Michael Adducts of (Alkynylcarbene)pentacarbonylchromium Complexes: Formation, Stereochemistry, and Thermal Rearrangement☆

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Received January 28, 1992

Key Words: Chromium, alkynylcarbene complexes / Vinylcarbenechromium complexes, β-donor-substituted / Carbene complexes, vinyl, chelated

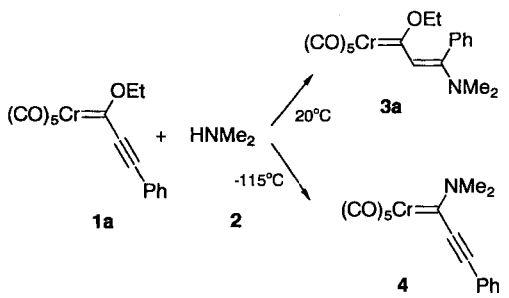
β-Donor-substituted α,β-unsaturated chromium carbene complexes $(CO)_5CrC(OEt)C=CR(XR'_n)$ (X = N, O, S; **3**, **9**, **11**–**16**, **22**–**25**) have been synthesized by Michael addition of amines, alcohols, and thiols to alkynylcarbene complexes $(CO)_5CrC(OEt)C\equiv CR$ (**1**). The configurations of the newly formed C–C double bonds have been determined by NOE/NOESY measurements and X-ray crystal structure analysis. These vinylcarbene complexes lose one carbonyl ligand in refluxing tetrahydrofuran to give tetracarbonyl complexes $(CO)_4CrC(OEt)C=CR(XR'_n)$ (X = N, O, S; **26**–**28**).

The chemistry of Fischer carbene complexes has been an ever expanding field since their discovery in 1964[1]. Apart from being of continual interest to inorganic chemists, they have found their way into the hands of synthetically oriented organic chemists. A number of elegant carbene complex-based approaches to various types of natural products, including vitamines[2], β-lactams[3], and tetracycline precursors[4], have been reported to date. Some antibiotics, such as deoxyfrenolicin[5] and daunomycinone[6], have been prepared via carbene complexes as well. Among the carbene complexes, which show the greatest synthetic potential, those with a vinyl or phenyl group attached to the carbene center have attracted most attention. In these cases the β-substituent is the pivotal point in determining the outcome of a ring-closing reaction with an alkyne. While hydrogen or silyl groups can easily shift around a newly formed ring to give a stabilized aromatic derivative[7], the presence of two β-alkyl substituents enforces the formation of cyclohexadienones[8]. Only recently have compounds with different types of substituents at this crucial point in the molecule been reported in the literature. In our work with β-donor-substituted Fischer vinylcarbene complexes we did not find any products as defined by Dötz[7] or Wulff[8]. In the presence of an amino, alkoxy, or arylthio group in the β-position, the formation of some unexpected compounds was observed. For example, with a secondary amino group and a non-quaternary carbon adjacent to the β-position, the reactions with alkynes yielded cyclopentadienes[9]. Pyridines or phenols were obtained with a primary amino or a phenylthio group, respectively[10]. However, the complexes with a tertiary alkyl substituent and a secondary amino or ethoxy group at the β-carbon reacted with twofold insertion of an alkyne to eventually give cyclopenta[*b*]pyranes in good yields[11]. Although β-aminovinyl-substituted Fischer carbene complexes are well documented[12], no systematic study of the stereochemical implications has been carried out.

In order to be able to test the scope and limitations of the newly observed reactions of such complexes with alkynes[9–11], we have investigated the addition of nucleophiles to alkynyl-substitued chromiumcarbene complexes in more detail and on a wider scope.

β-Donor-substituted (Vinylcarbene)chromium Complexes

Fischer et al.[12g,h] have observed that the (alkynylcarbene)chromium complex **1a** easily adds dimethylamine in a Michael-type reaction. They already established the temperature dependence of this reaction and the competing substitution of the alkoxy group at the carbene carbon. Low temperatures favor the formation of the aminolysis product **4**, whereas the Michael addition is preferred at higher tem-



[+] Crystal structure analysis.

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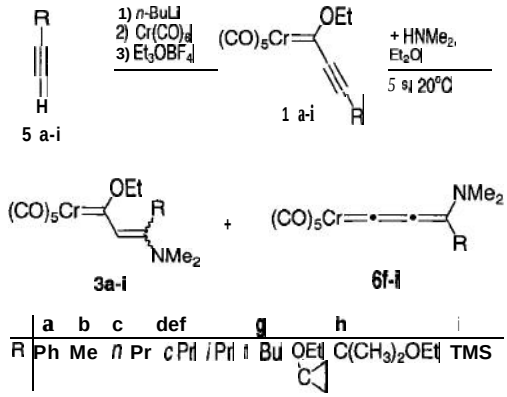
peratures. Surprisingly, no comment was given on the configuration of the newly formed C-C double bond.

While working with complex **1d**, we accidentally rediscovered this type of reaction and were immediately intrigued by the properties of the products and their potential use as building blocks in organic synthesis.

Therefore, we first synthesized a number of (ethynylcarbene)chromium complexes 1 a-i, some of which were previously unknown. All of these complexes (see Table 1) are readily available by the standard route[13] from hexacarbonylchromium and the corresponding 1-alkynes **5a–i**. All aryl- and alkyl-substituted complexes 1 a-h reacted with dimethylamine (2) very rapidly (within 5 s at 20°C) to give Michael adducts **3a–h** in very good yields (Table 1). With bulky tertiary substituents R at the acetylenic terminus as in 1 **f-h,** allenylidenechromium complexes **6f – h** were formed as byproducts[14].

Scheme 3



The trimethylsilyl-substituted complex **1i**[15] was markedly more reluctant than any of the others in its reaction with 2, even at room temperature, and gave about equal amounts of allenylidene complex 6i and Michael addition products **3i.**

None of the Michael adducts 3 showed any sign of being a mixture of stereoisomers or undergoing stereoisomerization at room temperature, as was observed by Aumann et al.[12a] for some analogous compounds.

The configuration of the newly formed C-C double bond in complexes 3d and **3h** was established by NOE measurements[18]. The configurations of the other complexes 3 were confirmed by NOESY measurements. All the experiments

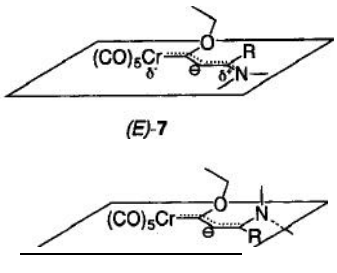


Figure 1. Steric implications for electronic interactions in intermediate vinyl anions (*E*)- and (Z)-7 generated from alkynylcarbene complexes 1

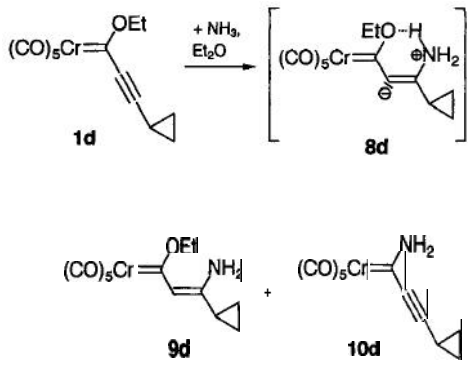
Table 1: Formation of (alkynylcarbene)chromium complexes 1 **a – i** and their reactions with dimethylamine (see Scheme 1)

Starting material	Complex (% yield)	Product (% yield)	Configuration	Product (% yield)
5a	**1a** (60[12h])	**3a** (96[12h])	*E*	**6a** (0)
5b	**1b** (62[15])	**3b** (98[12b])	*E*	**6b** (0)
5c	**1c** (57[16])	**3c** (93)	*E*	**6c** (0)
5d[17a]	**1d** (65)	**3d** (96)	*E*	**6d** (0)
5e	**1e** (66)	**3e** (91)	*E*	**6e** (0)
5f[15]	**1f** (63)	**3f** (84)	*Z*	**6f** (8)
5g[17a]	**1g** (64)	**3g** (85)	*Z*	**6g** (13)
5h	**1h** (78)	**3h** (80)	*Z*	**6h** (13)
5i	**1i** (73[15])	**3i** (27)	*Z*	**6i** (30)

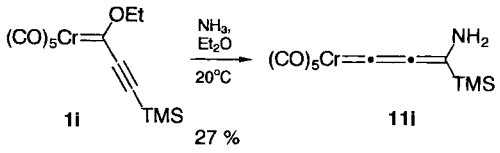
showed unequivocally that the configurations were uniform in each case. Surprisingly, though, on going from similar **1 e** with an isopropyl to **1f** with a *tert*-butyl substituent, the configuration in the adduct **3e/3f** switches completely from ***E*** to *Z*.

On the path to the (E)-configurated carbanion intermediate 7 upon addition of $HNMe_2$ to **1,** the system experiences the best possible stabilization by the donor ability of the Me_2N group in complete coplanar arrangement with the rest of the conjugated system (see Figure 1). With a bulky group R at the terminus, attack by Me_2NH apparently occurs only in such a fashion as to bring the more sterically demanding R into the anti-position, albeit at the expense of conjugative stabilization of the intermediate 7. Another description has been used for the analogous addition of dimethylamine to phenylethynyl phenyl ketone[19].

Because primary amino groups have a different synthetic potential, we proceeded with the addition of ammonia to **Id. To** our surprise, a mixture of the aminolysis product **10d** and the Michael addition product **9d** was obtained, with the latter predominating.

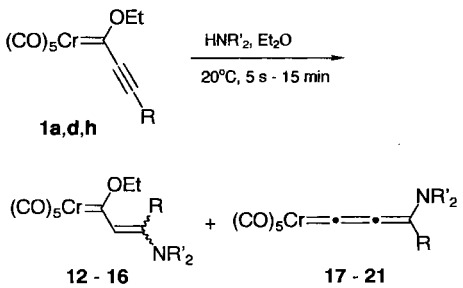


The ^{1}H-NMR spectrum of **9d** is extremely interesting. The signals of the NH_2 protons are more than 3.5 ppm apart (δ = 3.78 and 7.33 in C_6D_6). This and the signal of a vinylic proton at δ = 6.16 shows that **9d** is a primary enamine and not the tautomeric imine, and that its double bond is (*Z*)-configurated. A hydrogen bridge between N and OEt is the only possible explanation for the low-field shift of the signal of one NH_2 proton. These suppositions were confirmed by NOE measurements. The favorable hydrogen bridging in the intermediate **8d** could be the reason for the sole formation of the (*Z*)-isomer **9d**.



Furthermore, ammonia was allowed to react with the silyl-substituted complex **1i**. As expected, the two trends unfavorable for the Michael addition combined, and only the allenylidene complex **10i** was formed. A partial protiodesilylation could be a reason for the low yield in this transformation.

A series of different secondary amines was added to alkynylcarbene complexes **1a**, **1d**, and **1h** in order to test the scope and limitations of this simple route which affords high yields of diastereomerically pure [(β-aminovinyl)alkoxycarbene]pentacarbonylchromium complexes of type **3** (Table 2).



1	R
a	Ph
d	*c*Pr
h	$C(CH_3)_2OEt$

	NR'2	
12	N	17
13	$N(i\,Pr)_2$	18
14	$N(\sim\!\!\sim)_2$	19
15	$N(Bn)_2$	20
16	N O	21

The observed (*E*)/(*Z*) diastereoselectivities were in agreement with those obtained for the addition of $HNMe_2$. With R = Ph or *c*Pr, (*E*)-configurated products are favored. With a bulky tertiary group adjacent to C-3 small yields of (*Z*)-isomeric adducts are obtained besides allenylidene complexes **18h**–**20h**. Surprisingly, the Michael addition of pyrrolidine to **1h** did not only lead to the (*Z*) isomer but to a 2:1 mixture of (*E*) and (*Z*) complexes (*E*/*Z*)-**12h**, in spite of the bulky isopropyl group.

Table 2. Michael addition of secondary amines to (alkynylcarbene)chromium complexes

Starting Material	Product	Yield (%)	Configuration	Product	Yield (%)
1a	**12a**	98	*E*	**17a**	0
1a	**13a**	44	*E*	**18a**	53
1a	**14a**	98	*E*	**19a**	0
1a	**15a**	99	*E*	**20a**	0
1d	**16d**	94	*E*	**21d**	0
1h	**12h**	92	*E* / *Z* 2 : 1	**17h**	0
1h	**13h**	0	-	**18h**	68
1h	**14h**	30	*Z*	**19h**	64
1h	**15h**	23	*Z*	**20h**	74

The (*E*) configuration of **13a** was established by an X-ray crystal structure analysis. This compound shows the typical bond lengths and angles for β-hetero-substituted complexes, like pentacarbonyl[(*E*)-3-(dimethylamino)-1-methoxypropenylidene]chromium of Licandro et al.[12e] But in contrast to the latter **13a** has an antiperiplanar (*ap*) conformation (see Figure 2).

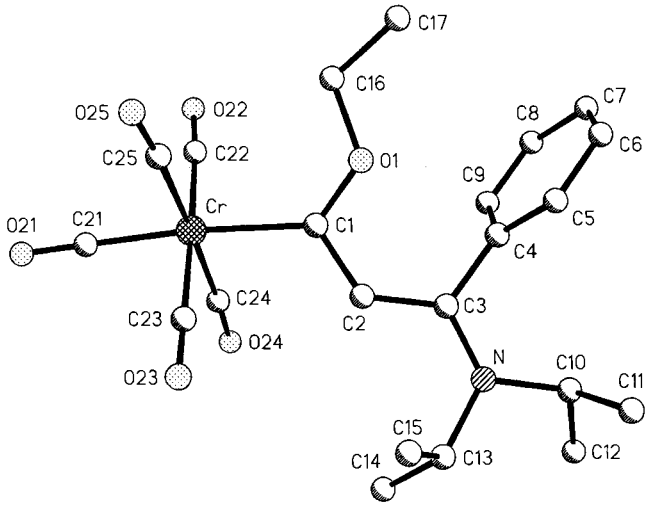


Figure 2. Structure of **13a** in the crystal

(*E*)- and (*Z*)-configurated complexes **3** and **12**–**16** can also be distinguished by their colors and UV/Vis absorption spectra. All (*Z*)-configurated complexes are orange-colored [(*Z*)-**3h**: λ_{max} (ε) = 237 nm (4.465), 340 (3.841), 420 (4.166)] while the others are light yellow [(*E*)-**3c**: λ_{max} (ε) = 241 nm (4.491), 313 (4.187), 401 (4.320)] (see Figure 3).

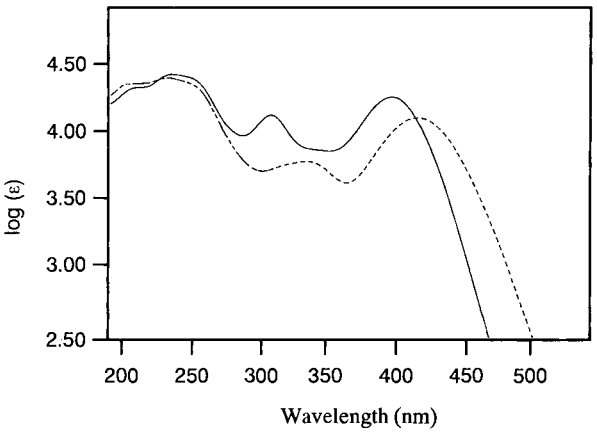
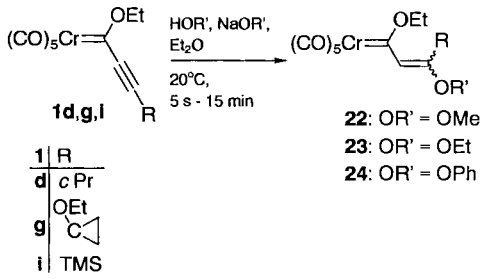


Figure 3. UV/Vis spectra of (*E*)-**3c** (—) and (*Z*)-**3h** (---) in acetonitrile

The reaction of **1h** with diisopropylamine gave an exceptionally low yield of addition product **13h** (0%), but a rather high percentage of allenylidene complex **18h**. As diisopropylamine is quite bulky, and furthermore a stronger base than some of the other amines, it apparently promotes the elimination of ethanol[14].



Next to amines, alcohols were tried as possible Michael donors. Ethanol or methanol alone add very slowly to **1**, but in the presence of a catalytic amount of alkoxide the reactions proceeded just as smoothly as with dimethylamine (Table 3). In these cases special precautions must be exercised in the addition of an alkoxy group which differs from that in the carbene position. When quenching the reaction mixture from **1d** and methanol with aqueous ammonium chloride, the isolated β-methoxy complex **22d** was contaminated with 4% of the 1,3-dimethoxy complex. Recently, Moreto et al.[16] reported on the addition of alcohols to alkynylcarbene complexes. Their conditions (alcohol with/without DBU) require long reaction times to complete the reaction (5—96 h), and the yields are lower than those reported here.

The trimethylsilyl derivatives **1i** and **6i** appeared to be a promising starting material for experiments with alcohols as well. Attempts were made to deprotect **1i** or **6i** with ethanol in the presence of a catalytic amount of ethoxide. Only the reaction with **6i** was successful, **6j** was obtained in 76% yield. By treatment with an equimolar amount of sodium ethoxide **1i** was converted into the desilylated adduct of ethanol **23j** in 46% yield in an (*E*)/(*Z*) ratio of 2:1.

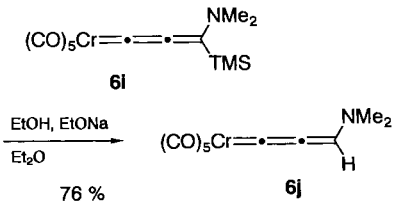


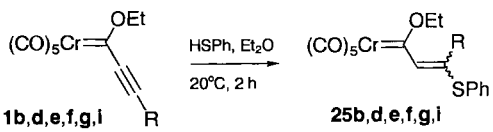
Table 3. Michael addition of alcohols to (alkynylcarbene)chromium complexes

Starting material	R	OR'	Product	Yield (%)	*E* / *Z* ratio (%)
1d	*c*Pr	OMe	**22d**	79[a]	100
1d	*c*Pr	OEt	**23d**	77	100
1h	$C(CH_3)_2OEt$	OEt	**23h**	76	60
1h	$C(CH_3)_2OEt$	OPh	**24h**	91	0
1i	H[b]	OEt	**23j**	46	67

[a] **22d** was contaminated with 4% of the 1,3-dimethoxy complex. — [b] The TMS group of **1i** was lost in the course of the reaction.

It is noteworthy, that β-amino- and β-alkoxyvinylcarbene complexes are similar in color appearance, stability, and elution behavior, but exhibit significantly different ^{13}C-NMR spectra. All the amino-substituted compounds show a substantial high-field shift of the carbene carbon signal as a consequence of the electron-donating effect of the β-amino groups. In the alkoxy derivatives this high-field shift is about 15 ppm smaller (see Table 5).

Ever since the beginning of carbene complex chemistry, this effect has been studied from various angles[1c,g]. One early procedure to bridge the gap between 1-amino- and 1-alkoxy groups has been the introduction of alkylthio groups attached to the carbene carbon as electron donors[20].



A number of variously substituted complexes **1** were treated with thiophenol; as in the case of amines, thiophenol added spontaneously (Table 4). A 1.5 molar excess of thiophenol is recommended for a rapid and total conversion. Unlike the amino and alkoxy derivatives listed above, the thiophenol adducts have exactly the same color as the starting materials and also display the same elution behavior in column chromatography.

Contrary to the addition of secondary amines, thiophenol gave mixtures of stereoisomers in all cases tested. Only for **25b** and **25e** could a separation of the diastereomers be accomplished. NOE measurements of the minor isomer of **25e** clearly pointed to the (*Z*) configuration of the product.

The ^{13}C-NMR chemical shifts for the carbene carbon in phenylthio-substituted complexes **25** are nearly the same as for the alkoxy-substituted analogues **22/23** (Table 5).

Table 4. Michael addition of thiophenol to (alkynylcarbene)chromium complexes

Starting material	R	Product	Yield (%)	*E* / *Z* ratio
1b	Me	**25b**	88	1 : 1.4
1d	*c*Pr	**25d**	75	1 : 0.8
1e	*i*Pr	**25e**	81	1 : 0.7
1f	*t*Bu	**25f**	88	1 : 1.0
1h	$C(CH_3)_2OEt$	**25h**	84[a]	1 : 1.7
1i	TMS	**25i**	26	1 : 3.0

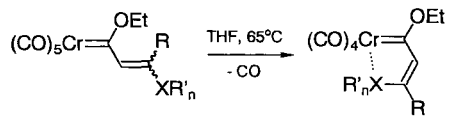
[a] The presence of a small amount of NaSPh gave rise to 98% (*E*/*Z* = 1:5) of **25h**.

Table 5. ^{13}C-NMR chemical shifts of C-1 in various β-donor-substituted (cyclopropylvinylcarbene)chromium complexes

Complex	XR'_n	δ
3d	NMe_2	284
9d	NH_2	292
22d	OMe	318
23d	OEt	317
25d	SPh	318

Chelated Vinylcarbene Complexes

In view of the fact that Fischer carbenechromium complexes of this kind readily lose a *cis*-carbonyl ligand at elevated temperatures, leaving a 16-electron complex ready to undergo further reactions[9a], a number of complexes **3**, **22**, **25** were heated in refluxing tetrahydrofuran under nitrogen. In all cases, new complexes were obtained, which were easily identified as the intramolecularly chelated complexes of type **26**–**28** (Table 6).



3: $XR'_n = NMe_2$
25: XR'_n = SPh
22: XR'_n = OMe

26: $XR'_n = NMe_2$
27: XR'_n = SPh
28: XR'_n = OMe

Similar chelatization phenomena are known for alkoxy-substituted phenylcarbene complexes[21] as well as for products of a special synthesis described by Raubenheimer[22]. Most of the newly formed chelate complexes exhibit an even higher stability than their precursors[21]. According to their ^{13}C-NMR data, **26**–**28** must contain even more electron-deficient carbene centers than most other complexes. The chemical shifts for these signals are larger than 330 ppm (Table 7). This reflects the reduced electron-donor properties of the heteroatom, the free p-electron pair of which is coordinated to chromium.

Table 6. Chelatization of various β-donor-substituted (vinylcarbene)chromium complexes

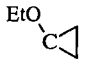
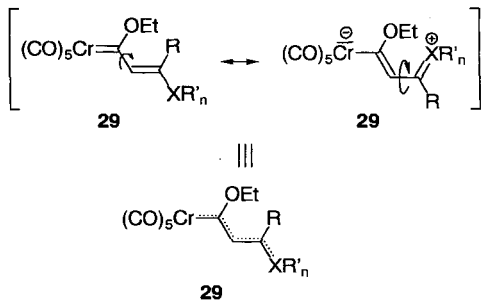
Starting material	β-Substituent	R	Product	Yield (conversion) (%)
3d	NMe_2	*c*Pr	**26d**	47 (62)
3e	NMe_2	*i*Pr	**26e**	76 (83)
3g	NMe_2		**26g**	44 (50)
3h	NMe_2	$C(CH_3)_2OEt$	**26h**	51 (53)
22d	OMe	*c*Pr	**28d**	73
25d	SPh	*c*Pr	**27d**	76
25f	SPh	*t*Bu	**27f**	81

Table 7. ^{13}C-NMR chemical shifts of C-1 in various β-donor-substituted (vinylcarbene)chromium complexes and their chelated counterparts in C_6D_6

Complex	β-Substituent	R	δ value of C-1	
			3,22,25	**26-28**
3d	NMe_2	*c*Pr	284	338
3e	NMe_2	*i*Pr	274	338
3g	NMe_2		287	337
3h	NMe_2	$C(CH_3)_2OEt$	277	338
22d	OMe	*c*Pr	318	331
25d	SPh	*c*Pr	318	335
25f	SPh	*t*Bu	324	340

In most cases, the pentacarbonylchromium complexes **3**, **22**, **25** were not heated until complete conversion had occurred, because decomposition accompanied the transformation at elevated temperatures.



29 **29**

29

It was possible to transform the (*Z*)- as well as the (*E*)-configurated complexes of type **3**, **22**, **25** into their chelated counterparts which indicates that rotations both around the single bond between C-1 and C-2 and the double bond between C-2 and C-3 must occur. This is in accord with the special electronic structure of Fischer carbene complexes. In a vinyl group adjacent to the carbene carbon, the C–C double bond has a considerable single-bond character as

caused by the strongly electron-withdrawing ability of the pentacarbonylchromium unit.

Conclusion

The Michael addition of amines, alcohols, and thiols to (alkynylcarbene)chromium complexes is a versatile route to β-donor-substituted (vinylcarbene)chromium complexes. The diastereoselectivity observed for the addition of amines and alcohols was established by NOE and NOESY experiments as well as an X-ray crystal structure analysis for one example. It depends only on the size of the group R at the terminal acetylenic position of the starting material.

The (*Z*)- as well as the (*E*)-β-donor-substituted (vinylcarbene)chromium complexes could be transformed to the corresponding chelate complexes in refluxing THF.

Many of these new β-donor-substituted vinylcarbene complexes undergo unique and synthetically useful further reactions, when treated with alkynes[9–11].

This work was supported by the *Volkswagen-Stiftung* (Schwerpunkt „Metallorganische Reaktionen für die Organische Synthese") and the *Fonds der Chemischen Industrie* as well as by the *Hoechst AG* and *Hüls AG* by generous gifts of chemicals. R. L., M. D., and E. P. are grateful to the *Studienstiftung des deutschen Volkes*, the *Deutsche Forschungsgemeinschaft* (Graduiertenkolleg „Kinetik und Selektivität chemischer Prozesse in verdichteter, fluider Phase"), and the *Stiftung Stipendienfonds des Verbandes der chemischen Industrie* for graduate fellowships.

Experimental

All operations were performed under nitrogen. Solvents were dried by distillation from sodium or potassium/benzophenone. – ^{1}H NMR: Bruker AM 250 (250 MHz), WM 270 (270 MHz), Varian XL 200 (200 MHz), VXR 200 (200 MHz), VXR 500 (500 MHz). – ^{13}C NMR: Bruker AM 250 (62.89 MHz), WM 270 (67.93 MHz), Varian XL 200 (50.31 MHz), VXR 500 (125.70 MHz), multiplicities were determined by APT (Attached Proton Test) or DEPT (Distortionless Enhancement by Polarization Transfer). Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual solvent signals. – IR: Perkin-Elmer 125, 297, 298, 399. – MS: Varian MAT CH 7, MAT 731. – HRMS: Varian MAT 311 A. – Melting points: Büchi 510, uncorrected. – Elemental analyses: Mikroanalytisches Laboratorium der Universität Hamburg, Mikroanalytisches Laboratorium der Universität Göttingen.

General Procedure for the Preparation of Pentacarbonyl(ethoxyalkynylcarbene)chromium Complexes **1**: 2.2 g (10 mmol) of hexacarbonylchromium was added to a solution of 10 mmol of alkynyllithium (from 10 mmol each of alkyne and of *n*BuLi in *n*-hexane) in 50 ml of diethyl ether at 0°C. 20 ml of tetrahydrofuran was added after 30 min, then the reaction mixture was stirred for 1.5 h at 0°C and for 1.5 h at 20°C. The resulting yellow-orange solution was treated with 11.5 mmol of triethyloxonium tetrafluoroborate, the reddish black mixture was filtered through silica gel (diethyl ether), and the solvents were removed under reduced pressure. Pure compounds were obtained by chromatography (200 g of silica gel, *n*-pentane) of the residue.

Pentacarbonyl(3-cyclopropyl-1-ethoxypropynylidene)chromium (**1d**): From 660 mg (10 mmol) of cyclopropylethyne (**5d**[17a]) was obtained 2.04 g (65%) of **1d**, $R_f = 0.43$, reddish black oil. – IR (film): $\tilde{\nu} = 2155$ cm^{-1} (C≡C), 2060 (C=O), 1930 (C=O), 1255, 1182, 1140, 1055, 900, 680, 650. – ^{1}H NMR (270 MHz, C_6D_6): δ = 0.57 (mc, 2H, cyclopropyl CH_2), 0.88 (m, 5H, cyclopropyl CH_2, OCH_2CH_3), 1.09 (mc, 1H, cyclopropyl CH), 3.89 (q, 2H, OCH_2, $^3J = 7.0$ Hz). – ^{13}C NMR (67.93 MHz, C_6D_6, plus DEPT): δ = 12.65 (–, cyclopropyl CH_2), 14.52 (+, CH_3), 75.85 (–, OCH_2), 83.36 (C_{quat}, C-2), 149.50 (C_{quat}, C-3), 217.05, 225.35 (C_{quat}, C=O), 315.16 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 314 (11) [M^+], 258 (16) [M^+ – 2 CO], 230 (29) [M^+ – 3 CO], 202 (26) [M^+ – 4 CO], 174 (75) [M^+ – 5 CO], 146 (72) [M^+ – 5 CO – C_2H_4], 52 (100) [Cr^+].

$C_{13}H_{10}CrO_6$ Calcd. 313.9882 Found 313.9882 (HRMS)

Pentacarbonyl(1-ethoxy-4-methyl-2-pentynylidene)chromium (**1e**): From 670 mg (10 mmol) of 3-methyl-1-butyne (**5e**) was obtained 2.09 g (66%) of **1e**, $R_f = 0.39$, reddish black oil. – IR (film): $\tilde{\nu} = 2993$ cm^{-1}, 2178 (C≡C), 2076 (C=O), 1973 (C=O), 1936 (C=O), 1311, 1241, 1177, 1120, 1068, 904, 686, 654, 597. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.89 (t, 3H, OCH_2CH_3, $^3J = 7.0$ Hz), 0.97 [d, 6H, $CH(CH_3)_2$, $^3J = 6.8$ Hz], 2.54 [sept, 1H, $CH(CH_3)_2$, $^3J = 6.8$ Hz], 3.96 (q, 2H, OCH_2, $^3J = 7.0$ Hz). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 14.44 (+, CH_3), 21.68 [+, $CH(CH_3)_2$], 23.19 (+, C-4), 75.75 (–, OCH_2), 85.95 (C_{quat}, C-2), 146.30 (C_{quat}, C-3), 216.99, 225.61 (C_{quat}, C=O), 318.25 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 316 (11) [M^+], 260 (12) [M^+ – 2 CO], 232 (13) [M^+ – 3 CO], 204 (21) [M^+ – 4 CO], 176 (92) [M^+ – 5 CO], 119 (29), 96 (18), 80 (26), 52 (100) [Cr^+].

$C_{13}H_{12}CrO_6$ Calcd. 316.0039 Found 316.0036 (HRMS)

Pentacarbonyl[1-ethoxy-3-(1-ethoxycyclopropyl)propynylidene]chromium (**1g**): From 940 mg (10 mmol) of (1-ethoxycyclopropyl)ethyne (**5g**[17b]) was obtained 2.30 g (64%) of **1g**, $R_f = 0.29$, reddish black oil. – IR (film): $\tilde{\nu} = 2970$ cm^{-1}, 2965, 2916, 2158 (C≡C), 2068 (C=O), 1951 (C=O), 1938 (C=O), 1450, 1373, 1321, 1294, 1229, 1091, 1069, 903, 688, 660. – ^{1}H NMR (500 MHz, C_6D_6): δ = 0.84 (t, 3H, OCH_2CH_3, $^3J = 7.0$ Hz), 1.02 (t, 3H, OCH_2CH_3, $^3J = 7.0$ Hz), 1.10 (mc, 2H, cyclopropyl CH_2), 1.13 (mc, 2H, cyclopropyl CH_2), 3.39 (q, 2H, OCH_2, $^3J = 7.0$ Hz), 3.85 (q, 2H, OCH_2, $^3J = 7.0$ Hz). – ^{13}C NMR (125.70 MHz, C_6D_6, plus APT): δ = 14.36 (+, CH_3), 15.25 (+, CH_3), 19.91 (–, cyclopropyl CH_2), 52.03 (–, cyclopropyl $COCH_2CH_3$), 64.89 (–, OCH_2), 76.03 (–, OCH_2), 88.88 (–, C-2), 164.36 (–, C-3), 216.83, 225.08 (–, C=O), 312.56 (–, C-1). – MS (EI, 70 eV): *m/z* (%) = 358 (19) [M^+], 302 (6) [M^+ – 2 CO], 274 (1) [M^+ – 3 CO], 246 (38) [M^+ – 4 CO], 218 (100) [M^+ – 5 CO], 52 (46) [Cr^+].

$C_{15}H_{14}CrO_7$ Calcd. 358.0147 Found 358.0147 (HRMS)

Pentacarbonyl(1,4-diethoxy-4-methyl-2-pentynylidene)chromium (**1h**): From 960 mg (10 mmol) of 3-ethoxy-3-methyl-1-butyne (**5h**) was obtained 2.81 g (78%) of **1h**, $R_f = 0.23$, reddish black oil. – IR (film): $\tilde{\nu} = 2990$ cm^{-1}, 2947, 2910, 2891, 2180 (C≡C), 2072 (C=O), 2010 (C=O), 1960 (C=O), 1450, 1374, 1258, 1220, 1118, 1078, 1004, 974, 918, 690, 660. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.88 (t, 3H, OCH_2CH_3, $^3J = 7.0$ Hz), 1.13 (t, 3H, OCH_2CH_3, $^3J = 7.0$ Hz), 1.41 (s, 6H, CH_3), 3.44 (q, 2H, OCH_2CH_3, $^3J = 7.0$ Hz), 3.96 (q, 2H, OCH_2CH_3, $^3J = 7.0$ Hz). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 14.46 (+, OCH_2CH_3), 15.82 (+, OCH_2CH_3), 28.01 (+, CH_3), 60.42 (–, OCH_2), 71.32 (C_{quat}, C-4), 76.06 (–, OCH_2), 87.73 (C_{quat}, C-2), 164.42 (C_{quat}, C-3), 216.69, 225.44 (C_{quat}, C=O), 317.03 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 360 (4) [M^+], 304 (3) [M^+ – 2 CO], 276 (2) [M^+ – 3 CO], 248 (7) [M^+ – 4 CO], 220 (5) [M^+ – 5 CO], 218 (100), 52 (14) [Cr^+].

$C_{15}H_{16}CrO_7$ Calcd. 360.0301 Found 360.0301 (HRMS)

General Procedure for the Preparation of β-Donor-substituted (Vinylcarbene)chromium Complexes: The nucleophiles were added

to a solution of 5 mmol of **1** in 50 ml of diethyl ether. When alcohols were used as nucleophiles **1** was dissolved in diethyl ether/alcohol (1:1), then 5% of the corresponding sodium alkoxide was added, and the reaction was subsequently quenched with a saturated solution of ammonium chloride. The reaction mixture was stirred at 20°C until no more starting material was detected by TLC. The solvents were removed under reduced pressure, and the residue was purified by chromatography over 100 g of silica gel to afford the pure complex.

Pentacarbonyl[(2E)-3-(dimethylamino)-1-ethoxy-2-hexenylidene]chromium (**3c**): To 1.58 g (5 mmol) of pentacarbonyl(1-ethoxy-2-hexynylidene)chromium (**1c**) was added dimethylamine until a change of color was observed. After purification 1.68 g (93%) of **3c** was obtained, R_f = 0.30 (pentane/diethyl ether, 1:1), yellow crystals, m.p. 99°C. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2046 (C=O), 1925 (C=O), 1893 (C=O), 1533, 1481, 1440, 1382, 1276, 1229, 1111, 1072, 933, 702, 671, 463. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.70 (t, 3H, $CH_2CH_2CH_3$, ^3J = 7.0 Hz), 1.11 (mc, 5H, $CH_2CH_2CH_3$, OCH_2CH_3), 2.04 [bs, 6H, $N(CH_3)_2$], 2.14 (t, 2H, $CH_2CH_2CH_3$, ^3J = 7.0 Hz), 4.67 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.37 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 14.04, 15.44 (+, C-6, OCH_2CH_3), 20.99 (–, C-5), 33.25 (–, C-4), 40.29 [+, $N(CH_3)_2$], 74.23 (–, OCH_2), 118.14 (+, C-2), 158.88 (C_{quat}, C-3), 220.35, 224.78 (C_{quat}, C=O), 286.76 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 361 (1) [M^+], 333 (5) [M^+ – CO], 305 (7) [M^+ – 2 CO], 277 (13) [M^+ – 3 CO], 249 (11) [M^+ – 4 CO], 221 (100) [M^+ – 5 CO], 164 (30), 136 (27), 94 (27), 52 (34) [Cr^+].

$C_{15}H_{19}CrNO_6$ (361.3) Calcd. C 49.87 H 5.30 N 3.88
Found C 49.61 H 5.35 N 3.73

Pentacarbonyl[(2E)-3-cyclopropyl-3-(dimethylamino)-1-ethoxy-2-propenylidene]chromium (**3d**): To 1.57 g (5 mmol) of **1d** was added dimethylamine until a change of color was observed. After purification 1.72 g (96%) of **3d** was obtained, R_f = 0.22 (pentane/diethyl ether, 4:1), yellow crystals. – IR (KBr): $\tilde{\nu}$ = 3008 cm^{-1}, 2925, 2043 (C=O), 1963 (C=O), 1914 (C=O), 1530, 1464, 1434, 1413, 1364, 1247, 1178, 1101, 1012, 955, 694, 668, 652, 520. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.22–0.68 (m, 4H, cyclopropyl CH_2), 1.15 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.19 (s, 6H, NCH_3), 4.64 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.01 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 9.92 (–, cyclopropyl CH_2), 15.26 (+, CH_3), 15.65 (+, cyclopropyl CH), 41.14 (+, NCH_3), 73.19 (–, OCH_2), 116.45 (+, C-2), 163.73 (C_{quat}, C-3), 220.55, 224.62 (C_{quat}, C=O), 283.93 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 359 (4) [M^+], 331 (4) [M^+ – CO], 303 (5) [M^+ – 2 CO], 275 (6) [M^+ – 3 CO], 247 (13) [M^+ – 4 CO], 219 (29) [M^+ – 5 CO], 191 (100) [M^+ – 5 CO – C_2H_4], 166 (13), 121 (17), 111 (13), 95 (26), 85 (15), 83 (17), 71 (26), 69 (20), 57 (37), 55 (15), 52 (30) [Cr^+].

$C_{15}H_{17}CrNO_6$ Calcd. 359.0461 Found 359.0459 (HRMS)

Pentacarbonyl[(2E)-3-(dimethylamino)-1-ethoxy-4-methyl-2-pentenylidene]chromium (**3e**): To 1.58 g (5 mmol) of **1e** was added dimethylamine until a change of color was observed. After purification 1.64 g (91%) of **3e** was obtained, R_f = 0.12 (pentane/diethyl ether, 1:1), yellow crystals, m.p. 79°C. – IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1}, 2043 (C=O), 1947 (C=O), 1882 (C=O), 1572, 1481, 1421, 1278, 1107, 662. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.79 [d, 6H, $CH(CH_3)_2$, ^3J = 6.8 Hz], 1.09 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.16 [s, 6H, $N(CH_3)_2$], 2.36 [sept, 1H, $CH(CH_3)_2$, ^3J = 6.8 Hz], 4.60 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.21 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.68 (+, OCH_2CH_3), 20.16 [+, $CH(CH_3)_2$], 31.58 (+, C-4), 42.87 [+, $N(CH_3)_2$], 72.83 (–, OCH_2), 114.36 (+, C-2), 169.35 (C_{quat}, C-3), 220.72, 224.86 (C_{quat}, C=O), 274.33 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 361 (1) [M^+], 333 (5) [M^+ – CO], 305 (7) [M^+ – 2 CO], 277 (10) [M^+ – 3 CO], 249 (12) [M^+ – 4 CO], 221 (100) [M^+ – 5 CO], 164 (32), 95 (35), 52 (50) [Cr^+].

$C_{15}H_{19}CrNO_6$ (361.3) Calcd. C 49.87 H 5.30 N 3.88
Found C 49.63 H 5.36 N 3.85

Pentacarbonyl[(2Z)-3-(dimethylamino)-1-ethoxy-4,4-dimethyl-2-pentenylidene]chromium (**3f**) *and Pentacarbonyl[3-(dimethylamino)-4,4-dimethyl-1,2-pentadienylidene]chromium* (**6f**): To 1.65 g (5 mmol) of pentacarbonyl(1-ethoxy-4,4-dimethyl-2-pentynylidene)-chromium (**1f**) was added dimethylamine until a change of color was observed. Purification yielded fraction I: 1.18 g (63%) of **3f**, R_f = 0.14 (pentane/diethyl ether, 1:1), yellow crystals, m.p. 78°C. – IR (KBr): $\tilde{\nu}$ = 2975 cm^{-1}, 2046 (C=O), 1922 (C=O), 1900 (C=O), 1544, 1461, 1397, 1256, 1102, 672. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.86 [s, 9H, $C(CH_3)_3$], 1.02 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.30 [s, 6H, $N(CH_3)_2$], 4.56 (q, ^3J = 7.0 Hz, 2H, OCH_2), 6.45 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.74 (+, OCH_2CH_3), 28.96 [+, $C(CH_3)_3$], 38.33 (C_{quat}, C-4), 45.55 [+, $N(CH_3)_2$], 72.44 (–, OCH_2), 115.93 (+, C-2), 171.60 (C_{quat}, C-3), 220.68, 224.60 (C_{quat}, C=O), 271.98 (C_{quat}, C-1). – MS (70 eV): *m/z* (%) = 375 (4) [M^+], 347 (18) [M^+ – CO], 319 (6) [M^+ – 2 CO], 291 (17) [M^+ – 3 CO], 263 (12) [M^+ – 4 CO], 235 (100) [M^+ – 5 CO], 178 (64), 150 (38), 95 (42), 52 (58) [Cr^+].

$C_{16}H_{21}CrNO_6$ (375.3) Calcd. C 51.20 H 5.64 N 3.73
Found C 51.07 H 5.80 N 3.65

II: 130 mg (8%) of **6f**, R_f = 0.07, orange crystals, m.p. 91°C. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2180 (C=C=C), 2072, 1995, 1930 (C=O), 1550, 1405, 1365, 910, 650. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.91 [s, 9H, $C(CH_3)_3$], 1.94 (s, 3H, NCH_3), 2.62 (s, 3H, NCH_3). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 29.02 [+, $C(CH_3)_3$], 38.47 (C_{quat}, C-4), 41.07, 46.83 [+, $N(CH_3)_2$], 122.77 (C_{quat}, C-2), 163.73 (C_{quat}, C-3), 218.72, 224.27 (C_{quat}, C=O), 229.42 (C_{quat}, C-1). – MS (70 eV): *m/z* (%) = 329 (6) [M^+], 273 (1) [M^+ – CO], 245 (2) [M^+ – 3 CO], 217 (5) [M^+ – 4 CO], 189 (38) [M^+ – 5 CO], 52 (100) [Cr^+].

$C_{14}H_{15}CrNO_5$ Calcd. 329.0355 Found 329.0355 (HRMS)

Pentacarbonyl[(2Z)-3-(dimethylamino)-1-ethoxy-3-(1-ethoxycyclopropyl)-2-propenylidene]chromium (**3g**) *and Pentacarbonyl[3-(dimethylamino)-3-(1-ethoxycyclopropyl)propadienylidene]chromium* (**6g**). To 1.79 g (5 mmol) of **1g** was added dimethylamine until a change of color was observed. Purification yielded fraction I: 1.71 g (85%) of **3g**, R_f = 0.24 (pentane/diethyl ether, 4:1), yellow crystals, m.p. 53°C. – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 2940, 2908, 2808, 2893, 2070 (C=O), 1968 (C=O), 1942 (C=O), 1626, 1448, 1398, 1308, 1262, 1074, 805, 697, 670. – ^{1}H NMR (500 MHz, C_6D_6): δ = 0.65 (m, 2H, cyclopropyl CH_2), 0.73 (m, 2H, cyclopropyl CH_2), 0.88 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.06 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.41 [bs, 6H, $N(CH_3)_2$], 3.19 (q, 2H, OCH_2, ^3J = 7.0 Hz), 4.63 (q, 2H, OCH_2, ^3J = 7.0 Hz, 6.25 (s, 1H, =CH). – ^{13}C NMR (125.79 MHz, C_6D_6, plus APT): δ = 15.31 (–, cyclopropyl CH_2), 15.50 (+, CH_3), 15.74 (+, CH_3), 42.15 [+, $N(CH_3)_2$], 60.29 (–, cyclopropyl $COCH_2CH_3$), 64.24 (–, OCH_2), 73.88 (–, OCH_2), 117.44 (+, C-2), 159.52 (–, C-3), 220.08, 224.61 (–, C=O), 287.43 (–, C-1). – MS (EI, 70 eV): *m/z* (%) = 403 (16) [M^+], 375 (8) [M^+ – CO], 347 (7) [M^+ – 2 CO], 319 (16) [M^+ – 3 CO], 291 (35) [M^+ – 4 CO], 263 (33) [M^+ – 5 CO], 191 (68), 166 (100), 52 (45) [Cr^+].

$C_{17}H_{21}CrNO_7$ (403.3) Calcd. C 50.62 H 5.25 N 3.47
Found C 50.67 H 5.51 N 3.52

II: 23 mg (13%) of **6g**, R_f = 0.34, orange crystals, m.p. 84°C. – IR (KBr): $\tilde{\nu}$ = 2976 cm^{-1}, 2918, 2154 (C=C=C), 2056, 2018, 1947

(C=O), 1895, 1574, 1404, 1272, 1168, 822, 798, 756, 672. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.81 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.14 (mc, 2H, cyclopropyl CH_2), 1.16 (mc, 2H, cyclopropyl CH_2), 2.52 (s, 3H, NCH_3), 2.63 (s, 3H, NCH_3), 3.44 (q, 2H, OCH_2, ^3J = 7.0 Hz). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 14.74 (+, OCH_2CH_3), 19.94 (–, cyclopropyl CH_2), 40.48, 46.36 (+, NCH_3), 52.14 (C_{quat}, $COCH_2CH_3$), 60.42 (–, OCH_2), 119.86 (C_{quat}, C-2), 161.34 (C_{quat}, C-3), 217.49, 228.04 (C_{quat}, C=O), 231.48 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 357 (10) [M^+], 329 (6) [M^+ – CO], 301 (1) [M^+ – 2 CO], 273 (1) [M^+ – 3 CO], 245 (4) [M^+ – 4 CO], 217 (19) [M^+ – 5 CO], 52 (100) [Cr^+].

$C_{15}H_{15}CrNO_6$ Calcd. 357.0304 Found 357.0304 (HRMS)

Pentacarbonyl[(2Z)-3-(dimethylamino)-1,4-diethoxy-4-methyl-2-pentenylidene]chromium (**3h**) *and Pentacarbonyl[3-(dimethylamino)-4-ethoxy-4-methyl-1,2-pentadienylidene]chromium* (**6h**): To 1.80 g (5 mmol) of **1h** was added dimethylamine until a change of color was observed. Purification yielded fraction I: 1.62 g (80%) of **3h**, R_f = 0.32 (pentane/diethyl ether, 4:1), orange crystals, m.p. 51°C. – IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1}, 2950, 2916, 2894, 2055 (C=O), 1968 (C=O), 1922 (C=O), 1560, 1464, 1408, 1262, 1190, 1109, 981, 922, 780, 692. – ^{1}H NMR (200 MHz, C_6D_6): δ = 0.83 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.02 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.17 (s, 6H, CH_3), 2.58 [s, 6H, $N(CH_3)_2$], 2.76 (q, 2H, OCH_2, ^3J = 7.0 Hz), 4.58 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.32 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.70 (+, OCH_2CH_3), 15.75 (+, OCH_2CH_3), 26.62 (+, CH_3), 45.08 [+, $N(CH_3)_2$], 59.02 (–, OCH_2), 72.76 (–, OCH_2), 78.74 [C_{quat}, $C(CH_3)_2$], 115.88 (C_{quat}, C-2), 165.71 (C_{quat}, C-3), 220.50, 224.55 (C_{quat}, C=O), 276.51 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 405 (3) [M^+], 377 (4) [M^+ – CO], 349 (6) [M^+ – 2 CO], 321 (27) [M^+ – 3 CO], 293 (4) [M^+ – 4 CO], 265 (32) [M^+ – 5 CO], 177 (80), 124 (100), 52 (74) [Cr^+].

$C_{17}H_{23}CrNO_7$ (405.1) Calcd. C 50.37 H 5.72
Found C 50.27 H 5.65

II: **6h**, 23 mg (13%), R_f = 0.07, orange crystals, m.p. 82°C. – IR (KBr): $\tilde{\nu}$ = 2998 cm^{-1}, 2955, 2921, 2880, 2150 (C=C=C), 2048 (C=O), 2025 (C=O), 1961 (C=O), 1895, 1618, 1582, 1407, 1400, 1277, 1178, 981, 824, 799, 760, 671. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.78 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.29 [s, 6H, $C(CH_3)_2$], 2.49 (s, 3H, NCH_3), 2.61 (s, 3H, NCH_3), 3.47 (q, 2H, OCH_2, ^3J = 7.0 Hz). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.37 (+, OCH_2CH_3), 26.73 (+, CH_3), 40.45 (+, NCH_3), 46.28 (+, NCH_3), 59.37 (–, OCH_2), 78.80 [C_{quat}, $C(CH_3)_2$], 123.86 (C_{quat}, C-2), 159.02 (C_{quat}, C-3), 218.49, 232.77 (C_{quat}, C=O), 232.07 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 359 (4) [M^+], 331 (1) [M^+ – CO], 303 (1) [M^+ – 2 CO], 275 (1) [M^+ – 3 CO], 247 (7) [M^+ – 4 CO], 219 (21) [M^+ – 5 CO], 52 (100) [Cr^+].

$C_{15}H_{17}CrNO_6$ Calcd. 359.0461 Found 359.0461 (HRMS)

Pentacarbonyl[3-(dimethylamino)-3-(trimethylsilyl)propadienylidene]chromium (**6i**) *and Pentacarbonyl[(2Z)-3-(dimethylamino)-1-ethoxy-3-(trimethylsilyl)-2-propenylidene]chromium* (**3i**): To 1.73 g (5 mmol) of pentacarbonyl[1-ethoxy-3-(trimethylsilyl)propynylidene]chromium (**1i**) was added dimethylamine until a change of color was observed. Purification yielded fraction I: 470 mg (27%) of **6i**, R_f = 0.33 (pentane/diethyl ether, 3:1), orange oil. – IR (film): $\tilde{\nu}$ = 2962 cm^{-1}, 2054 (C=O), 1937 (C=O), 1924 (C=O), 1530, 1403, 1252, 1163, 1049, 844, 660, 458. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.22 [s, 9H, $Si(CH_3)_3$], 2.48 (s, 3H, NCH_3), 2.98 (s, 3H, NCH_3). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = –0.75 [+, $Si(CH_3)_3$], 46.78 (+, NCH_3), 48.44 (+, NCH_3), 104.73 (C_{quat}, C-2), 136.78 (C_{quat}, C-3), 217.87, 224.34 (C_{quat}, C=O), 249.68 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 345 (2) [M^+], 289 (4) [M^+ – 2 CO], 261 (5) [M^+ – 3 CO], 233 (12) [M^+ – 4 CO], 206 (100) [M^+ – 5 CO], 52 (17) [Cr^+].

$C_{13}H_{15}CrNO_5Si$ Calcd. 345.0125 Found 345.0125 (HRMS)

II: 590 mg (30%) of **3i**, R_f = 0.17, orange crystals, m.p. 53°C. – IR (KBr): $\tilde{\nu}$ = 2945 cm^{-1}, 2043 (C=O), 1979 (C=O), 1913 (C=O), 1520, 1459, 1403, 1247, 1081, 850, 670. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.01 [s, 9H, $Si(CH_3)_3$], 1.11 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.14 [s, 6H, $N(CH_3)_2$], 4.61 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.44 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 0.97 [+, $Si(CH_3)_3$], 15.72 (+, OCH_2CH_3), 44.23 [+, $N(CH_3)_2$], 73.10 (–, OCH_2), 125.27 (+, C-2), 174.15 (C_{quat}, C-3), 220.42, 224.91 (C_{quat}, C=O), 278.53 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 307 (1) [M^+ – 3 CO], 279 (1) [M^+ – 4 CO], 251 (10) [M^+ – 5 CO], 184 (97), 154 (18), 109 (29), 94 (39), 73 (55), 52 (100) [Cr^+].

$C_{15}H_{21}CrNO_6Si$ (391.4) Calcd. C 46.03 H 5.41 N 3.58
Found C 46.27 H 5.52 N 3.52

Pentacarbonyl[3-(dimethylamino)propadienylidene]chromium (**6j**): To a solution of 173 mg (0.5 mmol) of **6i** in 10 ml of diethyl ether/ethanol (1:1) was added 1.2 ml of a 2 N solution of sodium ethoxide in ethanol. The mixture was filtered through silica gel (diethyl ether), and the solvents were removed under reduced pressure. The pure compound was obtained by chromatography (20 g of silicagel, pentane/diethyl ether) of the residue. Yield: 104 mg (76%) of **6j**, R_f = 0.23, orange oil. – IR (film): $\tilde{\nu}$ = 3430 cm^{-1}, 2926, 2058 (C=O), 1972 (C=O), 1919 (C=O), 1626, 1534, 1402, 998, 670, 461. – ^{1}H NMR (250 MHz, C_6D_6): δ = 2.30 (s, 3H, NCH_3), 2.90 (s, 3H, NCH_3), 5.03 (s, 1H, 3-H). – ^{13}C NMR (62.89 MHz, C_6D_6): δ = 46.72, 48.66 [$N(CH_3)_2$], 84.29 (C-2), 116.10 (C-3), 217.68, 223.99 (C=O), 250.08 (C-1).

$C_{10}H_7CrNO_7$ Calcd. 272.9729 Found 272.9725 (HRMS)

(1-Amino-3-cyclopropylpropynylidene)pentacarbonylchromium (**10d**) *and [(2Z)-3-Amino-1-ethoxy-3-cyclopropyl-2-propenylidene]-pentacarbonylchromium* (**9d**): To 1.57 g (5 mmol) of **1d** was added ammonia until a change of color was observed. Purification yielded fraction I: 400 mg (28%) of **10d**, R_f = 0.34 (pentane/diethyl ether, 1:1), orange crystals, m.p. 66°C. – IR (KBr): $\tilde{\nu}$ = 3428 cm^{-1} (NH), 3336 (NH), 3257 (NH), 2184 (C≡C), 2162 (C=O), 2058 (C=O), 1909 (C=O), 1650, 1407, 1346, 861, 701, 658, 456. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.49–0.59 (m, 2H, cyclopropyl CH_2), 0.77 (mc, 2H, cyclopropyl CH_2), 1.08 (mc, 1H, cyclopropyl CH), 6.52 (bs, 1H, NH), 6.92 (bs, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 1.59 (+, cyclopropyl CH), 11.20 (–, cyclopropyl CH_2), 82.39 (C_{quat}, C-2), 134.20 (C_{quat}, C-3), 217.51, 223.76 (C_{quat}, C=O), 265.81 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 285 (9) [M^+], 229 (10) [M^+ – 2 CO], 201 (15) [M^+ – 3 CO], 173 (18) [M^+ – 4 CO], 145 (53) [M^+ – 5 CO], 117 (60), 52 (100) [Cr^+].

$C_{11}H_7CrNO_5$ Calcd. 284.9729 Found 284.9724 (HRMS)

II: 1.16 g (70%) of **9d**, R_f = 0.11, yellow crystals, m.p. 116°C. – IR (KBr): $\tilde{\nu}$ = 3495 cm^{-1} (NH), 3370 (NH), 2048 (C=O), 1925 (C=O), 1893 (C=O), 1606, 1510, 1255, 1101, 1024, 671, 465. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.24–0.34 (m, 4H, cyclopropyl CH_2), 0.34–0.46 (m, 1H, cyclopropyl CH), 0.93 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 3.78 (bs, 1H, NH), 4.55 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.16 (s, 1H, =CH), 7.33 (bs, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 9.39 (–, cyclopropyl CH_2), 15.37, 16.23 (+, cyclopropyl CH, OCH_2CH_3), 73.82 (–, OCH_2), 115.20 (+, C-2), 157.66 (C_{quat}, C-3), 219.54, 224.21 (C_{quat}, C=O), 291.87 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 331 (0.2) [M^+], 303 (1) [M^+ – CO], 276 (37) [M^+ – 2 CO + H], 219 (5) [M^+ – 4 CO], 191

(55) [$M^+ - 5\,CO$], 163 (88), 149 (62), 105 (57), 80 (43), 68 (61), 52 (100) [Cr^+].

$C_{13}H_{13}CrNO_6$ (331.3) Calcd. C 47.14 H 3.93 N 4.23
Found C 46.95 H 3.91 N 4.15

[3-Amino-3-(trimethylsilyl)propadienylidene]pentacarbonylchromium (**11i**): To 1.73 g (5 mmol) of **1i** was added ammonia until a change of color was observed. After purification 430 mg (27%) of **11i** was obtained, R_f = 0.29 (pentane/diethyl ether, 1:1), orange oil. – IR (film): $\tilde{\nu}$ = 3453 cm^{-1} (NH), 3347 (NH), 2964, 2125 (C=C=C), 2060 (C=O), 1930 (C=O), 1906 (C=O), 1637, 1382, 1253, 1212, 974, 848, 652. – ^1H NMR (250 MHz, C_6D_6): δ = 0.20 [s, 9H, $Si(CH_3)_3$], 6.60 (bs, 1H, NH), 7.12 (bs, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = −0.91 [+, $Si(CH_3)_3$], 106.07 (C_{quat}, C-2), 131.71 (C_{quat}, C-3), 217.17, 223.87 (C_{quat}, C=O), 268.42 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 317 (3) [M^+], 233 (3) [$M^+ - 3\,CO$], 205 (16) [$M^+ - 4\,CO$], 177 (100) [$M^+ - 5\,CO$], 52 (33) [Cr^+].

$C_{11}H_{11}CrNO_5Si$ Calcd. 316.9812 Found 316.9811 (HRMS)

Pentacarbonyl[(2E)-3-cyclopropyl-1-ethoxy-3-morpholino-2-propenylidene]chromium (**16d**): To 1.57 g (5 mmol) of **1d** was added morpholine until a change of color was observed. Purification yielded 1.62 g (94%) of **16d**, R_f = 0.31 (pentane/diethyl ether, 4:1), yellow oil. – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 2930, 2870, 2050 (C=O), 1924 (C=O), 1900 (C=O), 1530, 1465, 1440, 1430, 1240, 1120, 665. – ^1H NMR (250 MHz, C_6D_6): δ = 0.32–0.43 (m, 4H, cyclopropyl CH_2), 0.54 (mc, 1H, cyclopropyl CH), 1.08 (t, 3H, CH_3, ^3J = 7.0 Hz), 2.75–2.81 (m, 4H, NCH_2), 2.92–2.98 (m, 4H, OCH_2CH_2N), 4.64 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.20 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 9.71 (−, cyclopropyl CH_2), 15.08 (+, CH_3), 15.62 (+, cyclopropyl CH), 50.05 (−, OCH_2CH_2N), 65.98 (−, OCH_2CH_2N), 73.52 (−, OCH_2), 115.83 (+, C-2), 162.69 (C_{quat}, C-3), 220.25, 224.73 (C_{quat}, C=O), 284.03 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 401 (2) [M^+], 345 (2) [$M^+ - 2\,CO$], 317 (21) [$M^+ - 3\,CO$], 289 (13) [$M^+ - 4\,CO$], 261 (58) [$M^+ - 5\,CO$], 233 (87) [$M^+ - 5\,CO - C_2H_4$], 175 (29), 163 (23), 119 (15), 82 (15), 74 (92), 69 (39), 59 (100), 52 (45) [Cr^+].

$C_{15}H_{19}CrNO_5$ [$M^+ - 2\,CO$] Calcd. 345.0668
Found 345.0637 (HRMS)

Pentacarbonyl[(2E)-1-ethoxy-3-phenyl-3-(1-pyrrolidinyl)-2-propenylidene]chromium (**12a**): To 1.75 g (5 mmol) of pentacarbonyl(1-ethoxy-3-phenylpropynylidene)chromium (**1a**) was added pyrrolidine until a change of color was observed. Purification yielded 2.07 g (98%) of **12a**, R_f = 0.21 (pentane/diethyl ether, 5:1), yellow crystals, m.p. 97°C. – IR (KBr): $\tilde{\nu}$ = 3012 cm^{-1}, 2994, 2971, 2953, 2050 (C=O), 1946 (C=O), 1901 (C=O), 1507, 1496, 1424, 1317, 1243, 1175, 1114, 1008, 940, 727, 700, 678, 650. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.52 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.78 (tt, 2H, NCH_2CH_2, ^3J = 7.2, ^3J = 7.2 Hz), 2.03 (tt, 2H, NCH_2CH_2, ^3J = 7.2, ^3J = 7.2 Hz), 3.06 (t, 2H, NCH_2CH_2, ^3J = 7.2 Hz), 3.58 (t, 2H, NCH_2CH_2, ^3J = 7.2 Hz), 4.12 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 6.38 (s, 1H, =CH), 6.98–7.16 (m, 2H, phenyl H), 7.28–7.42 (m, 3H, phenyl H). – ^{13}C NMR (62.89 MHz, C_6D_6, plus APT): δ = 14.10 (+, OCH_2CH_3), 24.57 (−, NCH_2CH_2), 25.04 (−, NCH_2CH_2), 49.16 (−, NCH_2CH_2), 50.26 (−, NCH_2CH_2), 73.17 (−, OCH_2CH_3), 118.66 (+, C-2), 126.85, 127.67, 127.99 (+, phenyl C), 138.99 (−, phenyl C), 152.73 (−, C-3), 220.28, 224.78 (−, C=O), 290.90 (−, C-1). – MS (EI, 70 eV): *m/z* (%) = 421 (20) [M^+], 393 (9) [$M^+ - CO$], 365 (1) [$M^+ - 2\,CO$], 337 (39) [$M^+ - 3\,CO$], 309 (44) [$M^+ - 4\,CO$], 281 (100) [$M^+ - 5\,CO$], 253 (62), 224 (36), 197 (66), 121 (41), 97 (74), 91 (53) [$C_7H_7^+$], 57 (49), 52 (40) [Cr^+].

$C_{20}H_{19}CrNO_6$ (421.4) Calcd. C 57.13 H 4.55 N 3.32
Found C 57.42 H 4.74 N 3.16

Pentacarbonyl[(2E)- and -(2Z)-1,4-diethoxy-4-methyl-3-(1-pyrrolidinyl)-2-pentenylidene]chromium (**12h**): To 1.80 g (5 mmol) of **1h** was added pyrrolidine until a change of color was observed. Purification yielded 1.98 g (92%) of **12h**, R_f = 0.36 (pentane/diethyl ether, 5:1), yellow crystals, m.p. 98°C, *E/Z* = 2:1. – IR (KBr): $\tilde{\nu}$ = 2973 cm^{-1}, 2930, 2862, 2039 (C=O), 1961 (C=O), 1904 (C=O), 1598, 1445, 1340, 1226, 1160, 1063, 922, 873, 755, 698, 673. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.07 (t, *E*, OCH_2CH_3, ^3J = 7.0 Hz), 1.12 (t, *E*, OCH_2CH_3, ^3J = 7.0 Hz), 1.32 (t, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 1.38 (t, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 1.44 [s, *E*, $C(CH_3)_2$], 1.49 [s, *Z*, $C(CH_3)_2$], 1.52–2.10 (m, *E*, NCH_2CH_2), 2.64 (bs, *Z*, NCH_2CH_2), 2.92 (bs, *Z*, NCH_2CH_2), 3.22 (q, *E*, OCH_2CH_3, ^3J = 7.0 Hz), 3.31 (q, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 3.43 (bs, *Z*, NCH_2CH_2), 3.65 (bs, *E*, NCH_2CH_2), 4.08 (q, *E*, OCH_2CH_3, ^3J = 7.0 Hz), 4.50 (q, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 5.68 (s, *E*, =CH), 6.07 (s, *Z*, =CH). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 15.54 (+, *E*, OCH_2CH_3), 15.62 (+, *E*, OCH_2CH_3), 15.68 (+, *Z*, OCH_2CH_3), 15.82 (+, *Z*, OCH_2CH_3), 24.20 (−, *E*, NCH_2CH_2), 25.47 (−, *Z*, NCH_2CH_2), 26.22 [+, *E*, $C(CH_3)_2$], 28.39 [+, *Z*, $C(CH_3)_2$], 50.62 (−, *E*, NCH_2CH_2), 54.64 (−, *Z*, NCH_2CH_2), 58.44 (−, *E*, OCH_2CH_3), 58.87 (−, *Z*, OCH_2CH_3), 72.24 (−, *E*, OCH_2CH_3), 72.53 (−, *Z*, OCH_2CH_3), 116.29 (+, *E*, C-2), 116.56 (+, *Z*, C-2), 143.78 (C_{quat}, *E*, C-3), 162.51 (C_{quat}, *Z*, C-3), 219.00 (C_{quat}, *E*, C=O), 219.67 (C_{quat}, *Z*, C=O), 224.16 (C_{quat}, *E*, C=O), 224.43 (C_{quat}, *Z*, C=O), 255.66 (C_{quat}, *E*, C-1), 273.78 (C_{quat}, *Z*, C-1). – MS (EI, 70 eV): *m/z* (%) = 431 (0.2) [M^+], 347 (18) [$M^+ - 3\,CO$], 291 (0.2) [$M^+ - 5\,CO$], 263 (5) [$M^+ - 5\,CO - C_2H_4$], 235 (8) [$M^+ - 5\,CO - 2\,C_2H_4$], 219 (100), 70 (20) [$NC_4H_8^+$], 52 (21) [Cr^+].

$C_{19}H_{25}CrNO_7$ Calcd. 431.1036 Found 431.1036 (HRMS)

Pentacarbonyl[(2E)-3-(di-2-propenylamino)-1-ethoxy-3-phenyl-2-propenylidene]chromium (**14a**): To 1.75 g (5 mmol) of **1a** was added di-2-propenylamine until a change of color was observed. Purification yielded 2.19 g (98%) of **14a**, R_f = 0.11 (pentane/diethyl ether, 5:1), yellow crystals, m.p. 75°C. – IR (KBr): $\tilde{\nu}$ = 3101 cm^{-1}, 3075, 2998, 2948, 2894, 2881, 2050 (C=O), 1956 (C=O), 1921 (C=O), 1649, 1500, 1422, 1280, 1238, 1179, 1116, 1023, 939, 880, 814, 779, 701, 676. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.62 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 3.57 (bs, 2H, NCH_2CHCH_2), 4.10 (bs, 2H, NCH_2CHCH_2), 4.21 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 5.32 [bs, 4H, $N(CH_2CHCH_2)_2$], 5.65 (bs, 1H, NCH_2CHCH_2), 5.88 (bs, 1H, NCH_2CHCH_2), 6.77 (s, 1H, =CH), 7.12 (mc, 2H, phenyl H), 7.39 (mc, 3H, phenyl H). – ^{13}C NMR (62.89 MHz, C_6D_6, plus APT): δ = 14.26 (+, OCH_2CH_3), 52.82 (−, NCH_2CHCH_2), 73.48 (−, OCH_2CH_3), 119.21 (+, C-2), 119.34 (−, NCH_2CHCH_2), 127.96, 129.31, 129.54 (+, phenyl C), 133.02 (+, NCH_2CHCH_2), 137.43 (−, phenyl C), 154.32 (−, C-3), 219.11, 224.38 (−, C=O), 298.08 (−, C-1). – MS (EI, 70 eV): *m/z* (%) = 447 (8) [M^+], 419 (6) [$M^+ - CO$], 363 (31) [$M^+ - 3\,CO$], 335 (7) [$M^+ - 4\,CO$], 307 (44) [$M^+ - 5\,CO$], 266 (36), 240 (61), 210 (58), 169 (62), 108 (65), 80 (96), 77 (29), 55 (23), 52 (100) [Cr^+].

$C_{22}H_{21}CrNO_6$ (447.1) Calcd. C 59.06 H 4.73 N 3.13
Found C 59.21 H 4.79 N 3.12

Pentacarbonyl[(2E)-3-(dibenzylamino)-1-ethoxy-3-phenyl-2-propenylidene]chromium (**15a**): To 1.75 g (5 mmol) of **1a** was added dibenzylamine until a change of color was observed. Purification yielded 2.71 g (94%) of **15a**, R_f = 0.30 (pentane/diethyl ether, 5:1), orange crystals, m.p. 103°C. – IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 3056, 2996, 2948, 2903, 2054 (C=O), 1962 (C=O), 1923 (C=O), 1500, 1461, 1386, 1241, 1174, 1124, 1101, 1038, 1016, 951, 839, 784, 740, 704, 682. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.62 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 4.24 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 4.28 (bs, 2H, CH_2Ph), 4.66 (bs, 2H, CH_2Ph), 6.89 (s, 1H, =CH),

7.04–7.49 (m, 15H, phenyl H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 14.08 (+, OCH_2CH_3), 53.81 (–, NCH_2Ph), 73.92 (–, OCH_2CH_3), 120.74 (+, C-2), 127.10, 127.59, 127.98, 128.14, 128.31, 128.39 (+, phenyl C), 128.59, 129.11 (C_{quat}, phenyl C), 219.35, 224.49 (C_{quat}, C=O), 287.16 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 491 (3) [M^+ – 2 CO], 463 (1) [M^+ – 3 CO], 435 (1) [M^+ – 4 CO], 407 (23) [M^+ – 5 CO], 363 (24) [M^+ – 5 CO – C_2H_4O], 310 (8), 272 (19), 218 (13), 180 (7), 155 (11), 91 (100) [$C_7H_7^+$], 80 (16), 52 (63) [Cr^+].

$C_{30}H_{25}CrNO_6$ (547.1) Calcd. C 65.81 H 4.60 N 2.56
Found C 65.92 H 4.77 N 2.56

Pentacarbonyl[(2Z)-3-(di-2-propenylamino)-1,4-diethoxy-4-methyl-2-pentenylidene]chromium (**14h**) *and Pentacarbonyl[3-(di-2-propenylamino)-4-ethoxy-4-methyl-1,2-pentadienylidene]chromium* (**19h**): To 1.80 g (5 mmol) of **1h** was added di-2-propenylamine until a change of color was observed. Purification yielded fraction I: 690 mg (30%) of **14h**, R_f = 0.31 (pentane/diethyl ether, 5:1), orange crystals, m.p. 76°C. – IR (KBr): $\tilde{\nu}$ = 2992 cm^{-1}, 2941, 2845, 2050 (C=O), 1997 (C=O), 1919 (C=O), 1707, 1605, 1458, 1257, 1216, 1174, 1105, 1070, 922, 671. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.21 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.55 [s, 6H, $C(CH_3)_2$], 3.47 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 4.20 (d, 4H, NCH_2CHCH_2, ^3J = 7.5 Hz), 4.78 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 5.27 (d, 4H, NCH_2CHCH_2), 5.52–5.77 (m, 2H, NH_2CHCH_3), 6.46 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 15.66 (+, OCH_2CH_3), 15.97 (+, OCH_2CH_3), 27.88 [+, $C(CH_3)_2$], 46.29 (–, NCH_2CHCH_2), 59.50 (–, $OCHCH_3$), 73.77 (+, OCH_2CH_3), 79.31 (C_{quat}, C-4), 115.67 (+, C-2), 126.17 (–, NCH_2CHCH_2), 135.76 (+, NCH_2CHCH_2), 162.37 (C_{quat}, C-3), 219.16, 224.12 (C_{quat}, C=O), 284.84 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 457 (18) [M^+], 429 (2) [M^+ – CO], 401 (4) [M^+ – 2 CO], 373 (9) [M^+ – 3 CO], 345 (3) [M^+ – 4 CO], 317 (86) [M^+ – 5 CO], 273 (46), 52 (100) [Cr^+].

$C_{21}H_{27}CrNO_7$ Calcd. 457.1193 Found 457.1193 (HRMS)

II: 1.32 g (64%) of **19h**, R_f = 0.16, orange crystals, m.p. 94°C. – IR (KBr): $\tilde{\nu}$ = 2999 cm^{-1}, 2980, 2895, 2087 (C=O), 2016 (C=O), 1935 (C=O), 1649, 1522, 1421, 1273, 1169, 1070, 944, 668. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.69 [s, 6H, $C(CH_3)_2$], 3.39 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 4.48–4.57 (m, 2H, NCH_2CHCH_2), 4.72–4.84 (m, 2H, NCH_2CHCH_2), 5.22–5.48 (m, 4H, NCH_2CHCH_2), 5.70–6.10 (m, 2H, NCH_2CHCH_2). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 15.50 (+, OCH_2CH_3), 27.45 [+, $C(CH_3)_2$], 53.13 (–, NCH_2CHCH_2), 57.69 (–, NCH_2CHCH_2), 59.71 (–, OCH_2CH_3), 79.17 (C_{quat}, C-4), 120.66 (–, NCH_2CHCH_2), 121.38 (–, NCH_2CHCH_2), 125.24 (+, C-2), 129.27 (+, NCH_2CHCH_2), 131.15 (+, NCH_2CHCH_2), 158.97 (C_{quat}, C-3), 217.38, 224.15 (C_{quat}, C=O), 238.32 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 411 (20) [M^+], 383 (1) [M^+ – CO], 355 (5) [M^+ – 2 CO], 327 (6) [M^+ – 3 CO], 299 (44) [M^+ – 4 CO], 271 (100) [M^+ – 5 CO], 237 (6), 185 (22), 158 (11), 145 (20), 119 (32), 75 (23), 57 (22), 52 (38) [Cr^+].

$C_{19}H_{21}CrNO_6$ Calcd. C 57.47 H 5.15 N 3.40
Found C 57.43 H 5.38 N 3.48

Pentacarbonyl[(2Z)-3-(dibenzylamino)-1,4-diethoxy-4-methyl-2-pentenylidene]chromium (**15h**) *and Pentacarbonyl[3-(dibenzylamino)-4-ethoxy-4-methyl-1,2-pentadienylidene]chromium* (**20h**): To 1.80 g (5 mmol) of **1h** was added dibenzylamine until a change of color was observed. Purification yielded fraction I: 640 mg (23%) of **15h**, R_f = 0.38 (pentane/diethyl ether, 5:1), orange crystals, m.p. 96°C. – IR (KBr): $\tilde{\nu}$ = 3086 cm^{-1}, 3052, 3012, 2996, 2948, 2911, 2050 (C=O), 1923 (C=O), 1902 (C=O), 1507, 1453, 1391, 1273, 1214, 1178, 1080, 979, 927, 884, 800, 756, 706, 680. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.96 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.24 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.65 [s, 6H, $C(CH_3)_2$], 3.46 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 4.57 (bs, 4H, CH_2Ph), 4.82 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 6.66 (s, 1H, =CH), 7.07–7.18 (m, 4H, phenyl H), 7.33–7.43 (m, 6H, phenyl H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 15.51 (+, OCH_2CH_3), 16.22 (+, OCH_2CH_3), 28.19 [+, $C(CH_3)_2$], 57.30 (–, NCH_2Ph), 59.66 (–, OCH_2CH_3), 74.33 (–, OCH_2CH_3), 79.74 (C_{quat}, C-4), 117.02 (+, C-2), 128.28, 128.39, 128.75 (+, phenyl C), 135.86 (C_{quat}, phenyl C), 162.91 (C_{quat}, C-3), 219.13, 224.20 (C_{quat}, C=O), 287.61 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 557 (1) [M^+], 529 (1) [M^+ – CO], 473 (19) [M^+ – 3 CO], 445 (1) [M^+ – 4 CO], 417 (2) [M^+ – 5 CO], 319 (54), 304 (55), 274 (54), 108 (75), 91 (69) [$C_7H_7^+$], 80 (100), 52 (77) [Cr^+].

$C_{29}H_{31}CrNO_7$ (557.6) Calcd. C 62.47 H 5.60 N 2.51
Found C 62.43 H 5.75 N 2.52

II: 1.89 g (74%) of **20h**, R_f = 0.27, orange crystals, m.p. 103°C. – IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 3082, 3052, 3008, 2996, 2951, 2925, 2880, 2098 (C=C=C), 2010 (C=O), 1948 (C=O), 1916 (C=O), 1512, 1458, 1440, 1248, 1204, 1186, 1094, 759, 699, 675. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.99 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.76 [s, 6H, $C(CH_3)_2$], 3.42 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 5.14 (s, 2H, NCH_2Ph), 5.32 (s, 2H, NCH_2Ph), 7.12–7.54 (m, 10H, phenyl H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus APT): δ = 15.32 (+, OCH_2CH_3), 27.56 [+, $C(CH_3)_2$], 53.14 (–, NCH_2Ph), 58.02 (–, NCH_2Ph), 59.81 (–, OCH_2CH_3), 79.43 [–, $C(CH_3)_2$], 125.65 (–, C-2), 127.10, 128.38, 128.72, 128.86, 129.06, 129.32 (+, phenyl C), 134.12, 134.24 (–, phenyl C), 160.02 (–, C-3), 217.24, 224.02 (–, C=O), 238.48 (–, C-1). – MS (EI, 70 eV): *m/z* (%) = 511 (7) [M^+], 427 (3) [M^+ – 3 CO], 399 (21) [M^+ – 4 CO], 371 (12) [M^+ – 5 CO], 327 (65) [M^+ – 5 CO – C_2H_4O], 304 (9), 274 (10), 184 (16), 168 (14), 143 (19), 108 (74), 91 (52) [$C_7H_7^+$], 80 (98), 52 (100) [Cr^+].

$C_{27}H_{25}CrNO_6$ (511.4) Calcd. C 63.40 H 4.93 N 2.74
Found C 63.41 H 5.06 N 2.75

Pentacarbonyl[3-(diisopropylamino)-3-phenylpropadienylidene]chromium (**18a**) *and Pentacarbonyl[(2E)-3-(diisopropylamino)-1-ethoxy-3-phenyl-2-propenylidene]chromium* (**13a**): To 1.75 g (5 mmol) of **1a** was added diisopropylamine until a change of color was observed. Purification yielded fraction I: 1.07 g (53%) of **18a**, R_f = 0.36 (pentane/diethyl ether, 5:1), orange crystals, m.p. 98°C. – IR (KBr): $\tilde{\nu}$ = 3025 cm^{-1}, 3007, 2990, 2950, 2204 (C=C=C), 2098 (C=O), 1976 (C=O), 1924 (C=O), 1540, 1453, 1358, 1318, 1251, 1159, 1008, 780, 717, 709, 688, 671. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28 [d, 6H, $NCH(CH_3)_2$, ^3J = 7.5 Hz], 1.91 [d, 6H, $NCH(CH_3)_2$, ^3J = 7.5 Hz], 4.02 (sept, 1H, NCH, ^3J = 7.5 Hz), 4.36 (sept, 1H, NCH, ^3J = 7.5 Hz), 7.32 (mc, 2H, phenyl H), 7.49 (mc, 3H, phenyl H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 19.34 [+, $NCH(CH_3)_2$], 19.69 [+, $NCH(CH_3)_2$], 51.72 (+, NCH), 55.31 (NCH), 65.84 (C_{quat}, C-2), 126.67, 128.92, 130.26 (+, phenyl C), 137.67 (C_{quat}, phenyl C), 151.98 (C_{quat}, C-3), 218.23, 224.53 (C_{quat}, C=O), 238.29 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 405 (19) [M^+], 377 (1) [M^+ – CO], 349 (3) [M^+ – 2 CO], 321 (4) [M^+ – 3 CO], 293 (26) [M^+ – 4 CO], 265 (100) [M^+ – 5 CO], 223 (21), 181 (18), 132 (12), 104 (55), 80 (39), 52 (74) [Cr^+].

$C_{20}H_{19}CrNO_5$ Calcd. 405.0668 Found 405.0668 (HRMS)

II: 990 mg (44%) of **13a**, R_f = 0.22, yellow crystals, m.p. 116°C. – IR (KBr): $\tilde{\nu}$ = 3025 cm^{-1}, 3010, 3000, 2990, 2945, 2900, 2050 (C=O), 1926 (C=O), 1905 (C=O), 1495, 1450, 1362, 1283, 1127, 1020, 939, 830, 775, 700, 689. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.55 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.09 [bs, 6H, $NCH(CH_3)_2$], 1.71 (bs, 6H, $NCH(CH_3)_2$], 3.42 [bs, 1H, $NCH(CH_3)_2$], 3.90 [bs, 1H, $NCH(CH_3)_2$], 4.12 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.86 (s, 1H,

=CH), 7.11 (mc, 2H, phenyl H), 7.40 (mc, 3H, phenyl H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 14.17 (+, OCH_2CH_3), 14.31 [+, $NCH(CH)_3)_2$], 20.19 [+, $NCH(CH)_3)_2$], 47.13 (+, NCH), 51.98 (+, NCH), 73.44 (–, OCH_2CH_3), 120.73 (+, C-2), 127.19, 127.63, 127.86 (+, phenyl C), 139.46 (C_{quat}, phenyl C), 152.77 (+, C-3), 219.95, 224.43 (C_{quat}, C=O), 291.44 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 451 (11) [M^+], 423 (8) [M^+ – CO], 395 (4) [M^+ – 2 CO], 367 (31) [M^+ – 3 CO], 339 (9) [M^+ – 4 CO], 311 (100) [M^+ – 5 CO], 283 (25) [M^+ – 5 CO – C_2H_4], 255 (21), 240 (23), 223 (14), 214 (41), 200 (17), 151 (48), 130 (29), 108 (19), 93 (17), 52 (36) [Cr^+].

$C_{22}H_{25}CrNO_6$ (451.4) Calcd. C 58.49 H 5.58 N 3.10
Found C 58.49 H 5.61 N 3.11

Pentacarbonyl[3-(diisopropylamino)-4-ethoxy-4-methyl-1,2-pentadienylidene]chromium (**18h**): To 1.80 g (5 mmol) of **1h** was added diisopropylamine until a change of color was observed. Purification yielded 1.41 g (68%) of **18h**, R_f = 0.11 (pentane/diethyl ether, 5:1), yellow crystals, m.p. 87°C. – IR (KBr): $\tilde{\nu}$ = 2986 cm^{-1}, 2940, 2858, 2076 (C=C=C), 2006 (C=O), 1938 (C=O), 1916 (C=O), 1516, 1464, 1392, 1356, 1170, 1151, 1113, 1067, 973, 675, 659. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.35 [d, 6H, $NCH(CH_3)_2$, ^3J = 7.5 Hz], 1.67 [s, 6H, $C(CH_3)_2$], 1.79 [d, 6H, $NCH(CH_3)_2$, ^3J = 7.5 Hz], 3.46 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 3.80 (sept, 1H, NCH, ^3J = 7.5 Hz), 5.11 (sept, 1H, NCH, ^3J = 7.5 Hz). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 14.03 (+, OCH_2CH_3), 19.41 [+, $NCH(CH_3)_2$], 20.18 [+, $NCH(CH_3)_2$], 27.76 [+, $C(CH_3)_2$], 52.91 (+, NCH), 53.31 (+, NCH), 59.83 (–, OCH_2CH_3), 79.56 (C_{quat}, C-4), 124.75 (+, C-2), 157.23 (C_{quat}, C-3), 217.48, 224.18 (C_{quat}, C=O), 235.89 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 415 (8) [M^+], 359 (2) [M^+ – 2 CO], 331 (3) [M^+ – 3 CO], 303 (21) [M^+ – 4 CO], 275 (100) [M^+ – 5 CO], 229 (24) [M^+ – 5 CO – C_2H_6O], 178 (11), 151 (29), 70 (10), 52 (47) [Cr^+].

$C_{19}H_{25}CrNO_6$ Calcd. 415.1087 Found 415.1087 (HRMS)

Pentacarbonyl[(2E)-3-cyclopropyl-1-ethoxy-3-methoxy-2-propenylidene]chromium (**22d**): To a solution of 1.57 g (5 mmol) of **1d** in 100 ml of diethyl ether/methanol (1:1) was added 7.5 ml of a 3.3 N solution of sodium methoxide in methanol. Purification yielded 1.37 g (79%) of **22d**, R_f = 0.54 (pentane/diethyl ether, 5:1), m.p. 99°C. – IR (KBr): $\tilde{\nu}$ = 3012 cm^{-1}, 2988, 2945, 2051 (C=O), 1974 (C=O), 1903 (C=O), 1532, 1441, 1364, 1310, 1255, 1192, 1136, 1105, 1018, 975, 893, 826, 801, 747, 715, 665, 460. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.44–0.54 (m, 2H, cyclopropyl CH_2), 0.78–0.86 (m, 2H, cyclopropyl CH_2), 0.97 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.34 (mc, 1H, cyclopropyl CH), 2.93 (s, 3H, OCH_3), 4.66 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 6.92 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 9.47 (–, cyclopropyl CH_2), 14.87 (+, OCH_2CH_3), 15.39 (+, cyclopropyl CH), 55.51 (+, OCH_3), 75.94 (–, OCH_2), 120.36 (+, C-2), 165.56 (C_{quat}, C-3), 218.46, 224.22 (C_{quat}, C=O), 318.17 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 346 (3) [M^+], 318 (12) [M^+ – CO], 290 (9) [M^+ – 2 CO], 262 (9) [M^+ – 3 CO], 234 (17) [M^+ – 4 CO], 206 (58) [M^+ – 5 CO], 178 (93) [M^+ – 5 CO – C_2H_4], 91 (31), 52 (100) [Cr^+].

$C_{14}H_{14}CrO_7$ Calcd. 346.0145 Found 346.0150 (HRMS)

Pentacarbonyl[(2E)-3-cyclopropyl-1,3-diethoxy-2-propenylidene]chromium (**23d**): To a solution of 1.57 g (5 mmol) of **1d** in 100 ml of diethyl ether/ethanol (1:1) was added 7.5 ml of a 3.3 N solution of sodium ethoxide in ethanol. Purification yielded 1.39 g (77%) of **23d**, R_f = 0.65 (pentane/diethyl ether, 5:1), m.p. 49°C. – IR (KBr): $\tilde{\nu}$ = 2985 cm^{-1}, 2942, 2097 (C=O), 2053 (C=O), 1975 (C=O), 1904 (C=O), 1537, 1472, 1446, 1428, 1386, 1307, 1251, 1191, 1138, 1105, 1060, 1019, 917, 881, 812, 799, 765, 716, 660, 459. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.47–0.55 (m, 2H, cyclopropyl CH_2), 0.66 (t, 3H, OCH_2CH_3, ^3J = 6.8 Hz), 0.82–0.88 (m, 2H, cyclopropyl CH_2), 0.98 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.34–2.44 (m, 1H, cyclopropyl CH), 3.39 (q, 2H, OCH_2CH_3, ^3J = 6.8 Hz), 4.67 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 6.98 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 9.67 (–, cyclopropyl CH_2), 13.60, 14.92 (+, CH_3), 15.48 (+, cyclopropyl CH), 64.76 (–, OCH_2CH_3), 75.92 (–, OCH_2CH_3), 121.31 (+, C-2), 165.60 (C_{quat}, C-3), 218.56, 224.28 (C_{quat}, C=O), 316.82 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 360 (7) [M^+], 332 (7) [M^+ – CO], 304 (6) [M^+ – 2 CO], 276 (5) [M^+ – 3 CO], 248 (19) [M^+ – 4 CO], 220 (76) [M^+ – 5 CO], 192 (100) [M^+ – 5 CO – C_2H_4], 174 (11), 148 (11), 135 (18), 96 (22), 93 (21), 91 (26), 80 (12), 69 (20), 52 (81) [Cr^+].

$C_{15}H_{16}CrO_7$ Calcd. 360.0301 Found 360.0303 (HRMS)

Pentacarbonyl[(2E)- and -(2Z)-1,3,4-triethoxy-4-methyl-2-pentenylidene]chromium (**23h**): To a solution of 1.80 g (5 mmol) of **1h** in 100 ml of diethyl ether/ethanol (1:1) was added 7.5 ml of a 3.3 N solution of sodium ethoxide in ethanol. Purification yielded 1.54 g (76%) of **23h**, R_f = 0.32 (pentane/diethyl ether, 3:1), red crystals, m.p. 56°C, *E*/*Z* = 1.5:1. – IR (KBr): $\tilde{\nu}$ = 2998 cm^{-1}, 2946, 2075 (C=O), 1983 (C=O), 1956 (C=O), 1929 (C=O), 1563, 1478, 1370, 1340, 1273, 1195, 1077, 919, 674. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.88 (t, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 0.89 (t, *E*, OCH_2CH_3, ^3J = 7.0 Hz), 0.99 (t, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 1.03 (t, *E*, OCH_2CH_3, ^3J = 7.0 Hz), 1.14 (t, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 1.18 (t, *E*, OCH_2CH_3, ^3J = 7.0 Hz), 1.20 [s, *Z*, $C(CH_3)_2$], 1.22 [s, *E*, $C(CH_3)_2$], 3.08 (q, *Z*, OCH_2, ^3J = 7.0 Hz), 3.28 (q, *E*, OCH_2, ^3J = 7.0 Hz), 3.34 (q, *Z*, OCH_2, ^3J = 7.0 Hz), 3.58 (q, *E*, OCH_2, ^3J = 7.0 Hz), 4.49 (q, *Z*, OCH_2, ^3J = 7.0 Hz), 4.50 (q, *Z*, OCH_2, ^3J = 7.0 Hz), 7.17 (s, *E*, =CH), 7.46 (s, *Z*, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 14.21 (+, *Z*, OCH_2CH_3), 14.70 (+, *E*, OCH_2CH_3), 14.93 (+, *Z*, OCH_2CH_3), 15.12 (+, *Z*, OCH_2CH_3), 15.20 (+, *E*, OCH_2CH_3), 15.71 (+, *E*, OCH_2CH_3), 24.96 (+, *Z*, CH_3), 25.68 (+, *E*, CH_3), 58.10 (–, *Z*, OCH_2), 58.75 (–, *E*, OCH_2), 64.44 (–, *E*, OCH_2), 64.95 (–, *Z*, OCH_2), 70.67 (–, *E*, OCH_2), 70.78 (–, *Z*, OCH_2), 75.57 [C_{quat}, *Z*, $C(CH_3)_2$], 75.95 [C_{quat}, *E*, $C(CH_3)_2$], 117.54 (+, *Z*, C-2), 119.95 (+, *E*, C-2), 158.70 (C_{quat}, *E*, C-3), 160.03 (C_{quat}, *Z*, C-3), 217.21 (C_{quat}, *E*, C=O), 217.61 (C_{quat}, *Z*, C=O), 224.21 (C_{quat}, *E*, C=O), 224.64 (C_{quat}, *Z*, C=O), 305.44 (C_{quat}, *E*, C-1), 313.99 (C_{quat}, *Z*, C-1). – MS (EI, 70 eV): *m/z* (%) = 406 (6) [M^+], 378 (2) [M^+ – CO], 350 (5) [M^+ – 2 CO], 322 (31) [M^+ – 3 CO], 294 (18) [M^+ – 4 CO], 266 (44) [M^+ – 5 CO], 222 (100), 178 (92), 96 (98), 52 (59) [Cr^+].

$C_{17}H_{22}CrO_8$ Calcd. 406.0720 Found 406.0720 (HRMS)

Pentacarbonyl[(2Z)-1,4-diethoxy-4-methyl-3-phenoxy-2-pentenylidene]chromium (**24h**): To a solution of 1.80 g (5 mmol) of **1h** and 1.0 g of phenol in 200 ml of diethyl ether was added 8 ml of a 3.0 N solution of sodium phenoxide in diethyl ether. Purification yielded 2.07 g (98%) of **24h**, R_f = 0.22 (pentane/diethyl ether, 30:1), orange crystals, m.p. 89°C. – IR (KBr): $\tilde{\nu}$ = 2944 cm^{-1}, 2995, 2040 (C=O), 1998 (C=O), 1921 (C=O), 1595, 1585, 1480, 1313, 1249, 1204, 1053, 900, 742, 654. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.11 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.19 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.38 [s, 6H, $C(CH_3)_2$], 3.52 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 4.34 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 6.73 (d, 2H, *o*-H, ^3J = 7.5 Hz), 6.92 (t, 1H, *p*-H, ^3J = 7.5 Hz), 7.21 (t, 2H, *m*-H, ^3J = 7.5 Hz), 7.35 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 14.69 (+, OCH_2CH_3), 15.73 (+, OCH_2CH_3), 25.62 [+, $C(CH_3)_2$], 58.94 (–, OCH_2), 77.06 (–, OCH_2), 77.57 (C_{quat}, C-4), 115.43, 122.82, 123.55, 129.72 (+, phenyl C, C-2), 151.06 (C_{quat}, phenyl C), 157.06 (C_{quat}, C-3), 216.64, 223.91 (C_{quat}, C=O), 332.58

(C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 454 (4) [M^+], 426 (2) [M^+ – CO], 398 (1) [M^+ – 2 CO], 370 (17) [M^+ – 3 CO], 342 (2) [M^+ – 4 CO], 314 (26) [M^+ – 5 CO], 285 (18), 234 (19), 191 (100) [$Cr(CO)_5^+$], 145 (20), 95 (30), 87 (42), 59 (50), 52 (29) [Cr^+].

$C_{21}H_{22}CrO_8$ Calcd. 454.0720 Found 454.0720 (HRMS)

Pentacarbonyl[(2Z)- and -(2E)-1,3-diethoxy-2-propenylidene]chromium (**23j**): To a solution of 1.66 g (5 mmol) of **1i** in 100 ml of diethyl ether/ethanol (1:1) was added 7.5 ml of a 3.3 N solution of sodium ethoxide in ethanol. Purification yielded fraction I: 490 mg (30%) of (*E*)-**23j**, R_f = 0.33 (pentane/diethyl ether, 3:1), brown oil[12b].

II: 260 mg (16%) of (*Z*)-**23j**, R_f = 0.18, brown oil. – IR (film): $\tilde{\nu}$ = 2977 cm^{-1}, 2045 (C=O), 1970 (C=O), 1915 (C=O), 1582, 1310, 1008, 673. – ^1H NMR (250 MHz, C_6D_6): δ = 0.69 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.04 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 3.09 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 4.42 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 5.02 (d, 1H, 2-H, ^3J = 6.8 Hz), 5.99 (d, 1H, 3-H, ^3J = 6.8 Hz). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 14.70, 14.85 (+, CH_3), 71.87, 75.25 (–, OCH_2), 120.48 (+, C-2), 150.07 (+, C-3), 218.08, 224.62 (C_{quat}, C=O), 287.15 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 320 (18) [M^+], 292 (7) [M^+ – CO], 264 (6) [M^+ – 2 CO], 236 (6) [M^+ – 3 CO], 208 (21) [M^+ – 4 CO], 180 (100) [M^+ – 5 CO], 151 (43), 123 (24), 52 (29) [Cr^+].

$C_{12}H_{12}CrO_7$ Calcd. 319.9988 Found 319.9988 (HRMS)

Pentacarbonyl[(2E)-and-(2Z)-1-ethoxy-3-(phenylthio)-2-butenylidene]chromium (**25b**): To 288 mg (1 mmol) of pentacarbonyl(1-ethoxy-2-butynylidene)chromium (**1b**) was added 170 mg (1.5 mmol) of thiophenol. Purification yielded fraction I: 146 mg (37%) of (*E*)-**25b**, R_f = 0.23 (pentane), red crystals, m.p. 90 °C. – IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1}, 2054 (C=O), 1983 (C=O), 1919 (C=O), 1529, 1237, 1093, 1013, 657, 457. – ^1H NMR (250 MHz, C_6D_6): δ = 0.89 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.88 (s, 3H, CH_3), 4.57 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.97–7.20 (m, 4H, phenyl H, =CH), 7.33–7.45 (m, 2H, phenyl H). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.09 (+, OCH_2CH_3), 23.12 (+, C-4), 76.50 (–, OCH_2), 128.96, 129.24, 130.53 (+, phenyl C, C-2), 130.96 (C_{quat}, phenyl C), 136.11 (+, phenyl C), 150.51 (C_{quat}, C-3), 217.52, 224.27 (C_{quat}, C=O), 321.57 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 398 (3) [M^+], 370 (4) [M^+ – CO], 342 (5) [M^+ – 2 CO], 314 (6) [M^+ – 3 CO], 286 (16) [M^+ – 4 CO], 258 (59) [M^+ – 5 CO], 201 (88), 161 (100) [$PhSCr^+$], 52 (70) [Cr^+].

II: 204 mg (51%) of (*Z*)-**25b**, R_f = 0.21, red crystals, m.p. 93 °C. – IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1}, 2056 (C=O), 1983 (C=O), 1919 (C=O), 1511, 1236, 1094, 1021, 671. – ^1H NMR (250 MHz, C_6D_6): δ = 1.25–1.41 (m, 6H, OCH_2CH_3, 4-H), 4.87 (q, 2H, OCH_2), 6.83–7.13 (m, 5H, Ph), 7.63 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.80 (+, OCH_2CH_3), 25.84 (+, C-4), 77.30 (–, OCH_2), 129.58, 129.97 (+, phenyl C), 131.03 (C_{quat}, phenyl C), 135.57 (+, phenyl C), 138.62 (+, C-2), 147.53 (C_{quat}, C-3), 217.95, 224.41 (C_{quat}, C=O), 319.15 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 398 (0.4) [M^+], 370 (13) [M^+ – CO], 342 (5) [M^+ – 2 CO], 314 (9) [M^+ – 3 CO], 286 (10) [M^+ – 4 CO], 258 (56) [M^+ – 5 CO], 201 (86), 161 (100) [$PhSCr^+$], 52 (58) [Cr^+].

$C_{17}H_{14}CrO_6S$ Calcd. 397.9916 Found 397.9913 (HRMS)

Pentacarbonyl[(2E)- and -(2Z)-3-cyclopropyl-1-ethoxy-3-(phenylthio)-2-propenylidene]chromium (**25d**): To 314 mg (1 mmol) of **1d** was added 170 mg (1.5 mmol) of thiophenol. Purification yielded 298 mg (75%) of **25d**, R_f = 0.21 (pentane), red crystals, m.p. 47 °C, *E*/*Z* = 1:0.8. – IR (film): $\tilde{\nu}$ = 2985 cm^{-1}, 2053 (C=O), 1977 (C=O), 1936 (C=O), 1505, 1230, 1036, 664. – ^1H NMR (250 MHz, C_6D_6): δ = 0.17–0.26 (m, *Z*, cyclopropyl CH_2), 0.57–0.68 (m, cyclopropyl CH_2), 0.85–1.05 (m, *E*, cyclopropyl CH_2, OCH_2CH_3), 1.32 (t, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 2.17 (mc, *E*, cyclopropyl CH), 4.25 (q, *E*, OCH_2, ^3J = 7.0 Hz), 4.87 (q, *Z*, OCH_2, ^3J = 7.0 Hz), 6.90–7.48 (m, phenyl H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 9.40, 11.69 (–, cyclopropyl CH_2), 14.91 (+, *E*, OCH_2CH_3), 15.61 (+, *Z*, OCH_2CH_3), 18.01 (+, *E*, cyclopropyl CH), 19.29 (+, *Z*, cyclopropyl CH), 76.28 (–, *E*, OCH_2), 77.11 (–, *Z*, OCH_2), 128.62 (C_{quat}, phenyl C), 129.26, 129.66, 130.58 (+, phenyl C), 130.73 (C_{quat}, phenyl C), 133.34, 135.72, 137.97 (+, phenyl C), 136.16, 137.97 (+, C-2), 152.64 (C_{quat}, *Z*, C-3), 156.64 (C_{quat}, *E*, C-3), 217.39 (C_{quat}, *E*, C=O), 217.81 (C_{quat}, *Z*, C=O), 224.33 (C_{quat}, *E*, C=O), 224.57 (C_{quat}, *Z*, C=O), 315.88 (C_{quat}, *Z*, C-1), 317.93 (C_{quat}, *E*, C-1). – MS (EI, 70 eV): *m/z* (%) = 424 (0.3) [M^+], 396 (9) [M^+ – CO], 368 (5) [M^+ – 2 CO], 340 (9) [M^+ – 3 CO], 312 (6) [M^+ – 4 CO], 284 (64) [M^+ – 5 CO], 227 (32), 161 (74) [$PhSCr^+$], 52 (100) [Cr^+].

$C_{18}H_{16}CrO_5S$ [M^+ – CO] Calcd. 396.0124
Found 396.0112 (HRMS)

Pentacarbonyl[(2E)- and -(2Z)-1-ethoxy-4-methyl-3-(phenylthio)-2-pentenylidene]chromium (**25e**): To 316 mg (1 mmol) of **1e** was added 170 mg (1.5 mmol) of thiophenol. Purification yielded fraction I: 142 mg (34%) of (*E*)-**25e**, R_f = 0.28 (pentane), red crystals, m.p. 63 °C. – IR (KBr): $\tilde{\nu}$ = 2927 cm^{-1}, 2054 (C=O), 2013 (C=O), 1924 (C=O), 1506, 1475, 1365, 1226, 1036, 751, 665. – ^1H NMR (250 MHz, C_6D_6): δ = 0.98 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.14 [d, 6H, $CH(CH_3)_2$, ^3J = 6.8 Hz], 3.37 [sept, 1H, $CH(CH_3)_2$, ^3J = 6.8 Hz], 4.62 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.82–7.12 (m, 4H, phenyl H, =CH), 7.37–7.43 (m, 2H, phenyl H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 14.64 (+, OCH_2CH_3), 22.26 [+, $CH(CH_3)_2$], 33.52 (+, C-4), 76.53 (–, OCH_2), 128.84 (+, phenyl C), 129.28 (C_{quat}, phenyl C), 130.43, 136.07, 136.42 (+, phenyl C, C-2), 161.22 (C_{quat}, C-3), 217.22, 224.10 (C_{quat}, C=O), 324.04 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 426 (5) [M^+], 398 (7) [M^+ – CO], 370 (4) [M^+ – 2 CO], 342 (7) [M^+ – 3 CO], 314 (8) [M^+ – 4 CO], 286 (51) [M^+ – 5 CO], 161 (100) [$PhSCr^+$], 52 (57) [Cr^+].

II: 100 mg (23%) of (*Z*)-**25e**, R_f = 0.22, red crystals, m.p. 57 °C. – IR (KBr): $\tilde{\nu}$ = 2927 cm^{-1}, 2054 (C=O), 1975 (C=O), 1910 (C=O), 1511, 1448, 1236, 1020, 665. – ^1H NMR (250 MHz, C_6D_6): δ = 0.89 [d, 6H, $CH(CH_3)_2$, ^3J = 6.8 Hz], 1.78 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.37 (sept, 1H, 4-H, ^3J = 6.8 Hz), 4.83 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.88–6.98 (m, 3H, phenyl H), 7.14–7.23 (m, 2H, phenyl H), 7.71 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.45 (+, OCH_2CH_3), 23.09 [+, $CH(CH_3)_2$], 33.53 (+, C-4), 77.14 (–, OCH_2), 129.49, 130.52 (+, phenyl C), 131.15 (C_{quat}, phenyl C), 134.96 (+, phenyl C), 136.36 (+, C-2), 153.16 (C_{quat}, C-3), 217.66, 224.31 (C_{quat}, C=O), 322.4 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 426 (0.2) [M^+], 398 (10) [M^+ – CO], 370 (5) [M^+ – 2 CO], 342 (10) [M^+ – 3 CO], 314 (7) [M^+ – 4 CO], 286 (60) [M^+ – 5 CO], 161 (100) [$PhSCr^+$], 52 (80) [Cr^+].

$C_{19}H_{18}CrO_6S$ Calcd. 426.0229 Found 426.0225 (HRMS)

Pentacarbonyl[(2E)- and -(2Z)-1-ethoxy-4,4-dimethyl-3-(phenylthio)-2-pentenylidene]chromium (**25f**): To 330 mg (1 mmol) of **1f** was added 170 mg (1.5 mmol) of thiophenol. Purification yielded 360 mg (88%) of **25f**, R_f = 0.28 (pentane), red oil, *E*/*Z* 1:1.0. – IR (film): $\tilde{\nu}$ = 2967 cm^{-1}, 2061 (C=O), 1991 (C=O), 1914 (C=O), 1581, 1478, 1362, 1250, 1126, 1052, 1020, 740, 696, 662, 633. – ^1H NMR (250 MHz, C_6D_6): δ = 0.78 (t, *E*, OCH_2CH_3, ^3J = 7.0 Hz), 0.98 (t, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 1.13 [s, *E*, $C(CH_3)_3$], 1.25 [s, *Z*, $C(CH_3)_3$], 4.40 (q, *E*, OCH_2, ^3J = 7.0 Hz), 4.51 (q, *Z*, OCH_2, ^3J = 7.0 Hz), 6.81–7.18 (m, phenyl H, =CH), 7.38–7.48 (m,

phenyl H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ [(*E*)-**25f**] = 14.11 (+, OCH_2CH_3), 29.47 [+, $C(CH_3)_3$], 39.76 (C_{quat}, C-4), 77.58 (–, OCH_2), 125.79, 127.71, 128.82 (+, phenyl C), 137.13, 138.69 (C_{quat}, phenyl C, C-2), 146.38 (+, C-3), 216.66, 223.92 (C_{quat}, C=O), 326.61 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 412 (2) [M^+ – CO], 384 (4) [M^+ – 2 CO], 356 (10) [M^+ – 3 CO], 328 (4) [M^+ – 4 CO], 300 (66) [M^+ – 5 CO], 233 (75), 161 (100) [$PhSCr^+$], 52 (73) [Cr^+].

$C_{19}H_{20}CrO_5S$ [M^+ – CO] Calcd. 412.0437
Found 412.0434 (HRMS)

Pentacarbonyl[(2E)- and -(2Z)-1,4-diethoxy-4-methyl-3-(phenylthio)-2-pentenylidene]chromium (**25h**): To 360 mg (1 mmol) of **1h** was added 170 mg (1.5 mmol) of thiophenol. Purification yielded 380 mg (84%) of **25h**, R_f = 0.11 (pentane), orange oil, *E*/*Z* 1:1.7. – IR (film): ṽ = 3005 cm^{-1}, 2930, 2054, 1988, 1933 (C=O), 1591, 1439, 1363, 1238, 1107, 750, 711, 689, 662. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22 (t, *Z*, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.37 (t, *E*, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.42 [s, *E*, 6H, $C(CH_3)_2$], 1.51 [s, *Z*, 6H, $C(CH_3)_2$], 1.52 (t, *E*, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.55 (t, *Z*, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 3.50 (q, *E*, 2H, OCH_2, ^3J = 7.0 Hz), 3.54 (q, *Z*, 2H, OCH_2, ^3J = 7.0 Hz), 4.70 (q, *E*, 2H, OCH_2, ^3J = 7.0 Hz), 4.73 (bs, *Z*, 2H, OCH_2), 6.02 (bs, *E*, 1H, =CH), 7.20 (s, *Z*, 1H, =CH), 7.32–7.44 (m, 3H, phenyl H), 7.45–7.53 (m, 2H, phenyl H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 14.52 (+, *Z*, OCH_2CH_3), 14.68 (+, *E*, OCH_2CH_3), 15.29 (+, *Z*, OCH_2CH_3), 15.62 (+, *E*, OCH_2CH_3), 25.84 [+, *E*, $C(CH_3)_2$], 26.83 (+, *Z*, $C(CH_3)_2$), 58.45 (–, *E*, OCH_2), 58.61 (–, *Z*, OCH_2), 75.78 (–, *Z*, OCH_2), 77.51 (–, *E*, OCH_2), 78.68 (C_{quat}, *Z*, C-4), 79.81 (C_{quat}, *E*, C-4), 122.04 (+, *E*, C-2), 126.49 (+, *Z*, C-2), 128.56, 128.89, 129.58, 129.89 (+, phenyl C), 131.52 (C_{quat}, *Z*, phenyl C), 135.59, 135.67 (+, phenyl C), 136.53 (C_{quat}, *E*, phenyl C), 159.24 (C_{quat}, *E*, C-3), 164.74 (C_{quat}, *Z*, C-3), 216.12, 216.46, 223.71, 223.87 (C_{quat}, C=O), 286.87 (C_{quat}, *Z*, C-1), 291.41 (C_{quat}, *E*, C-1). – MS (EI, 70 eV): *m/z* (%) = 414 (1) [M^+ – 2 CO], 386 (38) [M^+ – 3 CO], 358 (2) [M^+ – 4 CO], 330 (79) [M^+ – 5 CO], 250 (61), 286 (58), 161 (62) [$CrSPh^+$], 109 (27) [SPh^+], 87 (100), 59 (81), 52 (58) [Cr^+].

$C_{19}H_{22}CrO_5S$ [M^+ – 2 CO] Calcd. 414.0593
Found 414.0593 (HRMS)

Pentacarbonyl[(2E)- and -(2Z)-1-ethoxy-3-(phenylthio)-3-(trimethylsilyl)-2-propenylidene]chromium (**25i**): To 350 mg (1 mmol) of **1i** was added 170 mg (1.5 mmol) of thiophenol. Purification yielded 100 mg (26%) of **25i**, R_f = 0.30 (pentane), red crystals, m.p. 61°C, *E*/*Z* 1:3.0. – IR (KBr): ṽ = 2949 cm^{-1}, 2052 (C=O), 1973 (C=O), 1936 (C=O), 1904, 1576, 1477, 1218, 1076, 740, 664. – ^{1}H NMR (250 MHz, C_6D_6): δ = –0.05 [s, *Z*, $Si(CH_3)_3$], 0.20 [s, *E*, $Si(CH_3)_3$], 1.03 (t, *E*, OCH_2CH_3, ^3J = 7.0 Hz), 1.19 (t, *Z*, OCH_2CH_3, ^3J = 7.0 Hz), 4.71 (q, *Z*, OCH_2, ^3J = 7.0 Hz), 4.73 (q, *E*, OCH_2, ^3J = 7.0 Hz), 6.80–6.91 (m, phenyl H), 7.03–7.11 (m, phenyl H), 7.26–7.46 (m, phenyl H), 7.48 (s, *E*, =CH), 7.79 (s, *Z*, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 0.19 [+, *E*, $Si(CH_3)_3$], 0.28 [+, *Z*, $Si(CH_3)_3$], 15.11 (+, *Z*, OCH_2CH_3), 15.25 (+, *E*, OCH_2CH_3), 76.80 (–, *E*, OCH_2), 77.27 (–, *Z*, OCH_2), 127.24, 127.62 (+, phenyl C), 128.69 (C_{quat}, phenyl C), 129.06, 129.27 (+, phenyl C), 129.52 (C_{quat}, phenyl C), 130.41, 133.78 (+, phenyl C), 135.86, 146.39 (+, C-2), 148.65 (C_{quat}, C-3), 153.64 (C_{quat}, *E*, C-3), 217.02 (C_{quat}, *E*, C=O), 217.16 (C_{quat}, *Z*, C=O), 224.25 (C_{quat}, C=O), 224.31 (C_{quat}, C=O), 322.64 (C_{quat}, C-1), 324.21 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* = 428 (1) [M^+ – CO], 372 (3) [M^+ – 3 CO], 316 (41) [M^+ – 5 CO], 161 (100) [$PhSCr^+$], 52 (74) [Cr^+].

