, M. Audouin, E. Chelain, B. Denise, R. Goumont, A. Massoud, A. Parlier, A. Pacreau, M. Rudler, R. Yefsah, C. Alvarez, F. Delgado-Reyes, *Chem. Soc. Rev.* **1991**, *20*, 503–531; g) W. D. Wulff in *Comprehensive Organometallic Chemistry II*, *Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, L. S. Hegedus), Pergamon, New York, **1995**, pp. 469–547; h) D. F. Harvey, D. M. Sigano, *Chem. Rev.* **1996**, *96*, 271–288; i) A. de Meijere, *Pure Appl. Chem.* **1996**, *68*, 61–72; j) R. Aumann, H. Nienaber, *Adv. Organomet. Chem.* **1997**, *41*, 163–242; k) F. Zaragoza-Dörwald, *Metal Carbenes in Organic Synthesis*, VCH, Weinheim, **1999**; l) A. de Meijere, H. Schirmer, M. Duetsch, *Angew. Chem.* **2000**, *112*, 4124–4162; *Angew. Chem. Int. Ed.* **2000**, *39*, 3964–4002; m) Y.-T. Wu, A. de-Meijere, *Top. Organomet. Chem.* **2004**, *13*, 21–57; n) *Metal Carbenes in Organic Synthesis*, *Vol. 13* (Ed.: K. H. Dötz), *Top. Organomet. Chem.*, Springer, Berlin **2004**.

[2] a) M. Buchert, H. U. Reissig, *Chem. Ber.* **1992**, *125*, 2723–2729; b) S. U. Tumer, J. W. Herndon, L. A. McMullen, *J. Am. Chem. Soc.* **1992**, *114*, 8394; c) T. Kurahashi, Y.-T. Wu, K. Meindl, S. Rühl, A. de Meijere, *Synlett* **2005**, 805–808.

[3] a) R. Aumann, H. Heinen, C. Krüger, P. Betz, *Chem. Ber.* **1990**, *123*, 599–604; b) R. Aumann, H. Heinen, R. Goddard, C. Krüger, *Chem. Ber.* **1991**, *124*, 2587–2593; c) F. Funke, M. Duetsch, F. Stein, M. Noltemeyer, A. de Meijere, *Chem. Ber.* **1994**, *127*, 911–920; d) R. Aumann, M. Kößmeier, K. Roths, R. Fröhlich, *Synlett* **1994**, 1041–1044; e) M. Duetsch, F. Stein, F. Funke, E. Pohl, R. Herbst-Irmer, A. de Meijere, *Chem. Ber.* **1993**, *126*, 2535–2541.

[4] a) J. S. McCallum, F. A. Kunng, S. R. Gilbertson, W. D. Wulff, *Organometallics* **1988**, *7*, 2346–2360; b) K. S. Chan, G. A. Peterson, T. A. Brandvold, K. L. Faron, C. A. Challenger, C. Hyldahl, W. D. Wulff, *J. Organomet. Chem.* **1987**, *334*, 9–56; c) K. H. Dötz, R. Dietz, D. Neugebauer, *Chem. Ber.* **1979**, *112*, 1486–1490; d) S. L. B. Wang, J. Su, W. D. Wulff, K. Hoogsteen, *J. Am. Chem. Soc.* **1992**, *114*, 10665–10666.

[5] a) L. S. Hegedus, M. A. McGuire, L. M. Schultze, C. Yijun, O. P. Anderson, *J. Am. Chem. Soc.* **1984**, *106*, 2680–2687; b) L. S. Hegedus, L. M. Schultze, J. Toro, C. Yijun, *Tetrahedron* **1985**, *41*, 5833–5838; c) C. Borel, L. S. Hegedus, J. Krebs, Y. Satoh, *J. Am. Chem. Soc.* **1987**, *109*, 1101–1105; d) L. S. Hegedus, S. D'Andrea, *J. Org. Chem.* **1988**, *53*, 3113–3116; e) L. S. Hegedus, R. Imwinkelried, M. Alarid-Sargent, D. Dvorak, Y. Satoh, *J. Am. Chem. Soc.* **1990**, *112*, 1109–1117.

[6] K. S. Chan, M. L. Yeung, W. Chan, R. Wang, T. C. W. Mak, *J. Org. Chem.* **1995**, *60*, 1741–1747.

[7] K. H. Dötz, A. Tiriliomis, K. Harms, *Tetrahedron* **1993**, *49*, 5577–5597.

[8] a) B. Denise, A. Parlier, H. Rudler, J. Vaissermann, J. C. Daran, *J. Chem. Soc. Chem. Commun.* **1988**, 1303–1305; b) S. Lafollée-Bezzenine, A. Parlier, H. Rudler, J. Vaissermann, J.-C. Daran, *J. Organomet. Chem.* **1998**, *567*, 83–100.

