Organic Syntheses via Transition Metal Complexes. 109.[1] Transfer of Carbene Ligands from Group VI Metals to Rhodium as the Key Step of a Rhodium-Catalyzed Reactivity Enhancement of Fischer Carbene Complexes

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Vinylcyclopentadienes **5a**−**h** were obtained under mild conditions at 20 °C in 71−78% yields by a rhodium-catalyzed condensation of 1-alken-3-ynes **4a**,**b** with 4-amino-1-metalla-1,3-butadienes $(OC)_5M{=}C(OEt)CH{=}C(Ph)NR_2$ (**3**; M = W, Cr). The key step of this transformation involves formation of a rhodaoctatetraene (type **B**) by transmetalation and a subsequent insertion of the alkyne unit into the Rh=C double bond. $RhCl_3{\cdot}3H_2O$ in CH_3-OH was found to be a simple and most efficient (pre)catalyst of this reaction. $[(COD)RhCl]_2$ and $[(OC)_2RhCl]_2$ have been also successfully applied as precatalysts.

Since the discovery of Fischer carbene complexes[2] much attention has been paid to the preparation of a great variety of new compounds as well as to the development of strategies for a potential application of such compounds to organic syntheses.[3,11] Surprisingly, only a few studies have been directed toward transfer reactions of carbene ligands from group VI Fischer carbene complexes to other metals as an approach to the generation of new carbene complexes as well as an attempt to properly adjust the reactivity of a carbene complex to the requirements of a special organic transformation.[4] Stoichiometric carbene transmetalation reactions have gained interest anew within the last 3 years.[5] A brand new focus toward an application of catalytic processes involving carbene transmetalation reactions to organic syntheses was brought up by Sierra et al.[6] in 1998 and Narasaka et al.[7] in 1999. Both groups, independently of each other, reacted Fischer carbene complexes with olefins in the presence of catalytic amounts of Pd(II) salts. They obtained coupling products between carbene ligands and olefins, which were thought to be generated rather by chemistry known of palladium- than of chromium carbene complexes. Somewhat later in 1999, in studies directed toward the generation of metallaoctatetraenes of type **A**−**E** (Chart 1) and the π-cyclization of 1-metalla-1,3,5-hexatriene subunits of these compounds to cyclopentadiene rings, it was shown by us that the condensation of alkynes with cross-conjugated metallatrienes $(OC)_5M{=}(OEt)C(=CHNR_2)C(Ph){=}CHR^1$ (M = Cr, W; NR_2 = morpholine) to vinylcyclopentadienes could be performed even at 20 °C (even in the case of otherwise rather unreactive tungsten derivatives), if $[(COD)RhCl]_2$ was added as catalyst.[8] To our knowledge, this was the first case reported in which a rhodium catalyst had been successfully applied to the reactivity enhancement of a Fischer carbene complex.

Cyclopentadiene formation by π-cyclization of a conjugated 1-metalla-1,3,5-hexatriene unit was typically observed in the case of group VI metal derivatives, which are readily accessible from the corresponding (1-

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(1) Part 108: Aumann, R.; Roths, K.; Fröhlich, R. *J. Organomet. Chem.*, in press.

(2) Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645−645; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580−580.

(3) For some recent reviews see: (a) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187−198. (b) Doyle, M. P. *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 12, Chapters 5.1 and 5.2. (c) Wulff, W. *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 12, Chapter 5.3. (d) Barluenga, J. *Pure Appl. Chem.* **1999**, *71*, 1385−1391. (e) Barluenga, J.; Fañanás, F. J. *Tetrahedron* **2000**, *56*, 4597−4628. (f) Herndon, J. W. *Coord. Chem. Rev.* **1999**, *181*, 177−242. (g) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257−1280. (h) de Meijere, A. *Pure Appl. Chem.* **1996**, *68*, 61−72.