$C_{16}H_{20}CrO_3SSi$ [M^+ – 3 CO] Calcd. 372.0298
Found 372.0289 (HRMS)

General Procedure for the Preparation of Chelated Tetracarbonyl(vinylcarbene)chromium Complexes: A solution of 2 mmol of the respective β-donor-substituted (vinylcarbene)chromium complex was heated in 50 ml of refluxing tetrahydrofuran for 5 h. After removal of the solvent, the residue was purified by chromatography over 50 g of silica gel.

Tetracarbonyl[(2Z)-3-(dimethylamino)-1-ethoxy-3-cyclopropyl-2-propenylidene-N]chromium (**26d**): From 720 mg (2 mmol) of **3d** was obtained 310 mg (47%) of **26d**, R_f = 0.45 (pentane/diethyl ether, 1:1), black crystals, m.p. 85°C. – IR (KBr): ṽ = 2939 cm^{-1}, 2006 (C=O), 1906 (C=O), 1821 (C=O), 1633, 1456, 1366, 1300, 1251, 1226, 1172, 1024, 872, 674. – ^{1}H NMR (250 MHz, C_6D_6): δ = –0.02–0.05 (m, 2H, cyclopropyl CH_2), 0.22–0.30 (m, 2H, cyclopropyl CH_2), 1.26 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.36 [s, 6H, $N(CH_3)_2$], 4.93 (q, 2H, OCH_2, ^3J = 7.0 Hz), 5.41 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 7.89 (+, cyclopropyl CH), 10.79 (–, cyclopropyl CH_2), 15.08 (+, OCH_2CH_3), 53.95 [+, $N(CH_3)_2$], 76.89 (–, OCH_2), 128.60 (+, C-2), 180.84 (C_{quat}, C-4), 217.62, 230.86, 234.30 (C_{quat}, C=O), 337.54 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 331 (3) [M^+], 303 (4) [M^+ – CO], 275 (5) [M^+ – 2 CO], 247 (9) [M^+ – 3 CO], 219 (16) [M^+ – 4 CO], 191 (100) [M^+ – 4 CO – C_2H_4], 52 (25) [Cr^+].

$C_{14}H_{17}CrNO_5$ Calcd. 331.0512 Found 331.0510 (HRMS)

Tetracarbonyl[(2Z)-3-(dimethylamino)-1-ethoxy-4-methyl-2-pentenylidene-N]chromium (**26e**): From 720 mg (2 mmol) of **3e** was obtained 510 mg (76%) of **26e**, R_f = 0.56 (pentane/diethyl ether, 1:1), black crystals, m.p. 73°C. – IR (KBr): ṽ = 2977 cm^{-1}, 2005 (C=O), 1908 (C=O), 1822 (C=O), 1644, 1466, 1298, 1040, 943, 675. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.54 [d, 6H, $CH(CH_3)_2$, ^3J = 6.8 Hz], 1.48 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.76 [sept, 1H, $CH(CH_3)_2$, ^3J = 6.8 Hz], 2.26 [s, 6H, $N(CH_3)_2$], 4.94 (q, 2H, OCH_2, ^3J = 7.0 Hz), 5.87 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.05 (+, CH_2CH_3), 24.37, 24.49 [+, $CH(CH_3)_2$], 52.81 [+, $N(CH_3)_2$], 76.98 (–, OCH_2), 132.48 (+, C-2), 185.36 (C_{quat}, C-3), 217.60, 230.84, 234.38 (C_{quat}, C=O), 338.33 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 333 (9) [M^+], 305 (14) [M^+ – CO], 277 (16) [M^+ – 2 CO], 249 (17) [M^+ – 3 CO], 221 (100) [M^+ – 4 CO], 164 (34), 136 (18), 95 (26), 52 (25) [Cr^+].

$C_{14}H_{19}CrNO_5$ Calcd. 333.0668 Found 333.0669 (HRMS)

Tetracarbonyl[(2Z)-3-(dimethylamino)-1-ethoxy-3-(1-ethoxycyclopropyl)-2-propenylidene-N]chromium (**26g**): From 810 mg (2 mmol) of **3g** was obtained 330 mg (44%) of **26g**, R_f = 0.57 (pentane/diethyl ether, 1:1), black crystals, m.p. 69°C. – IR (KBr): ṽ = 2995 cm^{-1}, 2950, 2015 (C=O), 1907 (C=O), 1840 (C=O), 1641, 1488, 1373, 1298, 1244, 1062, 888, 679, 658, 617. – ^{1}H NMR (200 MHz, C_6D_6): δ = 0.49–0.53 (m, 2H, cyclopropyl CH_2), 0.77–0.81 (m, 2H, cyclopropyl CH_2), 0.96 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.51 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.98 [s, 6H, $N(CH_3)_2$], 3.01 (q, 2H, OCH_2, ^3J = 7.0 Hz), 5.24 (q, 2H, OCH_2, ^3J = 7.0 Hz), 5.95 (s, 1H, =CH). – ^{13}C NMR (50.31 MHz, C_6D_6, plus APT): δ = 14.68 (–, cyclopropyl CH_2), 14.77 (+, OCH_2CH_3), 15.12 (+, OCH_2CH_3), 55.18 [+, $N(CH_3)_2$], 58.97 (–, cyclopropyl $COCH_2CH_3$), 63.14 (–, OCH_2), 77.09 (–, OCH_2), 134.28 (+, C-2), 184.62 (–, C-3), 218.11, 228.61, 232.50 (–, C=O), 336.72 (–, C-1). – MS (EI, 70 eV): *m/z* (%) = 375 (10) [M^+], 347 (5) [M^+ – CO], 319 (8) [M^+ – 2 CO], 291 (19) [M^+ – 3 CO], 263 (24) [M^+ – 4 CO], 166 (100), 52 (51) [Cr^+].

$C_{16}H_{21}CrNO_6$ Calcd. 375.0774 Found 375.0774 (HRMS)

Tetracarbonyl[(2Z)-3-(dimethylamino)-1,4-diethoxy-4-methyl-2-pentenylidene-N]chromium (**26h**): From 810 mg (2 mmol) of **3h** was obtained 600 mg (76%) of **26h**, R_f = 0.67 (pentane/diethyl

ether, 5:1), black crystals, m.p. 64°C. – IR (KBr): $\tilde{\nu}$ = 2996 cm^{-1}, 2951, 2906, 2018 (C=O), 1902 (C=O), 1844 (C=O), 1633, 1459, 1377, 1280, 1176, 1070, 894, 811, 673, 640. – ^1H NMR (250 MHz, C_6D_6): δ = 0.80 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 0.85 [s, 6H, $C(CH_3)_2$], 1.26 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 2.78 (q, 2H, OCH_2, ^3J = 7.0 Hz), 2.91 [s, 6H, $N(CH_3)_2$], 4.97 (q, 2H, OCH_2, ^3J = 7.0 Hz), 5.88 (s, 1H, =CH). – ^{13}C NMR (62.90 MHz, C_6D_6, plus DEPT): δ = 15.02 (+, OCH_2CH_3), 15.14 (+, OCH_2CH_3), 28.94 (+, $C(CH_3)_2$), 55.09 [+, $N(CH_3)_2$], 56.02 (–, OCH_2), 76.86 (–, OCH_2), 79.96 [C_{quat}, $C(CH_3)_2$], 134.58 (–, C-2), 179.21 (C_{quat}, C-3), 218.17, 231.85, 234.43 (C_{quat}, C=O), 338.43 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 377 (12) [M^+], 349 (9) [M^+ – CO], 321 (21) [M^+ – 2 CO], 293 (3) [M^+ – 3 CO], 265 (49) [M^+ – 4 CO], 176 (100), 52 (32) [Cr^+].

$C_{16}H_{23}CrNO_6$ Calcd. C 50.93 H 6.11 N 3.71
Found C 50.97 H 6.11 N 3.61

Tetracarbonyl[(2Z)-3-cyclopropyl-1-ethoxy-3-methoxy-2-propenyliden-O]chromium (**28d**): From 690 mg (2 mmol) pentacarbonyl[(2*E*)-3-cyclopropyl-1-ethoxy-3-methoxy-2-propenylidene]chromium (**22d**) was obtained 460 mg (73%) of **28d**, R_f = 0.45 (pentane/diethyl ether, 5:1), brownyellow oil. – IR (film): $\tilde{\nu}$ = 2975 cm^{-1}, 2005 (C=O), 1895 (C=O), 1835 (C=O), 1614, 1440, 1310, 1297, 1238, 1160, 1067, 673, 658. – ^1H NMR (250 MHz, C_6D_6): δ = 0.20–0.42 (m, 2H, cyclopropyl H), 0.47 (mc, 3H, cyclopropyl H), 1.32 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 3.52 (s, 3H, OCH_3), 5.00 (q, 2H, OCH_2CH_3, ^3J = 7.0 Hz), 5.43 (s, 1H, =CH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 8.42 (–, cyclopropyl CH_2), 10.56 (+, cyclopropyl CH), 15.17 (+, OCH_2CH_3), 64.50 (+, OCH_3), 76.89 (–, OCH_2), 116.41 (+, C-2), 184.27 (C_{quat}, C-3), 215.25, 230.99, 233.56 (C_{quat}, C=O), 331.29 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 318 (28) [M^+], 290 (11) [M^+ – CO], 262 (7) [M^+ – 2 CO], 234 (41) [M^+ – 3 CO], 206 (57) [M^+ – 4 CO], 204 (61), 178 (93), 52 (100) [Cr^+].

$C_{13}H_{14}CrO_6$ Calcd. 318.0195 Found 318.0195 (HRMS)

Tetracarbonyl[(2Z)-1-ethoxy-3-cyclopropyl-3-(phenylthio)-2-propenylidene-S]chromium (**27d**): From 210 mg (0.5 mmol) of pentacarbonyl[3-cyclopropyl-1-ethoxy-3-(phenylthio)-2-propenylidene]chromium (**25d**) was obtained 150 mg (76%) of **27d**, R_f = 0.10 (pentane), violet oil. – IR (film): $\tilde{\nu}$ = 2961 cm^{-1}, 2931, 2011 (C=O), 1908 (C=O), 1864 (C=O), 1762, 1589, 1443, 1281, 1206, 1148, 1093, 1023, 661. – ^1H NMR (250 MHz, C_6D_6): δ = 0.28–0.37 (m, 4H, cyclopropyl CH_2), 1.11–1.20 (m, 1H, cyclopropyl CH), 1.26 (t, 3H, CH_3, ^3J = 7.0 Hz), 4.95 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.26 (s, 1H, =CH), 6.82–6.97 (m, 3H, phenyl H), 7.19–7.26 (m, 2H, phenyl H). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 13.34 (–, cyclopropyl CH_2), 15.04 (+, OCH_2CH_3), 16.95 (+, cyclopropyl CH), 77.23 (–, OCH_2), 129.65, 129.75, 130.50 (+, phenyl C), 134.77 (C_{quat}, phenyl C), 141.00 (+, C-2), 175.24 (C_{quat}, C-3), 216.91, 231.28, 232.32 (C_{quat}, C=O), 334.74 (C_{quat}, C-1). – MS (EI, 70 eV): *m/z* (%) = 396 (14) [M^+], 368 (3) [M^+ – CO], 340 (6) [M^+ – 2 CO], 312 (6) [M^+ – 3 CO], 284 (73) [M^+ – 4 CO], 256 (18), 227 (43), 161 (88) [$PhSCr^+$], 52 (100) [Cr^+].

$C_{18}H_{16}CrO_5S$ Calcd. 396.0124 Found 396.0120 (HRMS)

Tetracarbonyl[(2Z)-1-ethoxy-4,4-dimethyl-3-(phenylthio)-2-pentenylidene-S]chromium (**27f**): From 180 mg (0.5 mmol) of pentacarbonyl[1-ethoxy-4,4-dimethyl-3-(phenylthio)-2-pentenylidene]chromium (**25f**) was obtained 170 mg (81%) of **27f**, R_f = 0.12 (pentane), violet oil. – IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 2014 (C=O), 1913 (C=O), 1865 (C=O), 1278, 1218, 1192, 1148, 665. – ^1H NMR (250 MHz, C_6D_6): δ = 0.84 [s, 9H, $C(CH_3)_3$], 1.28 (t, 3H, OCH_2CH_3, ^3J = 7.0 Hz), 4.99 (q, 2H, OCH_2, ^3J = 7.0 Hz), 6.78–6.84 (m, 4H, =CH, phenyl H), 6.99–7.06 (m, 2H, phenyl H). – ^{13}C NMR (62.89 MHz, C_6D_6): δ = 15.06 (OCH_2CH_3), 30.67 [$C(CH_3)_3$], 39.94 (C-4), 77.25 (OCH_2), 128.87, 129.14, 129.63, 137.65 (phenyl C), 148.08 (C-2), 176.32 (C-3), 217.27, 231.26, 233.64 (C=O), 339.75 (C-1). – MS (EI, 70 eV): *m/z* (%) = 412 (7) [M^+], 384 (2) [M^+ – CO], 356 (5) [M^+ – 2 CO], 328 (3) [M^+ – 3 CO], 300 (58) [M^+ – 4 CO], 243 (70) [M^+ – 4 CO – *t*Bu], 161 (100) [$PhSCr^+$], 52 (76) [Cr^+].

$C_{19}H_{20}CrO_5S$ Calcd. 412.0437 Found 412.0412 (HRMS)

X-ray Crystal Structure Determination of **13**[23]: A single crystal sized 0.4 × 0.5 × 0.6 mm was mounted in a capillary. The structure determination was carried out on a Stoe-Siemens-Huber-AED2 four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) at room temperature. $C_{22}H_{25}CrNO_6 \cdot C_6H_6$ (529.5), crystallizes in the space group $Pna2_1$ with cell dimensions a = 1305.3(2), b = 1940.7(2), c = 1127.6(2) pm, V = 2.870(1) nm^3, Z = 4, d_r = 1.225 Mg/m^3, μ = 0.437 mm^{-1}. 6898 reflections were measured for 2Θ < 55°. An empirical absorption correction was applied. After merging equivalents, 3841 independent data with $F > 4\sigma(F)$ were used for all calculations. The structure was solved by Direct Methods[24]. All nonhydrogen atoms were refined anisotropically[25]. A riding model with idealized hydrogen geometry was employed for H-atom refinement. An extinction correction was applied $\{\chi = 0.0005(1)$ with $F^* = F[1+0.002\chi F^2/\sin(2\Theta)]^{-1/4}\}$; η was refined to a value of 1.04(5)[26]. The full-matrix least-squares refinement of the 325 parameters converged to final residuals R = 0.053, wR = 0.043 with $w^{-1} = \sigma^2(F) + 0.0002F^2$. Largest difference peak and hole 0.59 and –0.43 10^{-6} epm^{-3}, respectively.

☆ Dedicated to Professor *Ekkehard Winterfeldt* on the occasion of his 60th birthday.

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