[9] a) F. Stein, M. Duetsch, R. Lackmann, M. Noltemeyer, A. de Meijere, *Angew. Chem.* **1991**, *103*, 1669–1671; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1658–1660; the first single example of an intermolecular double insertion was reported by Rudler et al., see ref. [8a].

[10] W. D. Wulff, R. W. Kaesler, G. A. Peterson, P. C. Tang, *J. Am. Chem. Soc.* **1985**, *107*, 1060–1062.

[11] a) G. V. Boyd, F. W. Clark, *J. Chem. Soc. C* **1966**, 859–861; b) R. Matusch, K. Hartke, *Chem. Ber.* **1972**, *105*, 2594–2603; c) Y. Aso, M. Iyoda, S. Fujisawa, S. Yamaguchi, M. Nakagawa, *Tetrahedron Lett.* **1981**, *22*, 3061–3064; d) M. Iyoda, Y. Aso, M. Nakagawa, *Heterocycles* **1982**, *18*, 137–143; e) K. V. Fedotov, N. N. Romanov, A. I. Tolmachev, *Chem. Heterocycl. Compd.* **1991**, *27*, 479–482; f) R. Borsdorf, G. H. Fischer, W. Schroth, *J. Prakt. Chem.* **1978**, *320*, 463–472.

[12] a) H.-J. Timpe, A. V. El′cov, N. I. Rtiscev, *Chimia* **1974**, *28*, 657–659; b) A. Olszowski, *Chem. Phys. Lett.* **1980**, *73*, 256–262; c) W. Treibs, *Naturwissenschaften* **1960**, *47*, 156; d) J. Fabian, A. Mehlhorn, R. Zahradník, *Theor. Chim. Acta* **1968**, *12*, 247–255.

[13] E. O. Fischer, H. J. Kalder, *J. Organomet. Chem.* **1977**, *131*, 57–64.

[14] a) M. Duetsch, F. Stein, R. Lackmann, E. Pohl, R. Herbst-Irmer, A. de Meijere, *Chem. Ber.* **1992**, *125*, 2051–2065; b) F. Stein, M. Duetsch, E. Pohl, R. Herbst-Irmer, A. de Meijere, *Organometallics* **1993**, *12*, 2556–2564.

[15] CCDC-208925 (**2ca**) and -208926 (**4i**-Ph) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[16] a) B. L. Flynn, F. J. Funke, C. C. Silveira, A. de Meijere, *Synlett* **1995**, 1007–1010; b) Y.-T. Wu, B. L. Flynn, H. Schirmer, F. Funke, S.

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Müller, T. Labahn, M. Nötzel, A. de Meijere, *Eur. J. Org. Chem.* **2004**, 724–748.
[17] F. Stein, M. Duetsch, M. Noltemeyer, A. de Meijere, *Synlett* **1993**, 486–488.
[18] M. Duetsch, R. Lackmann, F. Stein, A. de Meijere, *Synlett* **1991**, 324–326.
[19] a) H. Fischer, G. Roth, D. Reindl, C. Troll, *J. Organomet. Chem.* **1993**, *454*, 133–149, and references therein; b) H. Berke, P. Härter, G. Huttner, J. von Seyerl, *J. Organomet. Chem.* **1981**, *219*, 317–327.
[20] K. H. Dötz, *Angew. Chem.* **1975**, *87*, 672–673; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 644–645.
[21] a) W. D. Wulff, P. C. Tang, J. S. McCallum, *J. Am. Chem. Soc.* **1981**, *103*, 7677–7678; b) S. Chamberlin, M. L. Waters, W. D. Wulff, *J. Am. Chem. Soc.* **1994**, *116*, 3113–3114.
[22] T. Liese, F. Jaekel, A. de Meijere, *Org. Synth.* **1990**, *69*, 144–147.
[23] W. G. Dauben, R. A. Bunce, J. M. Gerdes, K. E. Henegar, A. F. Cunningham, Jr., T. B. Ottoboni, *Tetrahedron Lett.* **1983**, *24*, 5709–5712.
[24] K. C. Nicolaou, S. E. Webber, *Synthesis* **1986**, 453–461.
[25] H. R. Snyder, J. C. Robinson, *J. Am. Chem. Soc.* **1941**, *63*, 3279–3280.
[26] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.
[27] G. M. Sheldrick, SHELXL-92, Program for crystal structure refinement, University of Göttingen **1992**.

Received: January 14, 2005
Published online: April 28, 2005

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim