Organic Syntheses via Transition Metal Complexes, C[+]

Vinyl- and Divinylcyclopentadienes by Rhodium-Catalyzed Condensation of Alkynes with Cross-Conjugated Amino Metallahexatrienes [= (1-Amino-1,3-butadien-2-yl)carbene Complexes] (M = Cr, W)

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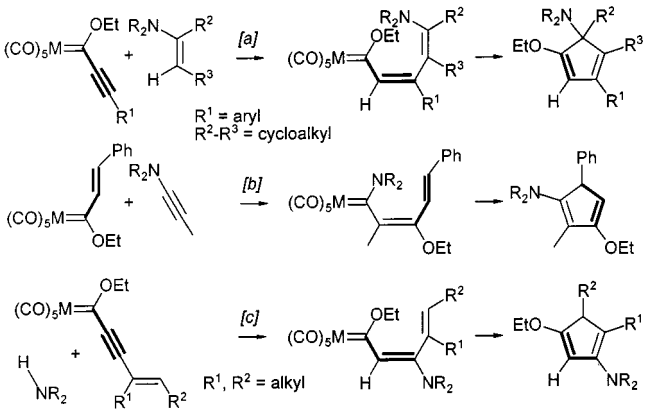
We report on the first example of a transition metal-catalyzed cyclization reaction of a Fischer carbene complex. It comprises the generation of vinyl- and divinyl cyclopentadienes under exceedingly mild conditions at 20 °C by condensation of (1-amino-1,3-butadien-2-yl)carbene complexes (= cross-conjugated metallahexatrienes) $(CO)_5M{=}C(OEt)C(=CHNR_2)CR^1{=}CHR^2$ **3** (M = Cr, W) with alkynes $R^3C{\equiv}CH$ **4** (R^3 = Ph, cyclohex-1-enyl, isopropenyl, methoxymethyl, 1-trimethylsiloxycyclohex-1-yl) in the presence of catalytic amounts of $[(COD)RhCl]_2$. The starting compounds **3** are accessible in high yields by addition of enamines (*E*)-$R_2NCH{=}CHR^2$ **2** to (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR^1$ **1** (M = Cr, W; R^1 = Ph, cyclohex-1-enyl).

Introduction

α,β-Unsaturated Fischer carbene complexes have been utilized as building blocks in a variety of cyclization reactions with alkynes and carbon monoxide. Above all, the Dötz reaction leading to formation of 1,4-dioxynaphthalenes has gained much interest and has found application in organic synthesis.[2] It has only recently been shown by de Meijere et al.[3] that reactions of alkynes with [(2-amino)alkenyl]carbene chromium complexes lead to amino cyclopentadienes,[4] methylenecyclopentenones,[5] or cyclopenta[*b*]pyrans[6] instead of Dötz products. It was pointed out that the amino group would play a pivotal role in this reaction. In independent studies it was demonstrated by our group that amino cyclopentadienes are generated by π-cyclization of 6-amino-1-metalla-1,3,5-hexatrienes. The latter compounds could be isolated and fully characterized spectroscopically as well as by crystal structure analyses. Whilst pursuing our studies, three different approaches to the formation of amino-1-metalla-1,3,5-hexatrienes became available in our hands (Scheme 1). They include an addition of enamines to (1-alkynyl)carbene complexes[7] (Scheme 1, path *a*), an insertion of electron-rich alkynes into the M=C bond (and C=C bond, respectively) of 1-metalla-1,3-butadienes[8] (path *b*), and an addition of amines R_2NH to 1-metalla-1,5-dien-3-ynes (= 3-buten-1-yn-1-yl)carbene complexes (path *c*).[1] A strong driving force for the cyclization of 1-metalla-1,3,5-trienes to cyclopentadienes is provided by amino substituents and especially 6-amino substituents. However, 2-amino and 4-amino substituents were also found to enhance this reaction. It should be noted that the reactions exemplified in Scheme 1 are complementary with respect to the connectivity of the building blocks of the 1-metalla-1,3,5-hexatrienes as well as the cyclopentadienes derived thereof.



Scheme 1. Different approaches to the generation of aminocyclopentadienes via 6-amino-, 2-amino- and 4-amino-1-metalla-1,3,5-hexatrienes

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[++] Crystal structure analysis.

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Results and Discussion

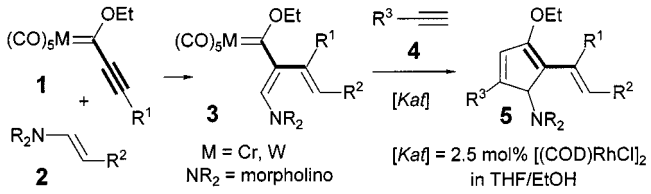
Vinylcyclopentadienes from Cross-Conjugated Aminometallahexatrienes (= 1-Amino-1,3-butadien-2-yl)carbene Complexes

Even though vinylcyclopentadienes must be considered valuable building-blocks in organic and organometallic syntheses, there are few reports on the preparation of such compounds. Furthermore, only in rare cases could these be generated isomerically pure,[9] but were obtained as mixture of isomeres[10] as is commonly observed with syntheses of other substituted cyclopentadienes.[11] Therefore, we now wish to report a method for the generation of vinylcyclopentadienes under conditions which lead to the formation of single isomers. Our reaction is based on the cyclization of (conjugated) 1-metalla-1,3,5-hexatrienes, which are generated by condensation of alkynes[4][8] with cross-conjugated aminometallahexatrienes [= (1-amino-1,3-butadien-2-yl)carbene complexes] $(CO)_5M{=}C(OEt){-}C(CR^1{=}CHR^2){=}CHNR_2$ (**3a**−**n**) of chromium and tungsten.[7e,12] The latter compounds were obtained by addition of enamines (*E*)-$R_2NCH{=}CHR^2$ (**2a**−**g**) (R_2N = Et_2N, Pr_2N, morpholino) to (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR^1$ (**1a**−**d**) (M = Cr, W; R^1 = Ph, cyclohex-1-enyl) in 83−95% yields (Table 1). They are quite stable and therefore well suited as depository compounds. The morpholino derivatives **3a**−**e** of tungsten, and **3l**,**m** of chromium, were shown to react smoothly with a variety of terminal alkynes $R^3C{\equiv}CH$ (**4a**−**e**) (R^3 = Ph, isopropenyl, cyclohex-1-enyl, methoxymethyl, and 1-trimethylsiloxycyclohex-1-yl) in the presence of 2.5 mol-% $[(COD)RhCl]_2$, to give vinyl- and divinylcyclopentadienes **5a**−**n**. The success of our synthesis rest on the fact that it could be catalyzed under exceedingly mild conditions (at 20°C), under which extensive isomerization or oligomerization of the highly sensitive vinyl cyclopentadienes can be avoided. The efficiency of our synthesis was exemplified by an ^{1}H-NMR study of the reaction of 2-methyl-1-buten-3-yne (**4c**) with the cross-conjugated tungstahexatriene **3b** in CD_2Cl_2. It was found that the expected divinylcyclopentadiene **5i** is generated within the first 15 h as the only organic product, while ca. 50% of starting complex **3b** is consumed. On extension of the reaction time to 40 h, the alkyne **4c** was consumed completely in a side-reaction, which does not involve consumption of cross-conjugated metallahexatriene **3b** and therefore does not lead to further amino cyclopentadiene **5i**. In order to obtain maximum relative yields, it is recommended to work up the reaction mixture after ca. 25−40 h at 20°C. The solvent was found to exhibit a remarkable influence on the reaction course. The best yields of vinyl and divinyl cyclopentadienes **5a**−**n** are obtained in THF/EtOH (5:1), whilst applying an excess of 1.5 equivalents of alkynes **4**.

Condensation of alkynes **4a**,**c**,**d** with the enantiomerically pure cross-conjugated metallahexatriene **3c** affords diastereomeric cyclopentadienes **5k**−**m**, but with very little diastereotopic excess, as might be anticipated from the distance between the chiral centers in these molecules.

There remains no doubt that a catalytic formation of vinylcyclopentadienes must be considered superior to a thermally-induced reaction of the starting compounds. Nevertheless, it was found that a thermal reaction of [(1,3-butadien-2-yl)carbene]chromium complexes **3l**,**m** (but not of the corresponding tungsten complexes) with alkynes, in the absence of the catalyst, does lead to cyclopentadienes **5**, albeit in small amounts.

The vinyl- and divinylcyclopentadienes **5a**−**m** were isolated in 53−73% yields. They form air-sensitive yellowish and pale orange oils, which were purified by flash column chromatography on alumina with degassed solvents. Spectroscopic features most characteristic of compounds **5** include singlets for 1-H and 4-H (with only minor coupling between each other, less than 1 Hz). Further proof of the substitution pattern is provided by NOE-DIFF studies of vinyl cyclopentadienes **5c**,**d**,**f**,**g**,**h**, in which an enhancement was found between the signals for the 1-H and the NCH_2 groups of the morpholine unit, as well as the hydrogen atoms of the neighboring substituents attached to C2 and C5. In line with the structural assignment given in Scheme 1 are NMR $^1J(^{13}C,^1H)$ and $^{2,3}J(^{13}C,^1H)$ correlation experiments of compounds **5b**,**f**,**g**,**l** as well as the chemical shifts of C1 in the narrow range of δ = 70−71 for all cyclopentadien-1-yl morpholine derivatives **5**. Furthermore, a $^4J(^1H,^1H)$ coupling could be detected between 1-H and 1′′-H_2 as well as between 4-H and 1′′-H_2 in case of the methoxymethyl cyclopentadienes **5d**,**j**,**m** by homo-decoupling experiments. The ^{13}C-NMR signals of C5 of the methoxymethyl cyclopentadienes **5d**,**j**,**m** (δ = 147) as well as the (1-trimethylsiloxycyclohex-1-yl)cyclopentadienes **5e** (δ = 154) are shifted downfield relative to other cyclopentadiene derivatives **5** (δ = 132−138). The assignment of the signals C1′ and 1′-(*i-C* Ph) is based on the reasonable assumption that the $^2J(^{13}C,^1H)$ coupling would be smaller than the $^3J(^{13}C,^1H)$ coupling of the aromatic system. The mass spectra of compounds **5** exhibit a base peak at $[M^+ - 85]$, except for the methoxymethyl derivatives **5d**,**j**,**m**, whose base peaks are observed at $[M^+ - MeOCH_2]$. A molecular peak of compounds **5h**,**n** could not be detected with conventional ionization methods, but it could be clearly observed on application of an electron-spray-ionization technique (ESI; solvent: acetonitrile/MeOH). Interestingly, compounds **5h**,**k**,**n** underwent a cone potential depending fragmentation, which is probably due to loss of morpholine. When cone potentials were lowered (**5h**: from 19 to 11 V, **5k**: from 31 to 20 V, **5n**: from 34 to 20 V), an increase in intensity was observed for the $[M + H^+]$ peaks, whilst the peaks $[M + H^+ - 87]$ became smaller. It should be mentioned that in ESI-based mass spectrometry, a fragmentation of organic molecules has been observed for very rare examples only. In our case, this observation may be associated with the fact that the fragmentation barrier between the protonated cyclopentadienes **5h**,**k**,**n** and the cations supposedly formed by loss of morpholine (and concomitant generation of vinyl cyclopentadienyl or tropylium cations) would be very small in terms of chemical bond energies.



Scheme 2. Generation of vinylcyclopentadienes from (1-alkynyl)-carbene complexes and enamines

Table 1. Cross-conjugated metallahexatrienes **3** from (1-alkynyl)-carbene complexes **1** and enamines **2**

1	M	R^1	2	NR_2	R^2	3	M	NR_2	R^1	R^2	3[%][a]
a	W	Ph	**a**	mor[b]	Me	**a**	W	mor[b]	Ph	Me	93
b	W		**b**	mor[b]	i-Pr	**b**	W	mor[b]	Ph	i-Pr	95
c	Cr	Ph	**d**	mor[b]	[c]	**c**	W	mor[b]	Ph	[c]	92
d	Cr		**e**	NEt_2	[c]	**d**	W	mor[b]		Me	95
			f	NEt_2	Me	**e**	W	mor[b]		i-Pr	95
			g	NPr_2	Me	**f**	W	NEt_2	Ph	Me	87
						g	W	NEt_2		Me	83
						h	W	NEt_2	Ph	[c]	86
						i	W	NEt_2		[c]	84
						j	W	NPr_2	Ph	Me	89
						k	W	NPr_2		Me	86
						l	Cr	mor[b]	Ph	Me	95
						m	Cr	mor[b]	Ph	i-Pr	94
						o	Cr	mor[b]		i-Pr	88
						n	Cr	NEt_2	Ph	[c]	87

[a] Isolated yield in%. – [b] Morpholino. – [c] (6*S*)-2-Methyl-2-hepten-6-yl.

Table 2. Vinylcyclopentadienes **5** by condensation of alkynes **4** with cross-conjugated tungstahexatrienes **3a**–**e**

1	M	R^1	2	NR_2	R^2	3	M	NR_2	R^1	R^2	3[%][a]
a	W	Ph	**a**	mor[b]	Me	**a**	W	mor[b]	Ph	Me	93
b	W		**b**	mor[b]	i-Pr	**b**	W	mor[b]	Ph	i-Pr	95
c	Cr	Ph	**d**	mor[b]	[c]	**c**	W	mor[b]	Ph	[c]	92
d	Cr		**e**	NEt_2	[c]	**d**	W	mor[b]		Me	95
			f	NEt_2	Me	**e**	W	mor[b]		i-Pr	95
			g	NPr_2	Me	**f**	W	NEt_2	Ph	Me	87
						g	W	NEt_2		Me	83
						h	W	NEt_2	Ph	[c]	86
						i	W	NEt_2		[c]	84
						j	W	NPr_2	Ph	Me	89
						k	W	NPr_2		Me	86
						l	Cr	mor[b]	Ph	Me	95
						m	Cr	mor[b]	Ph	i-Pr	94
						o	Cr	mor[b]		i-Pr	88
						n	Cr	NEt_2	Ph	[c]	87

[a] Isolated yield in%, in THF/EtOH (5:1), 2.5 mol-% $[(COD)RhCl]_2$, after 28–40 h at 20°C. – [b] (6*S*)-2-Methyl-2-hepten-6-yl.

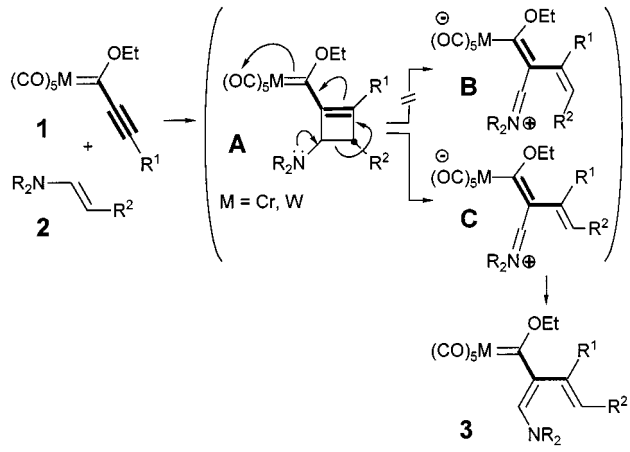
a) Generation of Cross-Conjugated Metallahexatrienes

Other than the vinyl- and divinylcyclopentadienes **5**, its cross-conjugated metallahexatriene precursors [= (1-amino-1,3-butadien-2-yl)carbene complexes] $(CO)_5M{=}C(OEt){-}C(=CHNR_2)\ CR^1{=}CHR^2$ (**3**) proved to be quite stable. The morpholino derivatives **3a**,**b**,**d**,**e**,**l**,**m**,**o** could be isolated as crystals[13] in nearly quantitative yields by addition of the enamines[14] (E)-$(R_2N)CH{=}CHR^2$ (**2**) (R_2N = morpholino) to (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR^1$ (**1**) in *n*-pentane (Scheme 2, Table 1).

The generation of cross-conjugated metallahexatrienes **3** involves a metathesis of the C=C double bond of the enamine **2** at the C≡C bond of the (1-alkynyl)carbene complex **1**, probably by formation of a (4-aminocyclobuten-1-yl)carbene complex **A** and a zwitterionic carbiminium carbonylmetallate **C** (not **B**) intermediate (Scheme 3).[7e,15] The reaction is highly stereoselective and in each case yields only one stereoisomer. The configurational assignment of these compounds rests on NOE-DIFF experiments performed on the cross-conjugated metallahexatrienes **3b**,**d**,**h**,**j** and crystal structure analyses of compounds **3j** and **3o** (Figures 1 and 2).

Cross-conjugated aminometallahexatrienes have been found to readily form highly polarized carbiminium carbonylmetallate structures $^{-}(OC)_5M{-}C{=}C{-}C{=}N^{+}$,[12] in which the ligand backbone is normally strongly distorted out of planarity due to the 1,3-allylic strain induced by substituents. The reactivity of the M–C bond of such molecules is strongly influenced by the degree of distortion. In the present case, cross-conjugated amino metallahexatrienes **3** were found to represent one of the rarer cases, in which the M–C–C–C(N) portion of the molecule is almost planar, since only little 1,3-allylic strain is induced by the steric interaction of the (small) hydrogen atom attached to the =CH(N) group (for example 9-H in Figure 1) and the $M(CO)_5$ moiety. Accordingly, these molecules are best represented by a resonance hybrid between a carbene complex $(CO)_5M{=}C{-}C{=}C{-}C{=}C(NR_2)$ and a carbiminium carbonylmetallate $^{-}(OC)_5M{-}C{=}C{-}C{=}C{-}C(=N^{+}R_2)$ which in this special case is almost planar. With respect to the ^{13}C-NMR shift of the M–C unit (e.g. W–C of **3j**: δ = 274.5, all other tungsten compounds **3**: δ = 273–278; Cr–C of **3o**: 297.2, all other chromium compounds **3**: δ = 292–298) and the C=*C*(N) group (e.g. **3j**: δ = 168.7, **3o**: δ = 164.2, all other compounds **3**: δ = 164–169) the metallahexatriene unit of compounds **3** should be much less polarized than, e.g., in the strongly distorted zwitterionic carbiminium carbonylmetallate $(2E)$-$[^{-}(OC)_5W{-}C(OEt){=}C(CPh{=}CHCO_2Me)C(Me){=}N^{+}(CH_2)_2]$ [W–C: δ = 245.0; C=*C*(N) δ = 181.0].[16]

The crystal structure analysis of the cross-conjugated aminotungstahexatriene **3j** (Figure 1) indicates the presence of an almost *syn*-planar M–C–C–C(N) backbone, W–C4–C5–C9: 3.95(0.46)°, and a W-shaped O–C–C–C–N unit, C4–C5–C9–N: 174.84(0.36)°. An essentially similar, although slightly more distorted M–C–C–C(N) unit is observed for the cross-conjugated amino chroma-



Scheme 3. Generation of cross-conjugated amino-metallahexatrienes **3** from (1-alkynyl)carbene complexes and enamines

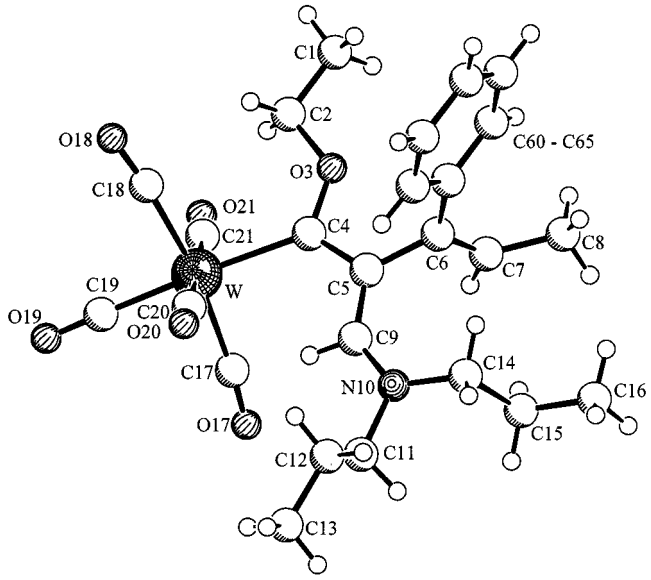


Figure 1. Molecular structure of cross-conjugated amino tungstahexatriene **3j** with selected bond lengths [Å] and angles [°]: W−C4 2.296(3), C4−C5 1.422(5), C5−C6 1.509(4), C6−C7 1.337(5), C6−C60 1.480(5), C5−C9 1.377(5), C9−N10 1.321(4); O3−C4−W 124.1(2), O3−C4−C5 106.9(3), C5−C4−W 129.0(2), C4−C5−C6 119.2(3), C6−C5−C9 123.2(3), C5−C9−N10 134.1(3), C5−C6−C7 117.4(3), C5−C6−C60 117.3(3)

hexatriene **3o** [Cr−C4−C5−C6: 26.58(0.33)° and C4−C5−C6−N: 174.80(0.26)°, Figure 2]. The stronger distortion of the latter compound is probably due to the increase in steric congestion induced by the shorter M=C distance of the chromium compound **3o** [Cr−C4 2.143(3) Å] compared to the tungsten compound **3j** [W−C4 2.296(3) Å]. The pattern of bond lengths observed for the tungsten compound **3j**, W−C4 2.296(3) Å, C4−C5 1.422(5), C5−C9 1.377(5), C9−N 1.321(4) is in line with the expected electron delocalization. A similar pattern of bond lengths is observed for the chromium compound **3o**, Cr−C4 2.143 (3) Å, C4−C5 1.440 (4), C5−C6 1.381 (4), C6−N 1.327 (3). The molecular structure of **3o** exhibits a positional disorder of the cyclohexenyl ring at C16 and C17, attributed to the statistic contribution of two different cyclohexenyl conformers.

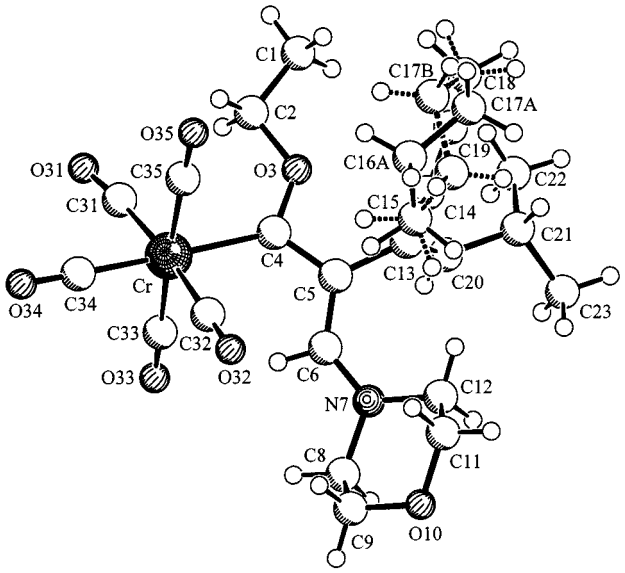
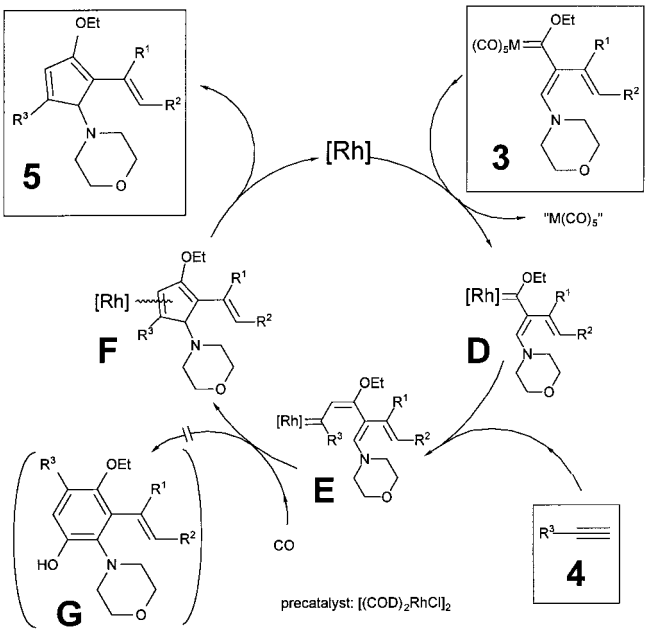


Figure 2. Molecular structure of cross-conjugated amino chromahexatriene **3o** with selected bond lengths [Å] and angles [°]: Cr−C4 2.143(3), C4−C5 1.440(4), C5−C6 1.381(4), C6−N7 1.327(3), C5−C13 1.508(3), C13−C14 1.497(3), C13−C20 1.331(4), C14−C19 1.336(4); O3−C4−C5 106.4(2), Cr−C4−C5 127.08(19), C4−C5−C6 117.2(2), C4−C5−C13 118.2(2), C5−C6−N7 132.4(2), C6−C5−C13 124.2(2), C5−C13−C14 115.7(2), C5−C13−C20 118.6(2), C13−C19−C18 121.8

b) Rhodium-Catalyzed Cyclopentadiene Formation

Based on earlier studies, it could be anticipated that reaction of a compound **3** with an alkyne **4** would lead to a 6-amino-1-metalla-1,3,5-hexatriene unit by insertion of the C≡C bond into the M=C bond (Scheme 1) and thus would finally produce a vinylcyclopentadiene. Furthermore, it could be anticipated that temperatures of 50−80°C would be required for the chromium complexes, and even 100°C for the tungsten complexes to react in this manner, and that these drastic conditions would be completely unsuitable for the preparation and isolation of highly sensitive vinylcyclopentadienes.

The success of our synthesis finally rests on the fact that it could be catalyzed by $[(COD)RhCl]_2$ under very mild conditions (at 20°C). Mechanistic speculations on the course of the Rh^I catalyzed insertion of alkynes **4** into compounds **3** are given in Scheme 4. They imply a transmetallation step of a metallahexatriene **3** to give a corresponding rhodium compound **D**,[17][18] from which a 1-rhoda-1,3,5-hexatriene **E**, is derived by insertion of an alkyne **4**. By a subsequent π-cyclization of compound **E** a vinyl cyclopentadiene rhodium complex **F** is assumed to be formed, from which the vinyl cyclopentadiene **5** is finally extruded by regeneration of the catalytic active rhodium species. A 2-amino-4-ethoxyphenol **G** (= Dötz product) is not obtained, though ample carbon monoxide is present for this reaction to occur. It should be noted that the reaction



Scheme 4. Rhodium-catalyzed generation of cyclopentadienes **5** from cross-conjugated metallahexatrienes **3**

shown in Scheme 4 represents the first example of a transition metal catalyzed reaction of a metal carbene complex.

Side Reactions

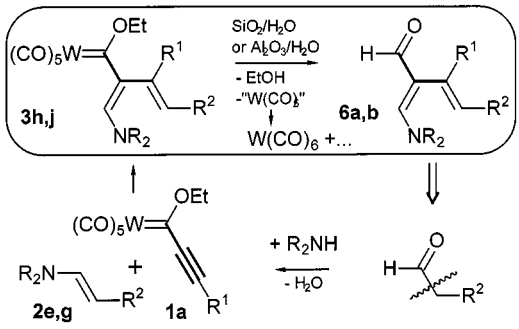
Three types of side reactions must be encountered on dealing with the reactions described above. These comprise a) a hydrolysis of a cross-conjugated metallahexatriene **3** on silica to give an aldehyde (Scheme 5); b) a thermally induced intramolecular transamination within a compound **3** (Scheme 6); and c) an isomerization of the π-system of divinyl cyclopentadienes (Scheme 7).

a) Aldehyde Formation by Hydrolysis of the M=C Bond

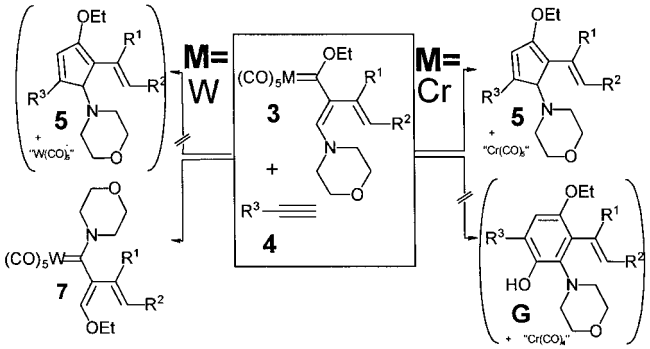
Cross-conjugated metallahexatrienes **3** were found to hydrolyze slowly on silica gel to give aldehydes **6** and the corresponding $M(CO)_6$ in a smooth reaction (Scheme 5).[19] Compounds **6a**,**b** (generated from **3h** and **3j**, respectively) have been characterized spectroscopically in order to exemplify this reaction mode. It should be noted that this process might be utilized for an overall C_2-homologization of aldehydes, from which the enamines **2** are obtained (Scheme 5).

b) Generation of Cross-Conjugated 2-Amino- from 4-Amino Tungstahexatrienes

Although a thermal reaction of alkynes **4** with the cross-conjugated chromahexatrienes **3l**,**m** at 65°C in THF/EtOH (5:1) was found to produce a small yield of vinyl cyclopentadienes **5**, no such reaction could be observed with the corresponding cross-conjugated tungstahexatrienes under similar conditions. On elevation of the reaction temperature to 75°C, the tungsten compounds **3a**,**b** were smoothly transformed into cross-conjugated tungstahexatrienes **7a**,**b** by an exchange of the 2-ethoxy- with the 4-morpholino group (Scheme 6).[20] The mechanism of the (4 to 2)-shift of the morpholino group has not been unravelled so far, except for the fact that it does not involve a concomitant rearrangement of the carbon skeleton nor a migration of the $W(CO)_5$ unit.[20]



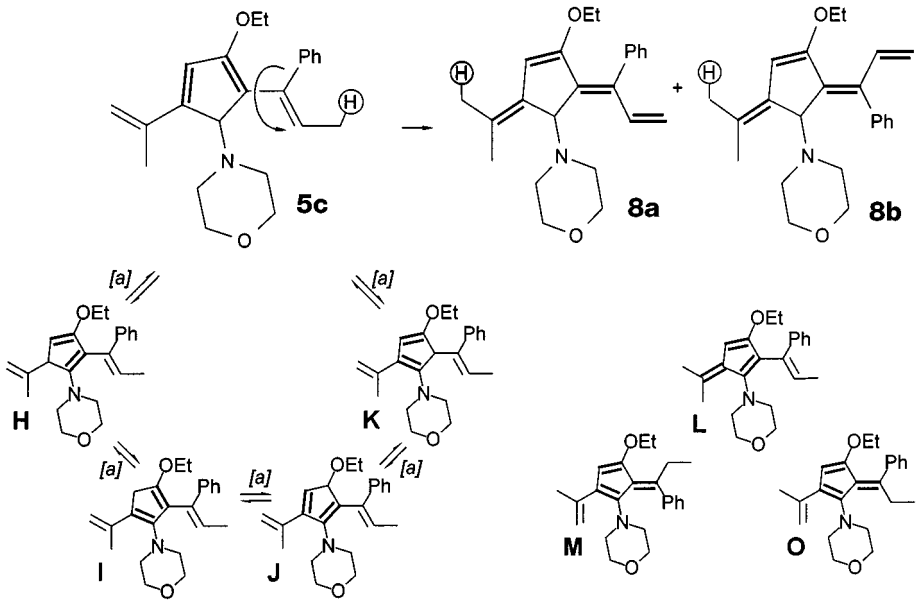
Scheme 5. Aldehydes by hydrolysis of cross-conjugated metallahexatrienes



Scheme 6. Different thermal behaviour of cross-conjugated metallahexatrienes **3** of chromium and tungsten in the presence of an alkyne

c) Rearrangement of Divinyl Cyclopentadiene 5c

The (uncatalyzed) reaction of 2-methyl-1-butene-3-yne (**4c**) with the chromium compound **3m** at 65°C was found to produce divinylcyclopentadiene **5c** (minor product) together with a 1:1-mixture of dialkylidene cyclopentenes **8a** and **8b** (major product, total yield ca. 25%) (Scheme 7). Since the latter compounds were not obtained under conditions of the rhodium catalysis at 20°C, it is assumed that compounds **8a**,**b** are generated by thermal rearrangement of the divinylcyclopentadiene **5c**. A transformation of this type could be acid- or base-catalyzed, but in principle it could also be achieved by two successive 1,5-sigmatropic hydrogen shifts, even though the latter process would be rather unfavorable owing to the transition state geometry which is forced by the rigid ring system.



Scheme 7. Thermal rearrangement of divinylcyclopentadiene **5c** – [a] Isomerization by sigmatropic H shift (not observed)

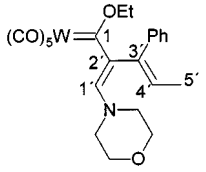
The structural assignment of compounds **8a**,**b** is based on their NMR spectra, which exhibit the expected features. Compounds **8a** and **8b** are most easily distinguished by the different chemical shifts of 2′-H (**8a**: δ = 7.02; **8b**: δ = 7.84) resulting from different anisotropic shielding by the neighboring phenyl group.

Since double bond isomerizations of cyclopentadienes by 1,5-hydrogen shifts[9][11] for certain cases are known to proceed at 20°C, it was not anticipated that compounds **5a**,**b**,**d**–**n** would be obtained as single isomers. Furthermore, it was not anticipated that compounds **5** would not readily yield mixtures of isomers, e.g. **H**–**O**, on heating up to 65°C. This observation is tentatively attributed to the increase of steric congestion, when a planar C(sp^2)–N enamine unit is forced into the cyclopentadiene ring of compounds **H**–**O**. It is therefore assumed that compounds **H**–**O** might be thermodynamically less stable than the other isomers **5** and **8**, which contain a C(sp^3)–N unit.

Experimental Section

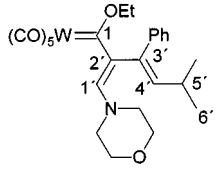
NMR: Bruker ARX 300, Bruker AM 360 and Varian U 600. – IR: FT-IR BIO-RAD DIGILAB DIVISION FTS-45. – MS and HRMS: FINNIGAN MAT8200. – ESI: Micromass Quattro LCZ – Elemental analyses: HERAEUS CHN-O-Rapid. – X-ray diffraction: Data sets were collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-97, structure refinement SHELXL-97, graphics SCHAKAL-92. – Melting points are uncorrected. – Column chromatography: ICN Alumina B, solvents were degassed by ultrasound in case of the cyclopentadiene isolation; flash chromatography was performed under an argon pressure of 1.4 bar within ca. 10 min for each cyclopentadiene; alumina was degassed at 10^{-3} mbar for several hours, stored over argon and then deactivated. – TLC: Merck Aluminiumoxide $60F_{254}$ neutral. – R_f values are based on TLC tests. – All reactions were performed under argon. – THF (p.a. quality), EtOH p.a., diethyl ether/*n*-pentane, C_6D_6, $CDCl_3$, and CD_2Cl_2 were used as purchased and not dried.

Pentacarbonyl[1-ethoxy-1-(1-morpholino-3-phenyl-1,3-pentadien-2-yl)methylene]tungsten(0) (3a): To pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)tungsten(0) (**1a**) (482 mg, 1.00 mmol) in a 5-mL screwtop vessel was added a solution of *N*-(propen-1-yl)morpholine (**2a**) (127 mg, 1.00 mmol) in 4 mL of *n*-pentane with vigorous stirring, at 20°C. The yellow precipitate was collected after 30 min by centrifuge and washed twice with *n*-pentane (2–3 mL) to give compound **3a** (568 mg, 93%, m.p. 104°C, dec., R_f = 0.4 on alumina, *n*-pentane/diethyl ether, 9:1). – ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 8.44 (1 H, s, 1′-H), 7.30 and 7.17 (2:3 H, m each, Ph), 5.51 (1 H, q, ^3J = 7.2 Hz, 4′-H), 4.45 (2 H, m dynamically broadened, OCH_2CH_3), 3.8–3.5 [8 H, dynamically broadened, $O(CH_2CH_2)_2N$], 1.90 (3 H, d, ^3J = 7.2 Hz, 5′-H_3), 1.01 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). – ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 277.8 (C_q, C1), 202.3 and 199.4 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 167.1 (CH, C1′); 139.8, 137.1 and 135.4 (C_q each, C2′, C3′, and *i*-C, Ph), 127.9 and 127.8 (CH each, *o*- and *m*-C Ph), 126.6 (CH, *p*-C Ph), 126.2 (CH, C4′), 76.0 (OCH_2CH_3), 66.7 [$O(CH_2CH_2)_2N$], 55–50 [dynamically broadened, $N(CH_2)_2$], 15.2 (CH_3, C5′), 14.7 (OCH_2CH_3). – IR (hexane/CH_2Cl_2), ṽ (%): 2056.6 cm^{-1} (16), 1962.0 (7), 1924.4 (100) (C≡O); 1586.7 (14). – MS (70 eV), ^{184}W, *m*/*z* (%): 609 (8) [M^+], 581 (9) [M^+ – CO], 525 (88) [M^+ – 3CO], 469 (10) [M^+ – 5 CO], 441 (44), 408 (29), 354 (36), 325 (53), 256 (25), 149 (35), 115 (76), 57 (100) – $C_{23}H_{23}NO_7W$ (609.3): calcd. C 45.34, H 3.80, N 2.30; found C 45.37, H 3.66, N 2.23.



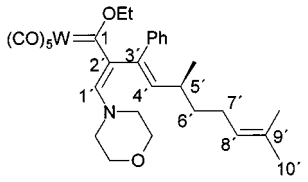
Pentacarbonyl[1-ethoxy-1-(5-methyl-1-morpholino-3-phenyl-1,3-hexadien-2-yl)methylene]tungsten(0) (3b): Pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)tungsten(0) (**1a**) (482 mg, 1.00

mmol) and *N*-[1-(3-methylbut-1-enyl)]morpholine (**2b**) (155 mg, 1.00 mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give a yellow precipitate of compound **3b**, which was collected after 30 min by centrifuge (602 mg, 95%, m.p. 96°C, R_f = 0.3 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 8.42 (1 H, s, 1′-H), 7.30, 7.22, and 7.14 (2:1:2 H, m each, Ph), 5.16 (1 H, d, ^3J = 10.4 Hz, 4′-H), 4.48 (2 H, dynamically broadened, OCH_2CH_3), 3.72 [8 H, dynamically broadened, $O(CH_2CH_2)_2N$], 2.87 (1 H, m, 5′-H), 1.14 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3), 1.04 (6 H, dynamically broadened, 6′-H_3 and 5′-CH_3). − ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 278.1 (C_q, C1), 202.2 and 199.4 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 166.8 (CH, C1′), 140.4 (C_q, *i*-C Ph), 139.7 (CH, C4′), 135.7 and 133.5 (C_q each, C2′ and C3′); 128.2, 128.0, and 126.7 (CH each, Ph), 76.1 (OCH_2CH_3), 66.8 [$O(CH_2CH_2)_2N$], 54 [dynamically broadened, $N(CH_2)_2$], 27.8 (CH, C5′), 23.0 (CH_3, C6′ and 5′-CH_3), 15.0 (OCH_2CH_3). − IR (hexane/CH_2Cl_2), ṽ (%): 2057.4 cm^{-1} (14), 1983.1 (11), 1961.9 (6), 1924.3 (100) (C≡O); 1588.8 (13), period − MS (70 eV), ^{184}W, *m/z* (%): 637 (7) [M^+], 609 (7) [M^+ − CO], 581 (7) [M^+ − 2 CO], 553 (100) [M^+ − 3 CO], 525 (11) [M^+ − 4 CO], 497 (15) [M^+ − 5 CO], 468 (41), 426 (21), 398 (40), 279 (40), 115 (41). − $C_{25}H_{27}NO_7W$ (637.3): calcd. C 47.11, H 4.27, N 2.20; found C 46.98, H 4.32, N 2.23.

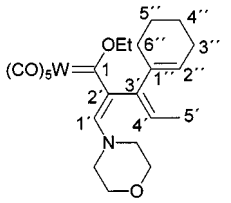


Pentacarbonyl{1-ethoxy-1-[(5*S*),9-dimethyl-1-morpholino-3-phenyl-1,3,8-decatrien-2-yl]methylene}tungsten(0) (3c): Pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)tungsten(0) (**1a**) (482 mg, 1.00 mmol) and *N*-{1-[(3*S*),7-dimethylocta-1,6-dienyl]}morpholine (**2d**) (223 mg, 1.00 mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give an orange oil of compound **3c** after separation by column chromatography on alumina (activity 3) (595 mg, 86%, R_f = 0.5 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.41 (1 H, s, 1′-H), 7.28 and 7.17 (2:3 H, m each, Ph), 5.19 (1 H, d, ^3J = 10.5 Hz, 4′-H), 5.08 (1 H, m, 8′-H), 4.54 (2 H, dynamically broadened, OCH_2CH_3), 3.69 [8 H, dynamically broadened, $O(CH_2CH_2)_2N$], 2.79 (1 H, m, 5′-H), 2.01 (2 H, m, 7′-H_2), 1.67 and 1.57 (3:3 H, s each, 10′-H_3 and 9′-CH_3), 1.39 (2 H, m, 6′-H_2), 1.18 (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3), 0.99 (3 H, dynamically broadened, 5′-CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 278.1 (C_q, C1), 202.2 and 199.4 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 166.8 (C_q, C1′), 140.1 (C_q, *i*-C Ph), 139.2 (CH, C8′); 136.0, 134.1, and 131.6 (C_q each, C2′, C3′, and C9′), 128.3 (CH); 127.9, 126.7, and 124.2 (CH each, *o*-, *m*-, and *p*-C Ph and C4′), 76.2 (OCH_2CH_3), 66.8 [$O(CH_2CH_2)_2N$], 53−52 [dynamically broadened, $N(CH_2)_2$], 37.5 (CH_2, C7′), 32.3 (CH, C5′), 25.7 (CH_2, C6′), 25.6 (CH_3 each, C10′), 20.2 (CH_3, 9′-CH_3), 17.6 (CH_3, 5′-CH_3), 15.0 (OCH_2CH_3). − IR (hexane), ṽ (%): 2057.9 cm^{-1} (13), 1962.3 (5), 1925.4 (100)(C≡O); 1589.2 (10). − MS (70 eV) *m/z* (%): 705 (4) [M^+], 677 (6) [M^+ − CO], 621 (65) [M^+ − 3 CO], 536 (10), 417 (7), 354 (6), 155 (12). − $C_{30}H_{35}NO_7W$ (705.5): calcd. C 51.08, H 5.00, N 1.99; found C 51.73, H 5.46, N 2.07.

Pentacarbonyl[1-ethoxy-1-(3-cyclohex-1-enyl-1-morpholino-1,3-pentadien-2-yl)methylene]tungsten(0) (3d): Pentacarbonyl(1-ethoxy-3-cyclohexen-1-yl-2-propyne-1-ylidene)tungsten(0) (**1b**) (486 mg, 1.00 mmol) and *N*-(propen-1-yl)morpholine (**2a**) (127 mg, 1.00

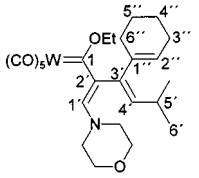


mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give a yellow precipitate of compound **3d**, which was collected after 30 min by centrifuge (582 mg, 95%, m.p. 98°C, R_f = 0.6 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 8.27 (1 H, s, 1′-H), 5.52 (1 H, m, 2′′-H), 5.13 (1 H, q, ^3J = 7.2 Hz, 4′-H), 4.61 (2 H, m dynamically broadened, OCH_2CH_3), 3.7−3.5 [8 H, m dynamically broadened, $O(CH_2CH_2)_2N$], 2.10 and 1.99 (2 H each, dynamically broadened each, 3′′-H_2 and 6′′-H_2), 1.79 (3 H, t, ^3J = 7.2 Hz, 5′-H_3), 1.54 (4 H, dynamically broadened, 4′′-H_2 and 5′′-H_2), 1.35 (3 H, t, ^3J = 7.0 Hz, OCH_3CH_3). − ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 277.7 (C_q, C1), 202.5 and 199.5 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 166.7 (CH, C1′); 139.3, 136.2, and 135.4 (C_q each, C2′, C3′, and C1′′), 127.4 (CH, C2′′), 124.5 (CH, C4), 76.0 (OCH_2CH_3), 66.9 [$O(CH_2CH_2)_2N$], 56−52 [dynamically broadened, $N(CH_2)_2$], 28.3 and 25.6 (CH_2 each, C3′′ and C6′′), 23.1 and 22.2 (CH_2 each, C4′′ and C5′′), 15.3 and 15.2 (CH_3 each, C5′ and OCH_2CH_3). − IR (hexane/CH_2Cl_2), ṽ (%): 2056.4 cm^{-1} (17), 1959.8 (7), 1923.2 (100) (C≡O); 1586.7 (16). − MS (70 eV), ^{184}W, *m/z* (%): 613 (6) [M^+], 585 (4) [M^+ − CO], 557 (8) [M^+ − 2 CO], 529 (6) [M^+ − 3 CO], 501 (9) [M^+ − 4 CO], 473 (20) [M^+ − 5 CO], 442 (30), 412 (17), 353 (23), 327 (18), 99 (67), 57 (100). − $C_{23}H_{27}NO_7W$ (613.3): calcd. C 45.04, H 4.44, N 2.28; found C 45.00, H 4.61, N 2.31.

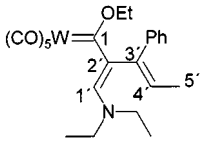


Pentacarbonyl[1-ethoxy-1-(3-cyclohex-1-enyl-5-methyl-1-morpholino-1,3-hexadien-2-yl)methylene]tungsten(0) (3e): Pentacarbonyl-(1-ethoxy-3-cyclohexen-1-yl-2-propyne-1-ylidene)tungsten(0) (**1b**) (486 mg, 1.00 mmol) and *N*-[1-(3-methylbut-1-enyl)]morpholine (**2b**) (155 mg, 1.00 mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give a yellow precipitate of compound **3e**, which was collected after 30 min by centrifuge (605 mg, 95%, m.p. 84°C, R_f = 0.4 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 8.25 (1 H, s, 1′-H), 5.50 (1 H, m, 2′′-H), 4.82 (1 H, d, ^3J = 10.9 Hz, 4′-H), 4.61 (2 H, m, dynamically broadened, OCH_2CH_3), 3.8−3.6 [8 H, dynamically broadened, $O(CH_2CH_2)_2N$], 2.81 (1 H, m, 5′-H), 2.10 and 1.94 (2:2 H, dynamically broadened each, 3′′-H_2 and 6′′-H_2), 1.59 (4 H, dynamically broadened, 4′′-H_2 and 5′′-H_2), 1.37 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3), 0.97 (6 H, d, dynamically broadened, 6′-H_3 and 5-′CH_3), period − ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 278.0 (C_q, C1), 202.4 and 199.5 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 166.5 (CH, C1), 138.6 (CH, C4′), 135.7 and 135.3 (C_q each, C2′ and C3′), 126.4 (CH, C2′′), 76.1 (OCH_2CH_3), 67.0 [$O(CH_2CH_2)_2N$], 54−51 [dynamically broadened, $O(CH_2CH_2)_2N$], 28.2 and 25.7 (CH_2 each, C3′′ and C6′′), 28.0 (CH, C5′), 23.2 (CH_3, dynamically broadened, C6′ and 5′-CH_3), 23.1 and 22.2 (CH_2 each, C4′′ and C5′′), 15.3 (OCH_2CH_3). − IR (hexane/

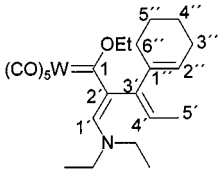
CH_2Cl_2), $\tilde{\nu}$ (%): 2056.8 cm^{-1} (13), 1959.9 (6), 1923.5 (100)(C≡O); 1588.4 (12). − MS (70 eV), ^{184}W, *m/z* (%): 641 (5) [M^+], 613 (4) [M^+ − CO], 585 (6) [M^+ − 2 CO], 557 (6) [M^+ − 3 CO], 529 (7) [M^+ − 4 CO], 501 (26) [M^+ − 5 CO], 470 (29), 442 (14), 379 (11), 365 (13), 355 (14), 317 (4), 155 (19), 91 (22), 57 (100). − $C_{25}H_{31}NO_7W$ (641.4): calcd. C 46.82, H 4.87, N 2.18; found C 46.95, H 5.02, N 2.26.



Pentacarbonyl[1-ethoxy-1-(1-*N*,*N*-diethylamino-3-phenyl-1,3-pentadien-2-yl)methylene]tungsten(0) (3f): To pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)tungsten(0) (**1a**) (482 mg, 1.00 mmol) in a 5-mL screwtop vessel was added a solution of *N*,*N*-diethyl-*N*-(propen-1-yl)amine (**2f**) (113 mg, 1.00 mmol) in 4 mL of *n*-pentane under vigorous stirring. The reaction mixture was stirred for 30 min at 20°C. Compound **3f** was obtained as an orange oil after separation by column chromatography on alumina (activity 3) and removal of the eluant (517 mg, 87%, R_f = 0.6 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.46 (1 H, s, 1′-H), 7.24 and 7.18 (2:3 H, m each, Ph), 5.50 (1 H, q, ^3J = 7.2 Hz, 4′-H), 4.47 (2 H, m dynamically broadened, OCH_2), 3.7−3.3 [4 H, dynamically broadened, $N(CH_2)_2$], 1.91 (3 H, d, ^3J = 7.2 Hz, 5′-H_3), 1.5−1.1 [6 H, dynamically broadened, $NCH_2CH_3)_2$], 1.04 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 273.8 (C_q, C1), 202.4 and 199.6 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 168.1 (CH, C1); 140.1, 139.1, and 137.0 (C_q each, C2′, C3′, and *i*-C Ph), 128.7 and 127.7 (CH each, *o*- and *m*-C Ph), 126.4 and 125.6 (CH each, C4′ and *p*-C Ph), 75.5 (OCH_2), 51.8 and 43.9 [CH_2 each, dynamically broadened each, $N(CH_2)_2$], 15.5 and 14.9 (CH_3 each, C5′ and OCH_2CH_3), 14.3 and 13.1 [CH_3 each, dynamically broadened each, $N(CH_2CH_3)_2$]. − IR (hexane), $\tilde{\nu}$ (%): 2058.2 cm^{-1} (12), 1959.0 (6), 1920.8 (100) (C≡O); 1585.9 (9). − MS (70 eV), ^{184}W, *m/z* (%): 595 (15) [M^+], 567 (16) [M^+ − CO], 539 (4) [M^+ − 2 CO], 511 (100) [M^+ − 3 CO], 483 (4) [M^+ − 4 CO], 455 (14) [M^+ − 5 CO], 426 (53), 394 (35), 364 (19), 339 (24), 325 (31), 313 (21), 298 (16), 128 (27), 56 (28). − $C_{23}H_{25}NO_6W$ (595.3): calcd. C 46.41, H 4.23, N 2.35; found C 46.79, H 4.42, N 2.42.



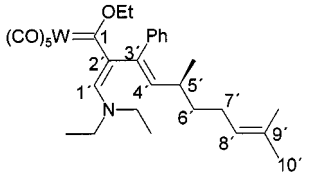
Pentacarbonyl[1-ethoxy-1-(3-cyclohex-1-enyl-1-*N*,*N*-diethylamino-1,3-pentadien-2-yl)methylene]tungsten(0) (3g): Pentacarbonyl(1-ethoxy-3-cyclohexen-1-yl-2-propyne-1-ylidene)tungsten(0) (**1b**) (486 mg, 1.00 mmol) and *N*,*N*-diethyl-*N*-(propen-1-yl)amine (**2f**) (113 mg, 1.00 mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give an orange oil of compound **3g** after separation by column chromatography on alumina (activity 3) and removal of the eluant (497 mg, 83%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.30 (1 H, s, 1′-H), 5.54 (1 H, m, 2′′-H), 5.12 (1 H, q, ^3J = 7.2 Hz, 4′-H), 4.58 (2 H, m, OCH_2), 3.45 [4 H, dynamically broadened, $N(CH_2)_2$], 2.11 and 2.00 (2:2 H, dynamically broadened, 3′′-H_2 and 6′′-H_2), 1.81 (3 H, d, ^3J = 7.2 Hz, 5′-H_3), 1.58 (4 H, dynamically broadened, 4′′-H_2 and 5′′-H_2), 1.33 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3), 1.24 [6 H, dynamically broadened, $N(CH_2CH_3)_2$]. − ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 273.3 (C_q, C1), 202.6 and 199.6 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 167.9 (CH, C1′); 139.3, 136.3, and 135.8 (C_q each, C2′, C3′, and C1′′), 127.2 and 124.0 (CH each, C4′ and C2′′), 75.4 (OCH_2), 51.4 and 43.7 [CH_2 each, dynamically broadened each, $N(CH_2)_2$], 29.5 and 28.2 (CH_2 each, C3′′ and C6′′), 25.6 and 23.2 (CH_2 each, C4′′ and C5′′), 15.5 and 15.3 (CH_3 each, OCH_2CH_3 and C5′), 13.8 [dynamically broadened, $N(CH_2CH_3)_2$]. − IR (hexane), $\tilde{\nu}$ (%): 2055.9 cm^{-1} (12), 1958.0 (6), 1920.3 (100) (C≡O); 1585.3 (10). − MS (70 eV), ^{184}W, *m/z* (%): 599 (23) [M^+], 571 (24) [M^+ − CO], 543 (28) [M^+ − 2 CO], 515 (21) [M^+ − 3 CO], 487 (19) [M^+ − 4 CO], 459 (85) [M^+ − 5 CO], 456 (100), 428 (95), 396 (79), 366 (30), 339 (39), 325 (42), 313 (32), 117 (18), 79 (28). − $C_{23}H_{29}NO_6W$ (599.3): calcd. C 46.09, H 4.88, N 2.34; found C 46.08, H 5.04, N 2.63.



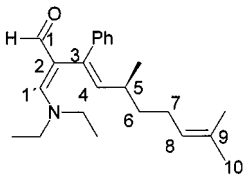
Pentacarbonyl{1-ethoxy-1-[1-*N*,*N*-diethylamino-(5*S*),9-dimethyl-3--phenyl-1,3,8-decatrien-2-yl]methylene}tungsten(0) (3h) and 2-Diethylaminomethylene-(5*S*),9-dimethyl-3-phenyldeca-3,8-dienal (6a): Pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)tungsten(0) (**1a**) (482 mg, 1.00 mmol) and *N*,*N*-diethyl-*N*-{1-[(3*S*),7-dimethylocta-1,6-dienyl]}amine (**2e**) (209 mg, 1.00 mmol) was treated as described above at 20°C in 4 mL of *n*-pentane to give an orange oil of compound **3h** after separation by column chromatography on alumina (activity 3) (595 mg, 86%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 9:1) and a pale yellowish oil of compound **6a** after elution with CH_2Cl_2/*n*-pentane 2:1 and removal of the eluant (27 mg, 8%, R_f = 0.4 on alumina, CH_2Cl_2/*n*-pentane 2:1).

3h: ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.43 (1 H, s, 1′-H), 7.27 (2 H, m, *o*-H Ph), 7.18 (3 H, m, *m*- and *p*-H Ph), 5.21 (1 H, d, ^3J = 9.5 Hz, 4′-H), 5.07 (1 H, m, 8′-H), 4.60 (2 H, m, OCH_2), 3.8−3.3 [4 H, dynamically broadened, $N(CH_2)_2$], 2.80 (1 H, m, 5′-H), 2.01 (2 H, m, dynamically broadened, 7′-H_2), 1.66 and 1.57 (3:3 H, s each, 10′-H_3 and 9′-CH_3), 1.40 (2 H, m, 6′-H_2), 1.24 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3), 1.17 [6 H, dynamically broadened, $N(CH_2CH_3)_2$], 1.03 (3 H, d, ^3J = 6.7 Hz, 5′-CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 273.6 (C_q, C1), 202.4 and 199.6 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 168.0 (CH, C1′), 140.1 (C_q, *i*-C Ph), 139.2 (CH, dynamically broadened, C8′); 136.5, 134.1, and 131.4 (C_q each, C2′, C3′, and C9′); 128.6, 127.8, 126.4, and 124.4 (CH each, *o*-, *m*-, *p*-C Ph and C4′), 75.8 (OCH_2), 51.6 and 43.6 [CH_2 each, dynamically broadened each, $N(CH_2)_2$], 37.6 (CH_2, C7′), 32.5 (CH, C5′), 25.6 (CH_2, C6′), 25.6 (CH_3, C10′), 20.3 (CH_3, 9′-CH_3), 17.5 (CH_3, 5′-CH_3), 15.3 (OCH_2CH_3), 14.1 [CH_3, dynamically broadened, $N(CH_2CH_3)_2$]. − IR (hexane), $\tilde{\nu}$ (%): 2056.7 cm^{-1} (14), 1960.0 (7), 1921.0 (100) (C≡O); 1588.4 (10). − MS (70 eV), ^{184}W, *m/z* (%): 691 (6) [M^+], 663 (9) [M^+ − CO], 607 (100) [M^+ − 3 CO], 551 (18) [M^+ − 5 CO], 522 (22), 490 (11), 417 (13), 365 (10), 338 (16), 97 (14), 83 (20). − $C_{30}H_{37}NO_6W$ (691.5): calcd. C 52.11, H 5.39, N 2.03; found C 51.85, H 5.30, N 2.05.

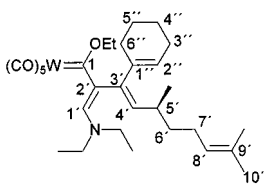
6a: ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): 9.02 (1 H, s, 1-H), 7.25 and 7.18 (3:2 H, m each, Ph), 6.63 (1 H, dynamically broadened, 1′-H), 5.40 (1 H, d, ^3J = 10.5 Hz, 4-H), 5.00 (1 H, m, 8-H), 3.30 [4 H, dynamically broadened, $N(CH_2CH_3)_2$], 2.70 (1 H, m, 5-H), 2.00 (2 H, m, dynamically broadened, 7-H_2), 1.60 and 1.54 (3:3 H,



s each, 10-H_3 and 9-CH_3), 1.35 and 1.20 (2:2 H, m each, 6-H_2 and 7-H_2), 1.06 (3 H, d, ^3J = 6.7 Hz, 5-CH_3), 1.03 [6 H, dynamically broadened, $N(CH_2CH_3)_2$]. − IR (diffuse reflection), $\tilde{\nu}$ (%): 2920 cm^{-1} (100), 2851 (73), 2694 (16), 1589 (92), 1423 (68), 1268 (62). − MS (70 eV), *m/z* (%): 339 (30) [M^+], 310 (26), 256 (33), 228 (100), 186 (32), 129 (17).



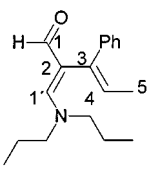
Pentacarbonyl{1-ethoxy-1-[3-cyclohexen-1-yl-1-*N*,*N*-diethylamino-(5*S*),9-dimethyl-1,3,8-decatrien-2-yl]methylene}tungsten(0) (3i): Pentacarbonyl(1-ethoxy-3-cyclohexen-1-yl-2-propyne-1-ylidene)tungsten(0) (**1b**) (486 mg, 1.00 mmol) and *N*,*N*-diethyl-*N*-{1-[(3*S*),7-dimethylocta-1,6-dienyl]}amine (**2e**) (209 mg, 1.00 mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give an orange oil of compound **3i** after separation by column chromatography on alumina (activity 3) (584 mg, 84%, R_f = 0.8 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.31 (1 H, s, 1′-H), 5.53 (1 H, m, 2′′-H), 5.10 (1 H, m, 8′-H), 4.84 (1 H, d, ^3J = 10.3 Hz, 4′-H), 4.62 (2 H, m, OCH_2), 3.9−3.2 [4 H, dynamically broadened, asymm., $N(CH_2)_2$], 2.75 (1 H, m, 5′-H), 2.09, 1.98, and 1.92 (2:2:2 H, m each, dynamically broadened each, 3′′-H_2, 6′′-H_2, and 7′-H_2), 1.68 (3 H, d,^4J = 1.0 Hz, 9′-H_3), 1.59 (3 H, d, ^4J = 1.0 Hz, 10′-H_3), 1.58 (4 H, m, dynamically broadened, 4′′-H_2 and 5′′-H_2), 1.34 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3), 1.30 (2 H, m, 6′-H_2), 1.23 [6 H, dynamically broadened, $N(CH_2CH_3)_2$], 0.96 (3 H, d, ^3J = 6.7 Hz, 5′-CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 273.8 (C_q, C1), 202.6 and 199.7 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 168.0 (CH, C1′), 137.9 (CH, C8′); 136.6, 135.5, and 131.2 (C_q each, 2:1:1, C1′′, C2′, C3′, and C9), 126.1 and 124.7 (CH each, C4′ and C2′′), 75.7 (OCH_2), 52−51 and 45−42 [dynamically broadened, $N(CH_2)_2$], 37.9 (CH_2, C7′), 32.6 (CH, C5′), 28.0, 25.9, and 25.7 (CH_2 each, C3′′, C6′′, and C6′), 25.6 (CH_3, C10′), 23.2 and 22.3 (CH_2 each, C4′′ and C5′′), 20.8 (CH_3, C9′-CH_3), 17.6 (CH_3, 5′-CH_3), 15.5 (CH_3, OCH_2CH_3), 14.3 [CH_3, $N(CH_2CH_3)_2$]. − IR (hexane), $\tilde{\nu}$ (%): 2056.2 cm^{-1} (13), 1959.3 (8), 1920.8 (100) (C≡O); 1586.8 (10). − MS (70 eV), ^{184}W, *m/z* (%): 695 (10) [M^+], 667 (14) [M^+ − CO], 639 (18) [M^+ − 2 CO], 611 (6) [M^+ − 3 CO], 583 (13) [M^+ − 4 CO], 557 (29) [M^+ − 5 CO], 553 (64), 524 (59), 492 (27), 417 (18), 365 (13), 352 (14), 339 (11), 326 (25), 109 (17), 86 (52), 69 (100), period − $C_{30}H_{41}NO_6W$ (695.5): C 51.81, H 5.94, N 2.01; found C 52.06, H 5.98; N 2.12.



Pentacarbonyl[1-ethoxy-1-(1-*N*,*N*-dipropylamino-3-phenyl-1,3-pentadien-2-yl)methylene]tungsten(0) (3j) and 2-Dipropylaminomethylene-3-phenylpent-3-enal (6b): Pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)tungsten(0) (**1a**) (482 mg, 1.00 mmol) and *N*,*N*-dipropyl-*N*-propen-1-ylamine (**2g**) (141 mg, 1.00 mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give an orange oil of compound **3j** after separation by column chromatography on alumina (activity 3) (553 mg, 89%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 9:1) and colorless needles of compound **6b** after elution with CH_2Cl_2/*n*-pentane, 2:1 and removal of the eluant (19 mg, 7%, R_f = 0.5 on alumina, CH_2Cl_2/*n*-pentane, 2:1). Precipitation of compound **3j** at −40°C in *n*-pentane for 1 day gives orange crystals (m.p. 65°C). − **3j**: ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.44 (1 H, s, 1′-H), 7.27 and 7.17 (2:3 H, each m, Ph), 5.49 (1 H, q, ^3J = 7.1 Hz, 4′-H), 4.48 (2 H, m dynamically broadened, OCH_2CH_3), 3.7−3.1 [4 H, dynamically broadened, $N(CH_2)_2$], 1.92 (3 H, d, ^3J = 7.1 Hz, 5′-H_3), 1.7−1.5 [4 H, dynamically broadened, $N(CH_2CH_2)_2$], 1.07 (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3), 1.0−0.7 [6 H, dynamically broadened, $N(CH_2CH_2CH_3)_2$]. − ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 274.5 (C_q, C1), 202.5 and 199.6 [C_q each, 1:4, *cis*- and *trans*-CO, $W(CO)_5$], 168.7 (CH, C1′); 140.0, 136.9, and 136.1 (C_q each, C2′, C3′, and *i*-C Ph), 128.8 and 127.8 (CH each, *o*- and *m*-C Ph), 126.4 and 125.9 (CH each, *p*-C Ph and C4′), 75.6 (OCH_2), 59.4 and 51.0 [dynamically broadened each, $N(CH_2)_2$], 22.4 and 21.2 [dynamically broadened each, $N(CH_2CH_2)_2$], 15.7 and 15.0 (OCH_2CH_3 and C5′), 10.8 [CH_3, $N(CH_2CH_2CH_3)_2$]. − IR (hexane/CH_2Cl_2), $\tilde{\nu}$ (%): 2058.6 cm^{-1} (13), 1959.9 (7), 1921.7 (100) (C≡O); 1585.2 (10). − MS (70 eV), ^{184}W, *m/z* (%): 623 (9) [M^+], 595 (11) [M^+ − CO], 539 (100) [M^+ − 3 CO], 483 (22) [M^+ − 5 CO], 453 (43), 380 (16), 354 (20), 325 (22), 312 (11), 115 (14). − $C_{25}H_{29}NO_6W$ (623.3): C 48.17, H 4.69, N 2.25; found C 48.27, H 4.70, N 2.00.

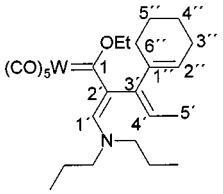
Crystal structure analysis of compound **3j**: Formula $C_{25}H_{29}NO_6W$, M = 623.34, yellow crystals, 0.60 × 0.50 × 0.40 mm, a = 9.783(1) Å, b = 12.046(1) Å, c = 12.780(1) Å, α = 103.03(1)°, β = 107.38(1)°, γ = 104.62(1)°, V = 1314.9(3) $Å^3$, $\rho_{calcd.}$ = 1.574 $g \cdot cm^{-3}$, $F(000)$ = 616 e, μ = 44.29 cm^{-1}, empirical absorption correction via φ scan data (0.935 ≤ C ≤ 0.997), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223 K, ω/2θ scans, 5625 reflections collected (−h, ±k, ±l), [(sinθ)/λ] = 0.62 $Å^{-1}$, 5301 independent and 4548 observed reflections [$I \geq 2\sigma(I)$], 302 refined parameters, R = 0.024, wR^2 = 0.051, max. residual electron density 0.57 (−0.59) $e \cdot Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.[21]

6b: ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.97 (1 H, s, 1-H), 7.28 (5 H, m, Ph), 6.66 (1 H, dynamically broadened, 1′-H), 5.74 (1 H, q, ^3J = 7.1 Hz, 4-H), 3.18 [4 H, dynamically broadened, $N(CH_2CH_2CH_3)_2$], 1.94 (3 H, d, ^3J = 7.1 Hz, 5-H_3), 1.47 [4 H, dynamically broadened, $N(CH_2CH_2CH_3)_2$], 0.79 [6 H, dynamically broadened, $N(CH_2CH_2CH_3)_2$]. − IR (diffuse reflection), $\tilde{\nu}$ (%): 2957 cm^{-1} (33), 2873 (19), 2701 (8), 1589 (100), 1421 (45), 1245 (42). − MS (70 eV), *m/z* (%): 271 (42) [M^+], 256 (15), 242 (15), 228 (24), 214 (100), 200 (45), 170 (22), 158 (29), 141 (44), 128 (75).



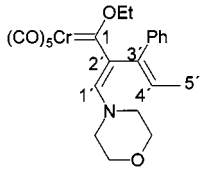
Pentacarbonyl[1-ethoxy-1-(3-cyclohex-1-enyl-1-*N*,*N*-dipropylamino-1,3-pentadien-2-yl)methylene]tungsten(0) (3k): Pentacar-

bonyl(1-ethoxy-3-cyclohexen-1-yl-2-propyne-1-ylidene)tungsten(0) (**1b**) (486 mg, 1.00 mmol) and *N*,*N*-dipropyl-*N*-propen-1-ylamine (**2g**) (141 mg, 1.00 mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give an orange oil of compound **3k** after separation by column chromatography on alumina (activity 3) (539 mg, 86%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.29 (1 H, s, 1′-H), 5.56 (1 H, m, 2′′-H), 5.12 (1 H, q, ^3J = 7.1 Hz, 4′-H), 4.58 (2 H, ^3J = 6.9 Hz, OCH_2), 3.7−3.1 [4 H, dynamically broadened, $N(CH_2)_2$], 2.11 and 1.99 (2:2 H, dynamically broadened each, 3′′-H_2 and 6′′-H_2), 1.91 (3 H, d, ^3J = 7.1 Hz, 5-H_3), 1.9−1.5 [8 H, dynamically broadened, $N(CH_2CH_2)_2$, 4′′-H_2 and 5′′-H_2], 1.33 (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3), 1.0−0.7 [6 H, dynamically broadened, $N(CH_2CH_2CH_3)_2$]. − ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 273.3 (C_q, C1), 202.5 and 199.6 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 168.5 (CH, C1′); 139.1, 136.2, and 135.5 (C_q each, C2′, C3′, and C1′′), 127.2 and 124.3 (CH each, C4′ and C2′′), 75.3 (OCH_2), 59.2 and 50.7 [dynamically broadened, $N(CH_2)_2$]; 28.1, 25.6, 23.9, 22.3, and 21.3 [CH_2 each, C3′′, C4′′, C5′′, C6′′, and $N(CH_2CH_2)_2$], 15.6 and 15.3 (OCH_2CH_3 and C5′), 10.7 [$N(CH_2CH_2CH_3)_2$]. − IR (hexane), ṽ (%): 2058.1 cm^{-1} (7), 1958.9 (4), 1921.0 (100) (C≡O); 1584.0 (6), period − MS (70 eV), ^{184}W, *m*/*z* (%): 627 (21) [M^+], 599 (21) [M^+ − CO], 571 (22) [M^+ − 2 CO], 543 (19) [M^+ − 3 CO], 515 (19) [M^+ − 4 CO], 487 (89) [M^+ − 5 CO], 485 (100), 454 (58), 422 (39), 379 (24), 353 (29), 325 (31), 274 (59), 69 (23). − $C_{25}H_{23}NO_6W$ (627.4): calcd. C 47.86, H 5.30, N 2.23; found C 47.72, H 4.99, N 2.41.

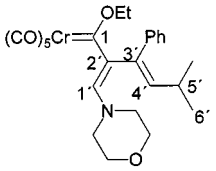


Pentacarbonyl[1-ethoxy-1-(1-morpholino-3-phenyl-1,3-pentadien-2-yl)methylene]chromium(0) (3l): Pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)chromium(0) (**1c**) (350 mg, 1.00 mmol) and *N*-(propen-1-yl)morpholine (**2a**) (127 mg, 1.00 mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give a yellow precipitate of compound **3l**, which was collected by centrifuge after 30 min (454 mg, 95%, m.p. 88°C (dec.), R_f = 0.6 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.37 (1 H, s, 1-H), 7.30 and 7.18 (2:3 H, m each, Ph), 5.46 (1 H, q, ^3J = 7.3 Hz, 4′-H), 4.57 (2 H, q, ^3J = 6.9 Hz, OCH_2CH_3), 3.68 [8 H, m, dynamically broadened, $O(CH_2CH_2)_2N$], 1.89 (3 H, d, ^3J = 7.3 Hz, 5′-H_3), 1.01 (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 297.9 (C_q, C1), 223.1 and 218.9 (C_q each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 165.0 (CH, C1′); 139.9, 137.7, and 135.9 (C_q each, C2′, C3′, and *i*-C Ph), 128.5, 127.9, 126.6, and 125.8 (CH each, C4′, *o*-, *m*-, and *p*-C Ph), 73.6 (OCH_2CH_3), 66.9 [$O(CH_2CH_2)_2N$], 52.6 [dynamically broadened, $N(CH_2)_2$], 15.2 and 14.9 (OCH_2CH_3 and C5′). − IR (hexane), ṽ (%): 2048.0 cm^{-1} (15), 1961.7 (6), 1925.2 (100) (C≡O); 1585.7 (12). − MS (70 eV), *m*/*z* (%): 421 (12) [M^+ − 2 CO], 393 (6) [M^+ − 3 CO], 365 (7) [M^+ − 4 CO], 337 (34) [M^+ − 5 CO], 281 (52), 251 (51), 195 (24), 180 (11), 128 (12), 115 (18), 80 (19), 52 (100). − $C_{23}H_{23}NO_7Cr$ (477.4): calcd. C 57.86, H 4.86, N 2.93; found C 57.88, H 4.93, N 3.05.

Pentacarbonyl[1-ethoxy-1-(5-methyl-1-morpholino-3-phenyl-1,3-hexadien-2-yl)methylene]chromium(0) (3m): Pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)chromium(0) (**1c**) (350 mg, 1.00 mmol) and *N*-[1-(3-methylbut-1-enyl)]morpholine (**2b**) (155 mg,

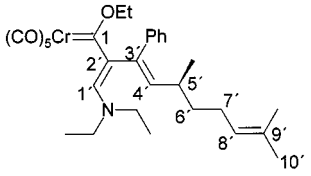


1.00 mmol) were treated as described above at 20°C in 4 mL of *n*-pentane to give a yellow precipitate of compound **3m**, which was collected after 30 min by centrifuge (476 mg, 94%, m.p. 105°C, R_f = 0.4 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 8.36 (1 H, s, 1′H), 7.30, 7.20, and 7.13 (2:1:2 H, m each, Ph), 5.13 (1 H, d, ^3J = 10.5 Hz, 4′-H), 4.60 (2 H, q, ^3J = 7.0 Hz, OCH_2CH_3), 3.71 [8 H, s, dynamically broadened, $O(CH_2CH_2)_2N$], 2.87 (1 H, m, 5′-H), 1.16 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3), 1.03 (6 H, d, ^3J = 6.7 Hz, 6′-H_3 and 5′-CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ = 298.0 (C_q, C1), 223.1 and 218.9 [C_q each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 164.5 (CH, C1′), 140.4 (C_q), 139.4 (CH, C4′), 136.1 and 134.0 (C_q each), 128.2, 128.0, and 126.7 (CH each, *o*-, *m*-, and *p*-C Ph), 73.7 (OCH_2CH_3), 66.9 [$O(CH_2CH_2)_2N$], 52.6 [dynamically broadened, $N(CH_2)_2$], 27.7 (CH, C5′), 23.0 (CH_3, C6′ and 5′-CH_3), 15.1 (OCH_2CH_3). − IR (hexane), ṽ (%): 2048.2 cm^{-1} (16), 1961.9 (7), 1925.5 (100) (C≡O); 1587.7 (10), period − MS (70 eV), *m*/*z* (%): 505 (1) [M^+], 449 (9) [M^+ − 2 CO], 421 (6) [M^+ − 3 CO], 393 (9) [M^+ − 4 CO], 365 (45) [M^+ − 5 CO], 335 (48), 321 (29), 309 (14), 263 (13), 248 (17), 236 (15), 221 (16), 155 (24), 52 (100). − $C_{25}H_{27}NO_7Cr$ (505.5): calcd. C 59.40, H 5.38, N 2.77; found C 59.38, H 5.51, N 2.90.

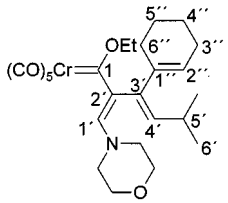


Pentacarbonyl{1-ethoxy-1-[1-*N*,*N*-diethylamino-(5*S*),9-dimethyl-3-phenyl-1,3,8-decatrien-2-yl]methylene}chromium(0) (3n): Pentacarbonyl(1-ethoxy-3-phenyl-2-propyne-1-ylidene)chromium(0) (**1c**) (350 mg, 1.00 mmol) and *N*,*N*-diethyl-*N*-{1-[(3*S*),7-dimethylocta-1,6-dienyl]}amine (**2e**) (209 mg, 1.00 mmol) were treated as described above in 4 mL of *n*-pentane to give an orange oil of compound **3n** after separation by column chromatography on alumina (activity 3) (487 mg, 87%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 9:1). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 8.38 (1 H, s, 1′-H), 7.27 and 7.16 (2:3 H, m each, Ph), 5.17 (1 H, d, ^3J = 10.4 Hz, 4′-H), 5.08 (1 H, m, 8′-H), 4.69 (2 H, m, OCH_2), 3.51 [4 H, m, dynamically broadened, assym., $N(CH_2)_2$], 2,79 (1 H, m, 5′-H), 2.00 (2 H, m, 7′-H_2), 1.66 and 1.56 (3:3 H, 10′-H_3 and 9′-CH_3), 1.40 (2 H, m, 6′-H_2), 1.24 (3 H, OCH_2CH_3), 1.16 [6 H, dynamically broadened, $N(CH_2CH_3)_2$], 1.02 (3 H, d, ^3J = 6.4 Hz, 5′-CH_3). − ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 291.9 (C_q, C1), 223.4 and 219.1 [C_q each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 165.7 (CH, C1′), 140.2 (C_q, *i*-C Ph), 138.8 (CH, dynamically broadened, C8′); 136.8, 134.6, and 131.5 (C_q each, C2′, C3′, and C9′); 128.6, 127.8, 126.4, and 124.4 (CH each, 2:2:1:1, *o*-, *m*-, *p*-C Ph and C4′), 79.3 (OCH_2), 51.6 and 43.3 [dynamically broadened each, $N(CH_2)_2$], 37.6 (CH_2, C7′), 32.4 (CH, C5′), 25.6 (CH_2 and CH_3, C6′ and C10′), 20.3, 17.5, 15.4, and 14.2 [CH_3 each, 9′CH_3, 5′-CH_3, OCH_2CH_3, and $N(CH_2CH_3)_2$]. − IR (hexane), ṽ (%): 2047.3 cm^{-1} (13), 1959.1 (6), 1922.6 (100) (C≡O); 1586.8 (9). − MS (70 eV), *m*/*z* (%): 559 (2)[M^+], 513 (4) [M^+ − 3 CO], 485 (32), [M^+ − 4 CO], 453 (41), [M^+ − 5 CO], 390 (30), 358 (16), 275 (12), 233 (15), 206 (11), 97

(27), 50 (100). − $C_{30}H_{37}NO_6Cr$ (559.6): calcd. C 64.39, H 6.66, N 2.50; found C 63.60, H 6.10, N 2.26.

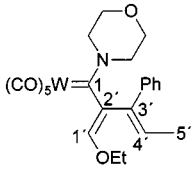


Pentacarbonyl[1-ethoxy-1-(3-cyclohex-1-enyl-5-methyl-1-morpholino-1,3-hexadien-2-yl)methylene]chromium(0) (3o): Pentacarbonyl-(1-ethoxy-3-cyclohexen-1-yl-2-propyne-1-ylidene)chromium(0) (**1d**) (354 mg, 1.00 mmol) and *N*-[1-(3-methylbut-1-enyl)]morpholine (**2b**) (155 mg, 1.00 mmol) were treated as described above at 20°C in 4 mL to give a yellow precipitate of compound **3o**, which was collected after 1 h by centrifuge (448 mg, 88%, m.p. 81°C, R_f = 0.5 on alumina, *n*-pentane/diethyl ether, 9:1). Single crystals for a crystal structure analysis were obtained by recrystallization from diethyl ether/*n*-pentane, 1:1, at −40°C. − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 8.09 (1 H, s, 1′-H), 5.40 (1 H, m, 2′′-H), 4.69 (1 H, d, ^3J = 10.1 Hz, 4′-H), 4.63 (2 H, q, dynamically broadened, ^3J = 6.9 Hz, OCH_2CH_3), 3.62 [8 H, s, dynamically broadened, $O(CH_2CH_2)_2N$], 2.72 (1 H, m, 5′-H), 1.99 and 1.85 (2:2 H, dynamically broadened each, 3′′-H_2 and 6′′-H_2), 1.48 (4 H, dynamically broadened, 4′′-H_2 and 5′′-H_2), 1.29 (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3), 0.83 (6 H, d, dynamically broadened, ^3J = 10.1 Hz, 6′-H_3 and 5′-CH_3). − ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 297.2 (C_q, C1), 223.2 and 219.0 [C_q each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 164.1 (CH, dynamically broadened, C1′), 138.2 (CH, dynamically broadened, C4′); 136.7, 136.2, and 135.7 (C_q each, C2′, C3′, and C1′′), 126.4 (CH, dynamically broadened, C2′′), 73.6 (dynamically broadened, OCH_2CH_3), 67.0 [$O(CH_2CH_2)_2N$], 52.5 [$O(CH_2CH_2)_2N$], 28.2 and 25.6 (CH_2 each, dynamically broadened, C3′′ and C6′′), 28.0 (CH, C5′), 23.2 (CH_3, C6′and 5-CH_3), 23.1 and 22.2 (CH_2 each, C4′′ and C5′′), 15.4 (OCH_2CH_3). − IR (hexane), $\tilde{\nu}$ (%): 2048.2 cm^{-1} (13), 1960.7 (4), 1924.9 (100) (C≡O); 1587.9 (10). − MS (70 eV) *m/z* (%): 509 (3) [M^+], 481 (5), [M^+ − CO], 453 (12), [M^+ − 2 CO], 425 (11), [M^+ − 3 CO], 397 (21), [M^+ − 4 CO], 369 (100), [M^+ − 5 CO], 333 (35), 321 (37), 288 (39), 260 (46), 173 (25), 131 (26). − $C_{25}H_{31}NO_7Cr$ (509.5): calcd. C 58.93, H 6.13, N 2.75; found C 58.82, H 6.47, N 2.50.

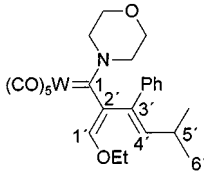


Crystal structure analysis of compound **3n**: Formula $C_{25}H_{31}NO_7Cr$, M = 509.51, orange crystals, 0.40 × 0.40 × 0.30 mm, a = 14.877(2) Å, b = 17.354(1) Å, c = 10.677(3) Å, β = 107.87(2)°, V = 2623.5(10) Å^3, $\rho_{calcd.}$ = 1.290 g·cm^{-3}, F(000) = 1072 e, μ = 4.78 cm^{-1}, empirical absorption correction via φ scan data (0.965 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223 K, ω/2θ scans, 5605 reflections collected (±h, +k, −l), [(sinθ)/λ] = 0.62 Å^{-1}, 5310 independent and 3576 observed reflections [$I \geq 2\sigma(I)$], 328 refined parameters, R = 0.051, wR^2 = 0.136, max. residual electron density 0.52 (−0.68) e·Å^{-3}, positional disorder at C16 and C17 (occupancy 50:50%), hydrogen atoms calculated and refined as riding atoms.[21]

Pentacarbonyl[1-morpholino-1-(1-ethoxy-3-phenyl-1,3-pentadien-2-yl)methylene]tungsten(0) (7a): A solution of pentacarbonyl[1-ethoxy-1-(1-morpholino-3-phenyl-1,3-pentadien-2-yl)methylene]tungsten(0) (**3a**) (122 mg, 0.2 mmol) in 1 mL of C_6D_6 was stirred for 14 h at 75°C in the absence as well as in the presence of 2-methyl-1-butene-3-yne (**4c**) (18 mg, 0.3 mmol). NMR spectroscopic analyses of the solutions indicated nearly quantitative transformation of **3a** into compound **7a**.[20] − ^{1}H NMR (360 MHz, C_6D_6, 303 K): δ = 7.36, 7.22, and 7.12 (2:2:1 H, m each, *o*-, *m*- and *p*-H Ph), 5.28 (1 H, s, 1′-H), 5.17 (1 H, q, ^3J = 7.0 Hz, 4′-H); 3.97, 3.39, 3.21, and 2.97 [2:2:2:2 H, m each, $O(CH_2CH_2)_2N$], 3.14 (2 H, m, OCH_2CH_3), 1.67 (3 H, d, ^3J = 7.0 Hz, 5′-H_3), 0.61 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). − ^{13}C NMR (90 MHz, C_6D_6, 303 K): δ = 252.9 (C_q, C1), 203.3 and 199.3 [C_q each 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 140.1 (C_q), 137.7 (CH, C1′), 135.3 and 131.7 (C_q each); 129.4, 128.7, 128.0, 127.4, and 126.7 (CH each, Ph and C4′); 68.5, 67.7, 67.5, 63.0, and 53.4 [CH_2 each, $O(CH_2CH_2)_2N$ and OCH_2CH_3], 15.0 and 14.7 (CH_3 each, OCH_2CH_3 and C5′).

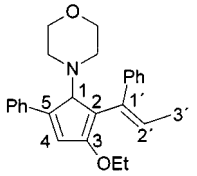


Pentacarbonyl[1-morpholino-1-(1-ethoxy-5-methyl-3-phenyl-1,3-hexadien-2-yl)methylene]tungsten(0) (7b): A solution of pentacarbonyl[1-ethoxy-1-(5-methyl-1-morpholino-3-phenyl-1,3-hexadien-2-yl)methylene]tungsten(0) (**3b**) (127 mg, 0.2 mmol) in 1 mL of C_6H_6 was stirred for 14 h at 75°C in the presence of 2-methyl-1-butene-3-yne (**4c**) (18 mg, 0.3 mmol). After removal of the solvent and the volatile alkyne, the residue (135 mg) was dissolved in $CDCl_3$ and measured by NMR spectroscopy indicating nearly quantitative formation of compound **7b**. − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 7.31 and 7.24 (2:3 H, m each, *o*-, *m*-, and *p*-H Ph), 5.64 (1 H, s, 1′-H), 4.90 (1 H, d, ^3J = 10.0 Hz, 4′-H); 4.49, 3.98, 3.90, and 3.68 [2:2:2:2 H, m each,$O(CH_2CH_2)_2N$], 3.42 (2 H, m, OCH_2CH_3), 2.33 (1 H, m, 5′-H), 0.92 and 0.88 (3:3 H, d each, ^3J = 6.5 and 7.4 H, 6′-H_3 and 5′-CH_3), 0.77 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). − ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 255.0 (C_q, C1), 203.4 and 198.8 [C_q each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 139.8 and 138.2 (CH each, C1′ and C4′); 131.5, 131.2, and 129.4 (C_q each, C2′ and C3′); 128.7, 127.6, and 126.4 (CH each, Ph); 68.6, 67.9, 67.8, 62.7, and 53.2 [CH_2 each, $O(CH_2CH_2)_2N$ and OCH_2CH_3], 27.8 (CH, C5′), 22.9 and 22.6 (CH_3 each, C6′ and 5′-CH_3), 14.5 (OCH_2CH_3).

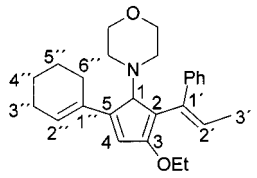


***N*-[3-Ethoxy-5-phenyl-2-(1-phenylpropenyl)cyclopenta-2,4-dienyl]-morpholine (5a):** To a solution of compound **3a** (609 mg, 1.00 mmol) and $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) in 4 mL of THF/EtOH (5:1) was added 1.5 equiv. of phenylacetylene (**4a**) (153 mg, 1.50 mmol). The reaction mixture was stirred for 36 h at 20°C. The solvent then removed under reduced pressure (20 mmbar, 20°C) and the residue extracted twice with 2 mL of *n*-pentane/diethyl ether (20:1) to separate the undissolved tungsten hexacarbonyl and small amounts of the oligomerized product. Compound **5a** was

isolated after double flash column chromatography on alumina (activity 3) and removal of the eluant (n-pentane/diethyl ether, 20:1) at 20°C as a yellow oil (268 mg, 69%, R_f = 0.3 on alumina, *n*-pentane/diethyl ether, 20:1). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 7.50 and 7.28 (2:8 H, m each, 1′- and 5-Ph), 6.62 (1 H, s, 4-H), 6.00 (1 H, q, ^3J = 7.1 Hz, 2′-H), 4.33 (1 H, s, 1-H), 3.95 (2 H, m, OCH_2CH_3), 3.46 [4 H, m, $O(CH_2CH_2)_2N$], 2.52 [4 H, m, $O(CH_2CH_2)_2N$], 1.79 (3 H, d, ^3J = 7.1 Hz, 3′-H_3), 1.18 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). ^{1}H NMR (360 MHz, C_6D_6, 303 K): δ = 7.46, 7.37, and 7.17 (2:2:6 H, m each, 5-Ph and 1′-Ph), 6.53 (1 H, s, 4-H), 6,14 (1 H, q, ^3J = 7.2 Hz, 2′-H), 4.38 (1 H, s, 1-H), 3.66 (2 H, m, OCH_2CH_3), 3.42 [4 H, m, $O(CH_2CH_2)_2N$], 2.54 [4 H, m, $O(CH_2CH_2)_2N$], 1.79 (3 H, d, ^3J = 7.2 Hz, 3′-H_3), 0.99 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). − ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 154.5 C_q, C3, 146.8 (C_q, *i*-C 5-Ph), 140.7 (C_q, C1′), 136.2 and 135.6 (C_q each, C5 and *i*-C 1′-Ph); 129.8, 128.0, 127.5, 127.0, 126.5, 126.1, 125.1, and 123.2 (CH each, 5-Ph, 1′-Ph, C4 and C2′), 122.3 (C_q, C2), 70.2 (CH, C1), 67.8 [$O(CH_2CH_2)_2N$], 65.4 (OCH_2CH_3), 48.7 [$O(CH_2CH_2)_2N$], 15.3 and 15.2 (CH_3 each, C3′ and OCH_2CH_3). − ^{13}C NMR (360 MHz, C_6D_6, 303 K): δ = 155.1 (C_q, C3), 147.6 (C_q, *i*-C 5-Ph), 141.5 (C_q, C1′), 137.0 and 136.2 (C_q each, C5 and *i*-C 1′-Ph); 130.3, 128.4, 127.9, 127.4, 127.1, 126.5, 125.3, and 123.5 (CH each, 5-Ph, 1′-Ph, C4 and C2′), 122.5 (C_q, C2), 70.7 (CH, C1), 67.8 [$O(CH_2CH_2)_2N$], 65.3 (OCH_2CH_3), 49.4 [$O(CH_2CH_2)_2N$], 15.4 and 15.3 (CH_3 each, OCH_2CH_3 and C3′). − IR (diffuse reflection), ṽ (%): 2975 cm^{-1} (35), 2850 (45), 1622 (38), 1597 (24), 1443 (36), 1337 (45), 1114 (100), 701 (56). MS (70 eV), *m*/*z* (%): 387 (20) [M^+], 358 (35), 302 (100), 273 (16), 228 (10), 215 (14), 131 (13), 115 (15). − HRMS: Calcd for $C_{26}H_{29}NO_2$ (387.21982); found: 387.22080 (+2.5 ppm, +1.0 mmu).

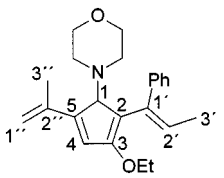


***N*-[5-(Cyclohex-1-enyl)-3-ethoxy-2-(1-phenylpropenyl)cyclopenta-2,4-dienyl]morpholine (5b):** Compound **3a** (609 mg, 1.00 mmol) and $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of 1-ethynylcyclohexene (**4b**) (159 mg, 1.50 mmol) were treated for 40 h at 20°C as described above to yield compound **5b** as a yellow oil after double flash column chromatography on alumina (activity 3) (244 mg, 62%, R_f = 0.5 on alumina, *n*-pentane/diethyl ether, 20:1). − ^{1}H NMR (300 MHz, C_6D_6, 303 K): δ = 7.35 (2 H, m, *o*-H Ph), 7.21 (2 H, m, *m*-H Ph), 7.09 (1 H, m, *p*-H Ph), 6.19 (1 H, m, 2′′-H), 6.17 (1 H, s, 4-H), 6.08 (1 H, q, ^3J = 7.1 Hz, 2′-H), 4.16 (1 H, s, 1-H), 3.70 (2 H, m, OCH_2CH_3), 3.54 [4 H, m, $O(CH_2CH_2)_2N$], 2.59 [4 H, m, $N(CH_2)_2$], 2.22 and 2.11 (1:3 H, m each, 3′′-H_2 and 6′′-H_2), 1.78 (3 H, d, ^3J = 7.1 Hz, 3′-H_3), 1.63 and 1.53 (2:2 H, m each, 4′′-H_2 and 5′′-H_2), 1.00 (3 H, t, ^3J = 7.0 Hz). − ^{13}C NMR (75 MHz, C_6D_6, 303 K): δ = 155.4 (C_q, C3), 149.1 (C_q, C1′′), 141.6 (C_q, C1′), 137.2 (C_q, *i*-C Ph), 132.0 (C_q, C5), 130.4 (CH, *o*-C Ph), 127.9 (CH, *m*-C Ph), 127.1 (CH, C2′′), 126.4 (CH, *p*-C Ph), 124.9 (CH, C2′), 121.7 (C_q, C2), 120.6 (CH, C4), 70.3 (CH, C1), 68.2 [$O(CH_2CH_2)_2N$], 65.2 (OCH_2CH_3), 49.4 [$N(CH_2)_2$], 26.4 and 26.1 (CH_2 each, C3′′ and C6′′), 23.3 and 22.7 (CH_2 each, C4′′ and C5′′), 15.4 (CH_3, C3′and OCH_2CH_3). − IR (diffuse reflection), ṽ (%): 2930 cm^{-1} (73), 2850 (68), 1610 (45), 1565 (22), 1444 (50), 1332 (63), 1115 (100), 703 (58). − MS (70 eV), *m*/*z* (%): 391 (13) [M^+], 362 (23), 306 (100), 277 (13). − HRMS: Calcd for $C_{26}H_{33}NO_2$ (391.25113); found: 391.25067 (−1.2 ppm, − 0.5 mmu).



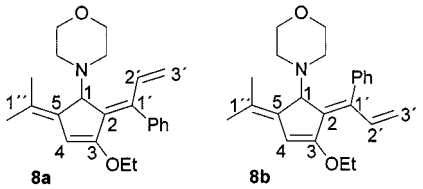
***N*-[3-Ethoxy-5-isopropenyl-2-(1-phenylpropenyl)cyclopenta-2,4-dienyl]morpholine (5c) and *N*-{1-[3-ethoxy-5-isopropylidene-2-(1-phenyl-1-prop-2-enylidene)]cyclopent-3-enyl}morpholine (8a and 8b):** Compound **3a** (609 mg, 1.00 mmol) and $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of 2-methyl-1-buten-3-yne (**4c**) (99 mg, 1.50 mmol) were treated for 32 h at 20°C as described above to yield compound **5c** as an orange oil after double flash column chromatography on alumina (activity 3) and removal of the eluant (n-pentane/diethyl ether, 20:1) at 20°C (238 mg, 68%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 20:1). Compound **5c** could be also obtained (though in ca. 10% only) by heating of a mixture of the chromium compound **3l** (505 mg, 1.00 mmol) and 2-methyl-1-buten-3-yne (**4c**) (99 mg, 1.50 mmol) in 4 mL of THF to 60°C for 12 h. Using the same workup conditions followed by column chromatography on alumina (activity 3), **5c** was obtained as mixture together with compounds **8a**,**b** (ca. 25%). **8a**,**b** could be isolated from this sample by a second flash chromatography on alumina (activity 3) after decomposition of **5c** within 4 d at 20°C in the sunlight (74 mg, 21%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 20:1). By a combination of homo-decoupling, NOE DIFF and long-range ^{1}H- and ^{13}C decoupling NMR experiments, it was possible to assign the NMR data of **8a** and **8b** in the area close to the diastereotopic centers.

5c: ^{1}H NMR (360 MHz, C_6D_6, 303 K): δ = 7.30 (2 H, m, *o*-H Ph), 7.18 (2 H, m, *m*-H Ph), 7.09 (1 H, m, *p*-H Ph), 6.23 (1 H, s, 4-H), 6.04 (1 H, q, ^3J = 7.2 Hz, 2′-H), 5.55 and 5.05 (1:1 H, m each, 1′′-H_2), 4.17 (1 H, s, 1-H), 3.63 (2 H, m, OCH_2CH_3), 3.54 [4 H, $O(CH_2CH_2)_2N$], 2.64 and 2.53 [2:2 H, m each, $N(CH_2)_2$], 1.89 (3 H, s, 3′′-H_3), 1.77 (3 H, d, ^3J = 7.2 Hz, 3′-H_3), .097 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). − ^{13}C NMR (90 MHz, C_6D_6, 303 K): δ = 155.1 (C_q, C3), 147.9 (C_q, C2′′), 141.2 (C_q, C1′), 137.5 and 137.0 (C_q each, C5 and *i*-C Ph), 130.3 (CH, *o*-C Ph), 128.0 (CH, *m*-C Ph), 126.6 (CH, *p*-C Ph), 125.6 (CH, C4), 123.9(CH, C2′), 123.4 (C_q, C2), 115,1 (CH_2, C1′′), 70.5 (CH, C1), 68.1 [$O(CH_2CH_2)_2N$], 65.2 (OCH_2CH_3), 49.4 [$N(CH_2)_2$], 21.3 (CH_3, C3′′), 15.4 and 15.3 (CH_3 each, C3′and OCH_2CH_3). − IR (diffuse reflection), ṽ (%): 2924 cm^{-1} (67), 2854 (68), 1621 (11), 1598 (30), 1443 (20), 1312 (34), 1116 (100), 703 (28), period − MS (70 eV), *m*/*z* (%):351 (13) [M^+], 322 (14), 266 (100), 237 (19), 115 (12), 91 (14). − $C_{23}H_{29}NO_2$ (351): calcd. C 78.63, H 8.26, N 3.99; found C 78.98, H 7.91, N 3.88.

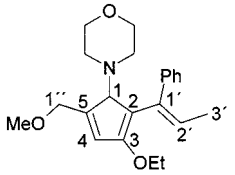


8a, **8b**: ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 7.84 (1 H, dd, ^3J = 17.1 Hz and 10.7 Hz, 2′-H of **8b**); 7.27, 7.17, and 7.02 (2:6:3 H, m:m:m and dd, ^3J = 17.1 Hz, 10.5 Hz, 1′-Ph of **8a**,**b** and 2′-H of **8a**), 5.77 (1 H, s, 4-H of **8b**), 5.60 (1 H, s, 4-H of **8a**), 5.08 (1 H, dd, ^2J = 1.7 Hz, ^3J = 10.5 Hz, 3′-H of **8a**), 5.01 (1 H, dd, ^2J =

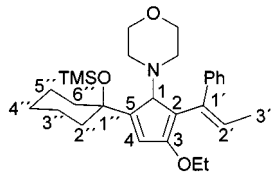
1.9 Hz, ^3J = 10.7 Hz, 3′-H of **8b**), 4.65 (1 H, dd, ^2J = 1.7 Hz, ^3J = 17.1 Hz, 3′-H of **8a**), 4.60 (1 H, dd, ^2J = 1.9 Hz, ^3J = 17.1 Hz, 3′-H of **8b**), 4.42 (1 H, s, 1-H of **8a**), 3.93 (2 H, q, ^3J = 7.0 Hz, OCH_2CH$_3$ of **8b**), 3.83 (1 H, s, 1-H of **8a**), 3.58 [4 H, m, O(CH_2CH$_2$)$_2$N of **8a**], 3.41 (2 H, m, diastereotopic OCH_2CH$_3$ of **8a**, 3.34 [4 H, m, O(CH_2CH$_2$)$_2$N of **8b**], 2.57 [4 H, m, N(CH$_2$)$_2$ of **8a**), 2.24 and 1.94 [2:2 H, m each, N(CH$_2$)$_2$ of **8b**], 1.80 and 1.74, [3:3 H, s each, 1′′-(CH$_3$)$_2$ of **8a**], 1.68 and 1.58 [3:3 H, s each, 1′′-(CH$_3$)$_2$ of **8b**], 1.39 (3 H, t, ^3J = 7.0 Hz, OCH$_2$CH_3 of **8b**), 0.63 (3 H, t, ^3J = 7.0 Hz, OCH$_2$CH_3 of **8a**). − ^{13}C NMR (90 MHz, CDCl$_3$, 303 K): δ = 161.6 (C$_q$, C3 of **8b**), 160.8 (C$_q$ each, C3 of **8a**), 139.7 and 139.3 (C$_q$ each, *i*-C Ph of **8a**,**b**), 138.0 (CH, C2′of **8a**), 136.3 (CH, C2′ of **8b**), 136.6 and 136.1 (C$_q$ each, C2 of **8a**,**b**), 135.9 and 134.2 (C$_q$ each, C1′ of **8a**,**b**), 133.0 (C$_q$, C5 of **8a**), 132.5 (C$_q$, C5 of **8b**); 130.6, 130.0, 127.6, 127.4, 126.4 and 126.0 (CH each, Ph of **8a**,**b**), 121.0 (C$_q$, C1′′ of **8a**), 120.9 (C$_q$, C1′′ of **8b**), 117.1 (CH$_2$, C3′ of **8a**), 117.0 (CH$_2$, C3′ of **8b**), 109.4 (CH, C4 of **8b**) 108.5 (CH, C4 of **8a**), 67.9 [O(*C*H$_2$CH$_2$)$_2$N of **8a**], 67.7 [O(*C*H$_2$CH$_2$)$_2$N of **8b**], 65.33 and 65.28 (CH$_2$ and CH, O*C*H$_2$CH$_3$ and C1 of **8b**), 64.3 and 64.2 (CH$_2$ and CH, O*C*H$_2$CH$_3$ and C1of **8a**), 49.3 [N(CH$_2$)$_2$ of **8a**], 49.2 [N(CH$_2$)$_2$ of **8b**]; 22.5 (CH$_3$, 1′′-CH$_3$ of **8b**), 21.8 and 20.9 [CH$_3$ each, 1′′-(CH$_3$)$_2$ of **8a**], 20.8 [CH$_3$, 1′′-CH$_3$ of **8b**], 14.7 (OCH$_2$*C*H$_3$ of **8b**), 13.7 (OCH$_2$*C*H$_3$ of **8a**). − IR (diffuse reflection), ṽ (%): 2850 cm^{-1} (75), 1599 (41), 1563 (69), 1443 (53), 1345 (63), 1116 (100), 702 (60). − MS (70 eV), *m*/*z* (%): 351 (29) [M$^+$], 298 (12), 280 (19), 264 (100), 251 (15), 235 (39), 221 (22), 207 (26), 195 (22), 178 (31), 165 (43).



***N*-[3-Ethoxy-5-methoxymethyl-2-(1-phenylpropenyl)cyclopenta-2,4-dienyl]morpholine (5d):** Compound **3a** (609 mg, 1.00 mmol) and [(COD)RhCl]$_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of methoxyprop-2-yne (**4d**) (108 mg, 1.50 mmol) were treated for 28 h at 20°C as described above to yield compound **5d** as a pale orange oil after flash column chromatography on alumina (activity 3) and removal of the eluant (*n*-pentane/diethyl ether, 7:3) at 20°C (220 mg, 63%, R_f = 0.5 on alumina, *n*-pentane/diethyl ether, 7:3). − ^{1}H NMR (360 MHz, C$_6$D$_6$, 303 K): δ = 7.31 (2 H, m, *o*-H Ph), 7.22 (2 H, m, *m*-H Ph), 7.11 (1 H, m, *p*-H Ph), 6.31 (1 H, m, 4-H), 6.13 (1 H, q, ^3J = 7.1 Hz, 2′-H), 4.03 (2 H, m, 1′′-H$_2$), 3.87 (1 H, d, ^4J = 0.9 Hz, 1-H), 3.62 (2 H, m, OCH_2CH$_3$), 3.53 [4 H, m, O(CH_2CH$_2$)$_2$N], 3.15 (3 H, s, OCH$_3$), 2.56 and 2.42 [2:2 H, m each, N(CH$_2$)$_2$], 1.76 (3 H, d, ^3J = 7.1 Hz, 3′-H$_3$), 0.94 (3 H, t, ^3J = 7.0 Hz, OCH$_2$CH_3). − ^{13}C NMR (90 MHz, C$_6$D$_6$, 303 K): δ = 154.2 (C$_q$, C3), 147.1 (C$_q$, C5), 141.7 (C$_q$, C1′), 137.0 (C$_q$, *i*-C Ph), 130.1 (CH, *o*-C Ph), 127.6 (CH, *m*-C Ph), 126.3 (CH, *p*-C Ph), 124.5 and 124.4 (CH each, C4 and C2′), 120.7 (C$_q$, C2), 71.2 (CH$_2$, C1′′), 70.9 (CH, C1), 67.9 [O(*C*H$_2$CH$_2$)$_2$N], 65.1 (O*C*H$_2$CH$_3$), 58.1 (OCH$_3$), 49.4 [N(CH$_2$)$_2$], 15.3 (CH$_3$, C3′ and OCH$_2$*C*H$_3$). − IR (diffuse reflection), ṽ (%): 2923 cm^{-1} (49), 2854 (63), 1638 (20), 1565 (32), 1443 (30), 1115 (100), 703 (30). − MS (70 eV), *m*/*z* (%): 355 (12) [M$^+$], 326 (13), 310 (100), 282 (17), 270 (21), 165 (14), 129 (21). − C$_{22}$H$_{29}$NO$_3$ (355.5): calcd. C 74.33, H 8.22, N 3.94; found: C 74.23, H 8.67, N 3.74.

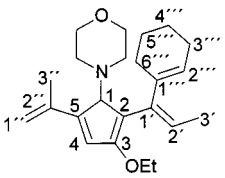


***N*-[3-Ethoxy-2-(1-phenylpropenyl)-5-(1-trimethylsiloxycyclohexyl)cyclopenta-2,4-dienyl]morpholine (5e):** Compound **3a** (609 mg, 1.00 mmol) and [(COD)RhCl]$_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of 1-ethynyl-1-trimethylsiloxycyclohexane (**4e**) (294 mg, 1.50 mmol) was treated for 38 h at 20°C as described above to yield compound **5e** as a pale orange oil after double flash column chromatography on alumina (activity 3) and removal of the eluant (*n*-pentane/diethyl ether, 20:1) at 20°C (293 mg, 61%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 20:1). − ^{1}H NMR (360 MHz, C$_6$D$_6$, 303 K): δ = 7.36 (2 H, m, *o*-H Ph), 7.22 (2 H, m, *m*-H Ph), 7.09 (1 H, m, *p*-H Ph), 6.42 (1 H, s, 4-H), 6.05 (1 H, q, ^3J = 7.1 Hz, 2′-H), 3.99 (1 H, s, 1-H), 3.72 (2 H, m, OCH_2CH$_3$), 3.55 [4 H, O(CH_2CH$_2$)$_2$ N], 2.76 and 2.51 [2:2 H, dynamically broadened each, N(CH$_2$)$_2$]; 1.98, 1.87, 1.78, 1.63, 1.52, and 1.29 [2:2:5:1:2:1 H; m,m,m,d (^3J = 7.1 Hz),m,m,m; 2′′-H$_2$, 3′′-H$_2$, 4′′-H$_2$, 5′′H$_2$, 6′′-H$_2$, and 3′-H$_3$], 1.00 (3 H, t, ^3J = 6.9 Hz, OCH$_2$CH_3), 0.21 [9 H, s, Si(CH$_3$)$_3$]. − ^{13}C NMR (90 MHz, C$_6$D$_6$, 303 K): δ = 155.6 and 154.7 (C$_q$ each, C3 and C5), 141.2 (C$_q$, C1′), 136.8 (C$_q$ each, *i*-C Ph), 130.3 (CH, *o*-C Ph), 128.0 (CH, *m*-C Ph), 126.7 (CH, *p*-C Ph), 125.8 (CH, C4), 123.8 (CH, C2′), 121.6 (C$_q$, C2), 76.3 (C$_q$, C1′′), 71.0 (CH, C1), 67.9 [O(*C*H$_2$CH$_2$)$_2$N], 65.2 (O*C*H$_2$CH$_3$), 51−49 [dynamically broadened, N(CH$_2$)$_2$], 40.0 and 36.6 (CH$_2$ each, C2′′ and C6′′); 26.3, 23.1, and 22.7 (CH$_2$ each, C3′′, C4′′, and C5′′), 15.5 and 15.4 (CH$_3$ each, C3′ and OCH$_2$*C*H$_3$), 2.8 [CH$_3$, Si(CH$_3$)$_3$]. − IR (diffuse reflection), ṽ (%): 2929 cm^{-1} (56), 2851 (43), 1629 (22), 1445 (21), 1333 (33), 1117 (68), 838 (100). − MS (70 eV), *m*/*z* (%): 481 (5) [M$^+$], 452 (4), 396 (27), 310 (39), 306 (10), 242 (7), 171 (100). − HRMS: Calcd for C$_{29}$H$_{43}$NO$_3$*S*i: 481.30121; found: 481.30231 (+2.3 ppm, +1.1 mmu). − C$_{29}$H$_{43}$NO$_3$Si (481.8): calcd. C 72.30, H 9.00, N 2.91; found C 71.75; H 8.93, N 3.05.

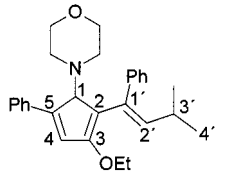


***N*-[2-(1-Cyclohex-1-enylpropenyl)-3-ethoxy-5-isopropenylcyclopenta-2,4-dienyl]morpholine (5f):** Compound **3d** (613 mg, 1.00 mmol) and [(COD)RhCl]$_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of 2-methyl-1-buten-3-yne (**4c**) (99 mg, 1.50 mmol) were treated for 28 h at 20°C as described above to give compound **5f** as a yellow oil after double flash column chromatography on alumina (activity 3) and removal of the eluant (*n*-pentane/diethyl ether, 20:1) at 20°C (210 mg, 59%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 20:1). − ^{1}H NMR (360 MHz, C$_6$D$_6$, 303 K): δ = 6.20 (1 H, s, 4-H), 5.64 (1 H, m, 2′′′-H), 5.61 (1 H, d, ^3J = 7.0 Hz, 2′′-H), 5.59 (1 H, s, 1′′-H), 5.10 (1 H, s, 1′′-H), 4.22 (1 H, s, 1-H), 3.59 [6 H, m, OCH_2CH$_3$ and O(CH_2CH$_2$)$_2$N], 2.69 [4 H, m, N(CH$_2$)$_2$], 2.14 (1 H, m, dynamically broadened, 6′′′-H), 2.10 (3 H, m, dynamically broadened. 6′′′-H and 3′′′-H$_2$), 1.91 (3 H, s, 3′′-H$_3$), 1.85 (3 H, d, ^3J = 7.0 Hz, 3′-H$_3$), 1.63 (4 H, m, 4′′′-H$_2$ and 5′′′-H$_2$), 1.07 (3 H, t, ^3J = 7.0 Hz, OCH$_2$CH_3). − ^{13}C NMR (90 MHz, C$_6$D$_6$, 303 K):

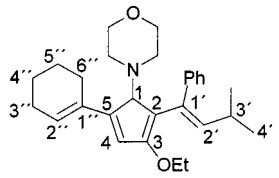
δ = 154.0 (C_q, C3), 147.8 (C_q, C2′′), 139.4 (C_q, C1′), 137.8 (C_q, C5), 137.4 (C_q, C1′′′), 125.6 (CH, C2′′′), 123.9 (CH, C4), 123.1 (CH, C2′), 122.9 (C_q, C2), 114.7 (CH_2, C1′′), 70.5 (CH, C1), 68.2 [O(*C*H_2CH$_2$)$_2$N], 65.3 (O*C*H_2CH$_3$), 49.5 [N(CH$_2$)$_2$], 29.4 (CH_2, C6′′′), 25.8 (CH_2, C3′′′), 23.6 and 22.9 (CH_2 each, C4′′′ and C5′′′), 21.3 (CH_3, C3′′), 15.5 (OCH$_2$*C*H_3), 15.2 (CH_3, C3′). − IR (diffuse reflection), ṽ (%): 2970 cm^{-1} (36), 2852 (69), 1597 (27), 1447 (25), 1342 (40), 1117 (100), 877 (21). − MS (ESI, 11 V, acetonitrile/MeOH): 356.5 [M + H$^+$]. − $C_{23}H_{33}NO_2$ (355.5): calcd. C 77.70, H 9.36, N 3.94; found C 77.96, H 9.34, N 3.65.



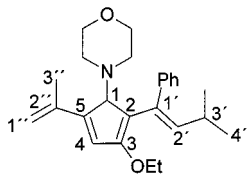
***N*-[3-Ethoxy-2-(3-methyl-1-phenylbut-1-enyl)-5-phenylcyclopenta-2,4-dienyl]morpholine (5g):** Compound **3b** (637 mg, 1.00 mmol), [(COD)RhCl]$_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of phenylacetylene (**4a**) (153 mg, 1.50 mmol) were treated for 36 h at 20°C as described above to yield compound **5g** as a yellow oil after double flash column chromatography on alumina (activity 3) and removal of the eluant (*n*-pentane/diethyl ether, 20:1) at 20°C (295 mg, 71%, R_f = 0.7, on alumina, *n*-pentane/diethyl ether, 20:1). Compound **5g** could also be obtained by heating a mixture of the chromium compound **3m** (505 mg, 1.00 mmol) and phenylacetylene (**4a**) (153 mg, 1.50 mmol) in 4 mL THF to 60°C for 12 h using the same workup conditions (141 mg, 34%). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 7.47, 7.28, and 7.21 (2:6:2 H, m each, 5-Ph and 1′-Ph), 6.56 (1 H, s, 4-H), 5.68 (1 H, d, ^3J = 10.2 Hz, 2′-H), 4.38 (1 H, s, 1-H), 3.92 and 3.82 (1:1 H, m each, diastereotopic OC*H*$_2$CH$_3$), 3.47 [4 H, m, O(C*H*$_2$CH$_2$)$_2$ N], 2.57 [4 H, m, N(CH$_2$)$_2$], 2.53 (1 H, m, 3′-H), 1.11 (3 H, d, ^3J = 6.6 Hz, 4′-H$_3$), 1.08 (3 H, t, ^3J = 7.1 Hz, OCH$_2$C*H*$_3$), 0.92 (3 H, d, ^3J = 6.6 Hz, 3′-CH$_3$). − ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 154.4 (C_q, C3), 147.4 (C_q, *i*-C Ph), 141.4 (C_q, C1′), 138.3 (CH, C2′), 136.0 (C_q, C5), 132.8 (C_q, *i*-C Ph); 129.4, 128.1, 127.4, 127.0, 126.6, and 126.1 (CH each, 2:2:2:1:2:1, 2′-, *o*-, *m*-, and *p*-C Ph), 123.7 (CH, C4), 122.2 (C_q, C2), 70.1 (CH, C1), 67.8 [O(*C*H$_2$CH$_2$)$_2$ N], 65.3 (O*C*H$_2$CH$_3$), 48.9 [N(CH$_2$)$_2$], 28.1 (CH, C3′), 23.4 and 23.3 (CH_3, C4′ and 3′-CH$_3$), 15.0 (OCH$_2$*C*H$_3$). − IR (diffuse reflection), ṽ (%): 3017 cm^{-1} (16), 2950 (100), 2852 (61), 1620 (30), 1597 (20), 1444 (27), 1343 (37), 1115 (70), 701 (46). − MS (70 eV), *m*/*z* (%): 415 (49.5) [M$^+$], 386 (73), 330 (100), 315 (19), 301 (20), 285 (19), 270 (14), 242 (15), 215 20), 145 (21), 131 (24), 115 (21), 91 (34), 56 (34). − HRMS: Calcd for $C_{28}H_{33}NO_2$ (415.25113); found: 415.25201(+2.1 ppm, +0.9 mmu).



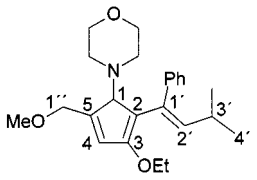
***N*-[5-(Cyclohex-1-enyl)-3-ethoxy-2-(3-methyl-1-phenylbut-1-enyl)-cyclopenta-2,4-dienyl]morpholine (5h):** Compound **3d** (613 mg, 1.00 mmol), [(COD)RhCl]$_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of 1-ethynylcyclohexene (**4b**) (159 mg, 1.50 mmol) was treated for 30 h at 20°C to yield compound **5h** as a yellow oil after double flash column chromatography on alumina (activity 3) (210 mg, 59%, R_f = 0.8 on alumina, *n*-pentane/diethyl ether, 20:1). Compound **5h** could be also obtained by heating of a mixture of the chromium compound **3m** (505 mg, 1.00 mmol) and 1-ethynylcyclohexene (**4b**) (159 mg, 1.50 mmol) in 4 mL THF to 60°C for 12 h (110 mg, 26%). − ^{1}H NMR (360 MHz, $CDCl_3$, 303 K): δ = 7.30 and 7.22 (2:3 H, m each, Ph), 6.12 (1 H, s, 4-H), 6.09 (1 H, m, 2′′-H), 5.58 (1 H, d, ^3J = 10.3 Hz, 2′-H), 4.08 (1 H, s, 1-H), 3.87 and 3.78 (1:1 H, m each, diastereotopic OC*H*$_2$CH$_3$), 3.53 [4 H, m, O(C*H*$_2$CH$_2$)$_2$N], 2.52 [5 H, m, N(CH$_2$)$_2$ and 3′-H); 2.27, 2.13, 1.67, and 1.59 (1:3:2:2 H, m each, 3′′-H$_2$, 4′′-H$_2$, 5′′-H$_2$, and 6′′-H$_2$), 1.09 (3 H, d, ^3J = 6.3 Hz, 4′-H$_3$), 1.06 (3 H, t, ^3J = 7.0 Hz, OCH$_2$C*H*$_3$), 0.90 (3 H, d, ^3J = 6.3 Hz, 3-′CH$_3$). − ^{13}C NMR (90 MHz, $CDCl_3$, 303 K): δ = 154.7 (C_q, C3), 148.9 (C_q, C1′′), 141.6 (C_q, C1′), 137.9 (CH, C2′), 133.1 (C_q, C5), 131.9 (Cq, *i*-C Ph); 129.5, 127.4, 127.0, and 126.0 (CH each, 2:2:1:1, *o*-, *m*-, *p*-C Ph and C2′′), 121.3 (C_q, C2), 120.5 (CH, C4), 69.4 (CH, C1), 68.1 [O(*C*H$_2$CH$_2$)$_2$N], 65.2 (OCH$_2$*C*H$_3$), 48.8 [N(CH$_2$)$_2$], 28.1 (CH, C3′), 26.3 and 25.8 (CH_2, C3′′ and C6′′), 23.5 and 23.3 (CH_3, C4′ and 3′-CH$_3$), 22.8 and 22.3 (CH_2, C4′′ and C5′′), 15.1 (OCH$_2$*C*H$_3$). − IR (diffuse reflection), ṽ (%): 2917 cm^{-1} (89), 2905 (94), 2862 (81), 1606 (43), 1445 (47), 1335 (60), 1116 (100), 704 (55). − MS (70 eV), *m*/*z* (%): 419 (25) [M$^+$], 390 (27), 334 (100), 319 (17), 305 (12), 289 (8), 155 (21), 129 (12), 105 (19), 91 (18). − HRMS: Calcd for $C_{28}H_{37}NO_2$: 419.28244; found: 419.28358 (+2.7 ppm, +1.1 mmu). − $C_{28}H_{37}NO_2$ (419.6): calcd. C 80.15, H 8.89, N 3.34; found C 80.02, H 9.38, N 3.42.



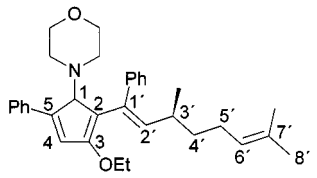
***N*-[5-(Isopropenyl)-3-ethoxy-2-(3-methyl-1-phenylbut-1-enyl)cyclopenta-2,4-dienyl]morpholine (5i):** Compound **3d** (613 mg, 1.0 mmol), [(COD)RhCl]$_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of 2-methyl-1-buten-3-yne (**4c**) (99 mg, 1.50 mmol) were treated for 30 h at 20°C as described above to yield compound **5i** as an orange oil (258 mg, 68%, R_f = 0.8 on alumina, *n*-pentane/diethyl ether, 20:1). − ^{1}H NMR (300 MHz, C_6D_6, 303 K): δ = 7.38, 7.21, and 7.11 (2:2:1 H, m each, Ph), 6.21 (1 H, s, 4-H), 5.72 (1 H, d, ^3J = 10.2 Hz, 2′-H), 5.48 (1 H, d, ^4J = 2.4 Hz, 1′′-H), 5.04 (1 H, m, 1′′-H), 4.17 (1 H, s, 1-H), 3.55 [6 H, m, OC*H*$_2$CH$_3$ and O(C*H*$_2$CH$_2$)$_2$N], 2.72 (1 H, m, 3′-H), 2.64 [4 H, m, N(CH$_2$)$_2$], 1.88 (3 H, s, 3′′-H), 1.11 (3 H, d, ^3J = 6.7 Hz, 4′-H$_3$), 0.95 (3 H, t, ^3J = 7.0 Hz, OCH$_2$C*H*$_3$), 0.92 (3 H, d, ^3J = 6.4 Hz, 3′-CH$_3$). − ^{13}C NMR (75 MHz, C_6D_6, 303 K): δ = 155.0 (C_q, C3), 148.4 (C_q, C2′′), 142.0 (C_q, C1′), 138.7 (CH, C2′), 137.9 and 133.9 (C_q each, C5 and *i*-C Ph); 129.9, 127.9, and 126.5 (CH each, Ph), 124.1 (CH, C4), 123.3 (C_q, C2), 114.9 (CH_2, C1′′), 70.4 (CH, C1), 68.1 [O(*C*H$_2$CH$_2$)$_2$N], 65.2 (O*C*H$_2$CH$_3$), 49.6 [N(CH$_2$)$_2$], 28.5 (CH, C3′), 23.5 and 23.4 (each CH$_3$, C4 and 3′-CH$_3$), 21.5 (CH_3, C3′′), 15.2 (OCH$_2$*C*H$_3$). − IR (diffuse reflection), ṽ (%): 2959 cm^{-1} (100), 2892 (60), 2847 (60), 1621 (31), 1598 (55), 1445 (39), 1339 (54), 1116 (92), 703 (54). − MS (70 eV), *m*/*z* (%): 379 (13) [M$^+$], 350 (22), 294 (100), 279 (17), 265 (16), 249 (9), 234 (7), 223 (7), 205 (7), 179 (10), 165 (12), 145 (13), 99 (16). − $C_{25}H_{33}NO_2$ (379.5): calcd. C 79.11, H 8.76, N 3.69; found C 79.13, H 8.82, N 3.71.



***N*-[3-Ethoxy-5-methoxymethyl-2-(3-methyl-1-phenylbut-1-enyl)-cyclopenta-2,4-dienyl}morpholine (5j):** Compound **3d** (613 mg, 1.00 mmol), $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of methoxyprop-2-yne (**4d**) (108 mg, 1.50 mmol) were treated for 28 h at 20°C as described above to yield compound **5j** as an orange oil (210 mg, 59%, R_f = 0.5 on alumina, *n*-pentane/diethyl ether, 7:3). − ^{1}H NMR (300 MHz, C_6D_6, 303 K): δ = 7.30 (2 H, m, *o*-H Ph), 7.22 (2 H, m, *m*-H Ph), 7.12 (1 H, m, *p*-H Ph), 6.26 (1 H, m, 4-H), 5.76 (1 H, d, ^3J = 10.0 Hz, 2′-H), 4.03 (2 H, m, 1′′-H_2), 3.85 (1 H, m, 1-H), 3.58 [6 H, m OCH_2CH_3 and $O(CH_2CH_2)_2N$], 3.11 (3 H, s, OCH_3), 2.63 and 2.46 [3:2 H, m each, 3′-H and $N(CH_2)_2$], 1.09 (3 H, d, ^3J = 6.7 Hz, 4′-H_3), 0.95 (3 H, d, ^3J = 6.7 Hz, 3′-CH_3), 0.90 (3 H, t, ^3J = 6.9 Hz). − ^{13}C NMR (MHz, C_6D_6, 303 K): δ = 154.0 (C_q, C3), 147.4 (C_q, C5), 142.3 (C_q, C1′), 137.9 (CH, C2′), 133.7 (C_q, *i*-C Ph), 129.8 (CH, *o*-C Ph), 127.7 (CH, *m*-C Ph), 126.3 (CH, *p*-C Ph), 125.0 (CH, C4), 120.8 (C_q, C2), 71.1 (CH, C1), 71.0 (CH_2, C1′′), 68.0 [$O(CH_2CH_2)_2N$], 65.1 (OCH_2CH_3), 58,0 (OCH_3), 49.5 [$N(CH_2)_2$], 28.4 (CH, C3′), 23.8 and 23.6 (CH_3, C4′ and 3′-CH_3), 15.2 (OCH_2CH_3). − IR (diffuse reflection), ṽ (%): 2959 cm^{-1} (64), 2851 (53),1634 (34), 1566 (22), 1445 (30), 1115 (100), 703 (44). − MS (70 eV), *m*/*z* (%): 383 (8), 354 (5), 338 (100), 298 (10). − HRMS: Calcd for $C_{24}H_{33}NO_3$ (383.24603); found: 383.24496 (−2.8 ppm, −1.1 mmu).

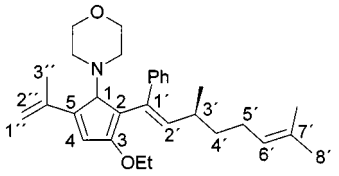


***N*-{(1*R*,*S*)-2-[(3*S*),7-Dimethyl-1-phenylocta-1,6-dien-1-yl]-3-ethoxy-5-phenylcyclopenta-2,4-dienyl}morpholine (5k):** Compound **3c** (705 mg, 1.00 mmol), $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of phenylacetylene (**4a**) (153 mg, 1.50 mmol) were treated for 36 h at 20°C as described above to yield compound **5k** (1:1 mixture of both diasteromers) as an orange oil after double flash column chromatography on alumina (activity 3) (333 mg, 69%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 20:1). − ^{1}H NMR (300 MHz, C_6D_6, 303 K, the second diasteromer in [ ]): δ = 7.38 [7.38] and 7.17 [7.17] (4:6 H, m each, 5-Ph and 1′-Ph), 6.48 [6.45] (1 H, s, 4-H), 5.88 [5.80] (1 H, d, ^3J = 10.4 Hz, 2′-H), 5.25 [5.08] (1 H, m, 6′-H), 4.37 [4.34] (1 H, s, 1-H), 3.66 [3.66] (2 H, m, OCH_2CH_3), 3.45 [3.45] [4 H, m, $O(CH_2CH_2)_2N$], 2.56 [2.56] [5 H, m, $N(CH_2)_2$ and 3′-H], 2.18 (2 H, m, 5′-H_2) [2.18 and 1.98 (1:1 H, m each, 5′-H_2)], 1.69 and1.61 [1.60 and 1.52] (3:3 H, s each, 8′-H_3 and 7′-CH_3), 1.42 (2 H, m, 4′-H_2), [1.42 and 1.25, (1:1 H, m each, 4′-H_2)] 1.17 [0.86] (3:3 H, d, ^3J = 6.6 Hz, 3′-CH_3), 0.99 [0.98] (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3). − ^{13}C NMR (75 MHz, C_6D_6, 303 K, the other diasteromer in [ ]): δ = 155.0 [154.9] (C_q, C3), 148.3 [148.3] (C_q, *i*-C 5-Ph), 142.3 [142.1] (C_q, C1′), 137.6 [137.4] (CH, C2′), 136.8 [136.7] (C_q, C5), 135.0 [134.8] (C_q, C7′), 131.1 [130.7] (C_q, *i*-C 1′-Ph); 130.1 [130.1], 128.4 [128.4], 127.8 [127.8], 127.4 [127.4], 127.2 [127.2] and 126.5 [126.5] (CH, 5-Ph and 1′-Ph), 125.5 [125.5] (CH, C6′), 124.0 [123.5] (CH, C4), 122.8 [122.6] (C_q, C2), 70.8 [70.5] (CH, C1), 67.9 [67.9] [$O(CH_2CH_2)_2N$], 65.3 [65.3] (OCH_2CH_3), 49.5 [49.5] [$N(CH_2)_2$], 38.7 [38.4] (CH_2, C5′), 33.3 [33.3] (CH, C3′), 26.8 [26.5] (CH_2, C4′), 25.8 [25.7] (CH_3, 7′-CH_3), 22.1 [21.5] (CH_3, 3′-CH_3), 17.9 [17.8] (CH_3, C8′), 15.2 [15.3] (OCH_2CH_3). − IR (diffuse reflection), ṽ (%): 2960 cm^{-1} (36), 2909 (42), 2850 (38), 1622 (26), 1446 (31), 1345 (35), 1115 (100), 701 (47). − MS (70 eV), *m*/*z* (%): 483 (100), 454 (57), 414 (17), 398 (14), 372 (34), 358 (17), 344 (14), 329 (11), 288 (10), 242 (12), 131 (24). − $C_{33}H_{41}NO_2$ (483.7): calcd. C 81.94, H 8.54, N 2.90; found C 81.90, H 8.75, N 3.05.

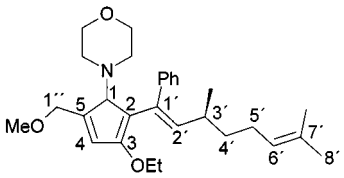


***N*-{(1*R*,*S*)-2-[(3*S*),7-Dimethyl-1-phenylocta-1,6-dien-1-yl]-3-ethoxy-5-isopropenylcyclopenta-2,4-dienyl}morpholine (5l):** Compound **3c** (705 mg, 1.00 mmol), $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of 2-methyl-1-buten-3-yne (**4c**) (99 mg, 1.50 mmol) were treated for 36 h at 20°C as described above to yield compound **5l** (1:1 mixture of both diasteromers) as orange oil (318 mg, 71%, R_f = 0.7 on alumina, *n*-pentane/diethyl ether, 20:1). − ^{1}H NMR (300 MHz, C_6D_6, 303 K, the other diasteromer in [ ]): δ = 7.40 [7.32] (2 H, m, *o*-H Ph), 7.22 [7.22] (4 H, m, *m*-H Ph), 7.12 [7.12] (1 H, m, *p*-H Ph), 6.23 [6.20] (1:1 H, s each, 4-H each), 5.76 [5.72] (1 H, d, ^3J = 10.2 Hz, 2′-H), 5.45 [5.45] (1 H, m, 1′′-H), 5.24 [5.04] (1 H, m, 6′-H), 5.03 [5.03] (1 H, m, 1′′-H), 4.15 [4.12] (1 H, s, 1-H), 3.63 [3.63] (2 H, m, OCH_2CH_3), 3.55 [3.55] [4 H, m, $O(CH_2CH_2)_2N$], 2.63 [2.63] [5 H, m, $N(CH_2)_2$ and 3′-H), 2.18 (2 H, m, 5′-H_2) [2.18 and 1.94 (1:1 H, m each, 5′-H_2)], 1.88 [1.88] (3 H, s, 3′′-H_3), 1.69 [1.58] (3 H, d, ^4J = 1.0 Hz, 7′-CH_3), 1.62 [1.49] (3 H, s, 8′-H_3), 1.45 [1.45] (4 H, m, 4′-H_2 and 5′-H_2 each), 1.16 [0.86] (3 H, d, ^3J = 6.7 Hz, 3′-CH_3), 1.02 [0.97] (3 H, OCH_2CH_3). ^{1}H NMR (600 MHz, C_6D_6, 303 K, the second diasteromer in [ ]): δ = 7.45 [7.37] (2 H, m, *o*-H Ph), 7.24 [7.21] (2 H, m, *m*-H Ph), 7.14 [7.12] (1 H, m, *p*-H Ph), 6.16 [6.13] (1 H, s, 4-H), 5.80 [5.78] (1 H, d, ^3J = 10.4 Hz, 2′-H), 5.52 [5.51] (1 H, "d", 1′′-H), 5.29 [5.09] (1 H, m, 6′-H), 5.06 [5.06] (1 H, "s", 1′′-H), 4.20 [4.16] (1 H, s, 1-H), 3.60 [3.60] [6 H, m, OCH_2CH_3 and $O(CH_2CH_2)_2N$], 2.66 [2.66] [5 H, m, $N(CH_2)_2$ and 3′-H), 2.24 (2 H, m, 5′-H_2) [2.24 and 2.00 (1:1 H, m each, 5′-H_2)], 1.92 [1.90] (3 H, "s", 3′′-H); 1.72, [1.61] (3 H, d, ^4J = 1.0 Hz, 7′-CH_3),1.65 [1.52] [3 H, s, 8′-H_3); 1.60 and 1.51 (1:1 H, m each, 4′-H_2) [1.41 (2 H, m, 4′-H_2)], 1.19 [0.97] (3 H, d, ^3J = 6.6 Hz, 3′-CH_3), 1.03 [0.97] (3 H, t, ^3J = 7.0 Hz, 2 ′ OCH_2CH_3) − ^{13}C NMR (75 MHz, C_6D_6, 303 K, the other diasteromer in [ ]): δ = 155.0 [155.0] (C_q, C3), 148.4 [148.4] (C_q, C2′′), 142.1 [141.9] (C_q, C1′), 137.9 [137.9] (C_q, dynamically broadened, C5), 137.9 [137.7] (CH, C2′), 135.0 [134.9] (C_q, C7′), 131.2 [130.7] (C_q, *i*-C Ph), 130.0 [130.0] (CH, *o*-C Ph), 127.9 [127.9] (CH, *m*-C Ph), 126.4 [126.4] (CH, *p*-C Ph), 125.5 [125.5] (CH, C6′), 124.0 [124.0] (CH, C4), 123.7 [123.7] (Cq, C2) 123.5 [123.5] (CH, C4), 115.0 [114.9] (CH_2, C1′′), 70.4 [70.2] (CH, C1), 68.0 [68.0] [$O(CH_2CH_2)_2N$), 65.2 [65.2] (OCH_2CH_3), 49.5 [49.5] [$N(CH_2)_2$], 38.7 [38.3] (CH_2, C5′), 33.2 [33.2] (CH, C3′), 26.7 [26.4] (CH_2, C4′), 25.8 [25.7] (CH_3, 7′-CH_3), 21.9 [21.4] (CH_3, C3′′), 21.2 [21.2] (CH_3, 3′-CH_3), 17.8 [17.7] (CH_3, C8′), 15.2 [15.2] (OCH_2CH_3). − ^{13}C NMR (150 MHz, C_6D_6, 303 K, the other diasteromer in [ ]): δ = 155.07 [155.01] (C_q, C3), 148.32 [148.27] (C_q, C2′′), 142.03 [141.84] (C_q, C1′), 137.90 [137.68] (CH, C2′), 137.79 [137.70] (C_q, C5), 134.98 [134.82] (C_q, C7′), 131.24 [130.73] (C_q, *i*-C Ph), 130.04 [130.00] (CH, *o*-C Ph), 127.89 [127.89] (CH, *m*-C Ph), 126.51 [126.47] (CH, *p*-C Ph), 125.45 [125.42] (CH, C6′), 124.00 [123.40] (CH, C4), 123.63 [123.45] (C_q, C2), 115.15 [115.05] (CH_2, C1′′), 70.31 [70.13] (CH, C1), 68.07 [68.04] [$O(CH_2CH_2)_2N$], 65.22 [65.21] (OCH_2CH_3), 49.49 [49.45] [$N(CH_2)_2$], 38.66 [38.28] (CH_2, C5′), 33.21 [33.21] (CH_3, C3′), 26.73 [26.40] (CH_2, C4′), 25.88 [25.77] (CH_3, 7′-CH_3), 21.93 [21.41] (CH_3, 3′-CH_3), 21.26 [21.26] (CH_3, C3′′), 17.85 [17.75] (CH_3, C8′), 15.26 [15.22] (OCH_2CH_3). − IR (diffuse reflection), ṽ (%): 2951 cm^{-1} (56), 2921

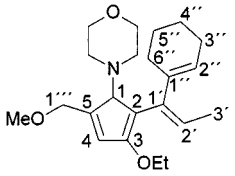
(58), 2851 (66), 1598 (32), 1448 (28), 1344 (36), 1116 (100), 703 (30). − MS (70 eV), *m/z* (%): 447 (33) [M^+], 418 (40), 362 (100), 336 (12), 319 (33), 293 (24), 279 (31), 252 (19), 239 (23), 206 (14), 179 (20), 165 (20),129 (17), 69 (63), period − MS (ESI, 20 V, acetonitrile/MeOH): 448.6 [M + H^+]. − $C_{30}H_{41}NO_2$ (447.7): calcd. C 80.49, H 9.23, N 3.13; found C 80.55, H 8.97, N 3.27.



***N*-{(1*R*,*S*)-2-[(3*S*),7-Dimethyl-1-phenylocta-1,6-dien-1-yl]-3-ethoxy-5-methoxymethylcyclopenta-2,4-dien-1-yl}morpholine (5m):** Compound **3c** (705 mg, 1.00 mmol), $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of methoxyprop-2-yne (**4d**) (108 mg, 1.50 mmol) were treated for 36 h at 20°C as described above to yield compound **5m** (1:1 mixture of both diasteromers) as an orange oil (316 mg, 70%, R_f = 0.4, on alumina, *n*-pentane/diethyl ether, 7:3). − ^{1}H NMR (300 MHz, C_6D_6, 303 K, the other diasteromer in [ ]): δ = 7.38 [7.33] (2 H, m, *o*-H Ph), 7.22 [7.22] (2 H, m, *m*-H Ph), 7.13 [7.13] (1 H, m, *p*-H Ph), 6.27 [6.26] (1 H, m, 4-H), 5.81 [5.74] (1 H, d, ^3J = 10.5 Hz, 2′-H), 5.23 [5.09] (1 H, m, 6′-H), 4.02 [4.02] (2 H, m, 2 ′ 1′′-H_2), 3.85 [3.84] (1 H, d, ^4J = 1.0 Hz, 1-H), 3.60 [3.60] [6 H, m, OCH_2CH_3 and $O(CH_2CH_2)_2N$], 3.15 [3.15] (3 H, t, ^4J = 1.8 Hz, OCH_3), 2.55 [2.55] [5 H, m, $N(CH_2)_2$ and 3′-H], 2.17 (2 H, m, 5′-H_2) [2.17 and 1.97 (1:1 H, m each, 5′-H_2)], 1.68 [1.60] (3 H, d, ^4J = 1.0 Hz, 2 ′ 7′-CH_3), 1.59 [1.52] (3 H, s, 8′-H_3), 1.45 [1.25] (4 H, m, 4′-H_2 and 5′-H_2), 1.13 [0.98] (3 H, d, ^3J = 6.7 Hz, 3′-CH_3), 0.93 [0.85] (3 H, t, ^3J = 6.9, OCH_2CH_3). − ^{13}C NMR (75 MHz, C_6D_6, 303 K, the other diasteromer in [ ]): δ = 154.0 [153.9] (C_q, C3), 147.4 [147.3] (C_q, C5), 142.4 [142.3] (C_q, C1′), 137.0 [136.7] (CH, C2′), 134.9 [134.7] (C_q, C7′), 131.0 [130.1] (C_q, *i*-C Ph), 130.1 [130.1] (CH, *o*-C Ph), 127.7 [127.7] (CH, *m*-C Ph), 126.3 [126.3] (CH, *p*-C Ph), 125.5 [125.5] (CH, C6′), 125.0 [124.6] (CH, C4), 121.1 [120.9] (C_q, C2), 71.2 [71.2] (CH_2, C1′′), 71.2 [71.0] (CH, C1), 68.0 [68.0] $[O(CH_2CH_2)_2N]$, 65.2 [65.2] (OCH_2CH_3), 58.0 [58.0] (OCH_3), 49.5 [49.5] $[N(CH_2)_2]$, 38.7 [38.5] (CH_2, C5′), 33.3 [33.3] (CH, C3′), 26.8 [26.5] (CH_2, C4′), 25.8 [25.7] (CH_3, 7-CH_3), 22.2 [21.7] (CH_3, 3′-CH_3), 17.8 [17.8] (CH_3, C8′), 15.2 [15.2] OCH_2CH_3). − IR (diffuse reflection), ṽ (%): 2926 cm^{-1} (72), 2853 (63), 1635 (25), 1449 (28), 1116 (100), 703 (33), period − MS (70 eV), *m/z* (%): 451 (9) [M^+], 422 (6), 406 (100), 366 (7), 308 (6), 294 (5), 270 (5), 178 (6), 165 (5). − $C_{29}H_{41}NO_3$ (451): calcd. C 77.12, H 9.15, N 3.10; found C 77.34, H 9.01, N 3.14.



***N*-[2-(1-Cyclohex-1-enylpropenyl)-3-ethoxy-5-methoxymethylcyclopenta-2,4-dienyl]morpholine (5n):** Compound **3d** (613 mg, 1.00 mmol), $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) and 1.5 equiv. of methoxyprop-2-yne (**4d**) (108 mg, 1.50 mmol) were treated for 36 h at 20°C as described above to yield compound **5n** as a pale orange oil (190 mg, 53%, R_f = 0.5, on alumina, *n*-pentane/diethyl ether, 7:3). − ^{1}H NMR (300 MHz, C_6D_6, 303 K): δ = 6.26 (1 H, m, 4-H), 5.76 (1 H, q, ^3J = 7.0 Hz, 2′-H), 5.61 (1 H, m, 2′′-H), 4.08 (2 H, m, 1′′′-H_2), 3.95 (1 H, m, 1-H), 3.65 (2 H, m, OCH_2CH_3), 3.60 [4 H, m, $O(CH_2CH_2)_2N$], 3.19 (3 H, s, OCH_3), 2.67 and 2.57 [2:2 H, m each, $N(CH_2)_2$], 2.23 and 2.11 (2:2 H, m each, 3′′-H_2 and 6′′-H_2), 1.87 (3 H, d, ^3J = 7.0 Hz, 3′-H_3), 1.66 (4 H, m, 4′′-H_2 and 5′′-H_2), 1.06 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). − ^{13}C NMR (75 MHz, C_6D_6, 303 K): δ = 153.1 (C_q, C3), 146.9 (C_q, C5), 139.0 and 137.9 (C_q each, C1′and C1′′); 124.9, 124.6 and 121.9 (CH each, C4, C2′and C2′′), 120.5 (C_q, C2), 71.2 (CH, C1), 71.1 (CH_2, C1′′′), 68.1 $[O(CH_2CH_2)_2N]$, 65.4 (OCH_2CH_3), 58.0 (OCH_3), 49.5 $[O(CH_2CH_2)_2N]$, 29.6 and 25.9 (CH_2 each, C3′′ and C6′′), 23.6 and 22.9 (CH_2 each, C4′′ and C5′′), 15.5 and 15.0 (CH_3 each, C3′ and OCH_2CH_3), period − MS (ESI, 20 V, acetonitrile/methanol): 360.4 [M + H^+]. − IR (diffuse reflection), ṽ (%): 2924 cm^{-1} (76), 2852 (76), 1635 (32), 1563 (25), 1447 (33), 1116 (100), 844 (30). − $C_{22}H_{33}NO_3$ (359): calcd. C 73.50, H 9.25, N 3.90; found C 73.31, H 9.69, N 3.92.



Acknowledgments

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[21] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114224 and -114225. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat). + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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