(4) (a) Fischer, E. O.; Beck, H.-J. *Angew. Chem.* **1970**, *82*, 44−45; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 72−73. (b) Öfele, K.; Herberhold, M. *Angew. Chem.* **1970**, *82*, 775−776; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 739−740. (c) Fischer, E. O.; Beck, H.-J.; Kreiter, C. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162−172. (d) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem Commun.* **1975**, 895−896. (e) Kreiter, C. G.; Öfele, K.; Wieser, G. W. *Chem. Ber.* **1976**, *106*, 1749−1758. (f) Ashworth, T.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1615−1624. (g) Berry, M.; Martin-Gil, J.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1625−1629. (h) Edwards, B. H.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *210*, 91−96. (i) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1981**, *114*, 1853−1857. (j) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148−155. (k) Thepold, K. H.; Bergmann, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464−475. (l) Aumann, R.; Heinrich, H.; Henkel, G.; Dartmann, M.; Krebs, B. *Z. Naturforsch.* **1983**, *38B*, 1325−1331. (m) Fischer, E. O.; Böck, M.; Aumann, R. *Chem. Ber.* **1983**, *116*, 3618−3623. (n) Fischer, E. O.; Böck, M. *Monatsh. Chem.* **1984**, *115*, 1159−1164. (o) Fehlhammer, W. P.; Achatz, D.; Plaia, U.; Völkl, A. *Z. Naturforsch.* **1987**, *42B*, 720−727. (p) Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Organometallics* **1992**, *11*, 3507−3510.

(5) (a) Liu, S.-T.; Hsieh, T.-Y.; Lee, G.-H.; Peng, S.-M. *Organomeallic.* **1998**, *17*, 993−995. (b) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972−975. (c) Ku, R.-Z.; Huang, J.-C.; Cho, J.-Y.; Kiang, F.-M.; Rajender Reddy, K.; Chen, Y.-C.; Lee, K.-J.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1999**, *18*, 2145−2154. (d) Liu, S.-T.; Rajender Reddy, K. *Chem. Soc. Rev.* **1999**, *28*, 315−322.

(6) Sierra, M. A.; Mancheño, M. J.; Sáenz, E.; del Amo, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 6812−6813.

(7) Sakurai, H.; Tanabe, K.; Narasaka, K. *Chem. Lett.* **1999**, 75−76.

(8) Aumann, R.; Göttker-Schnetmann, I.; Fröhlich, R.; Meyer, O. *Eur. J. Org. Chem.* **1999**, 2545−2561, 3209.

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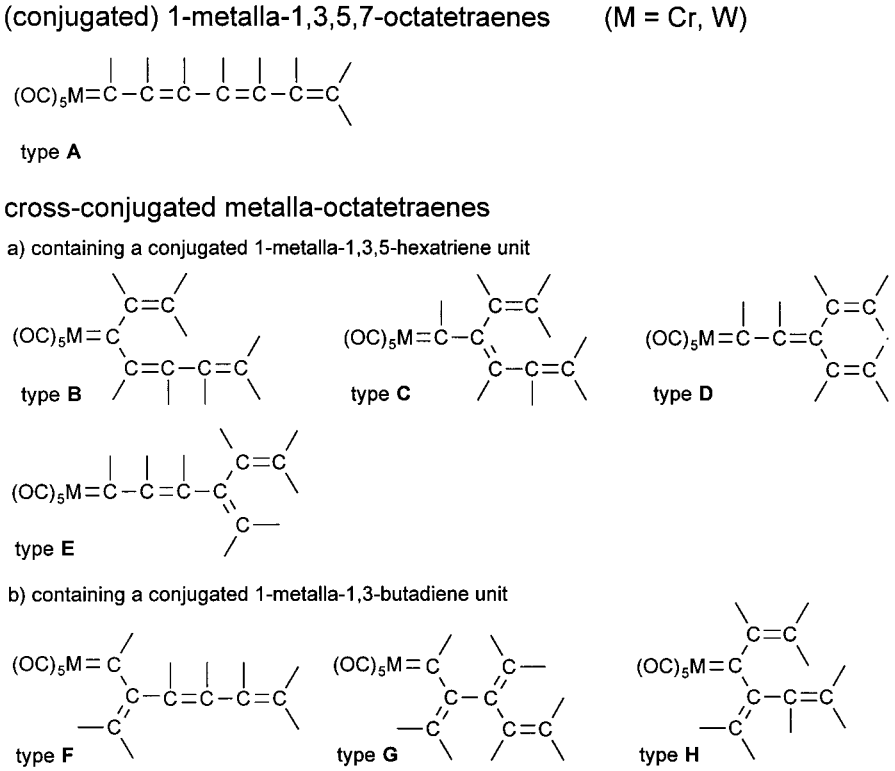
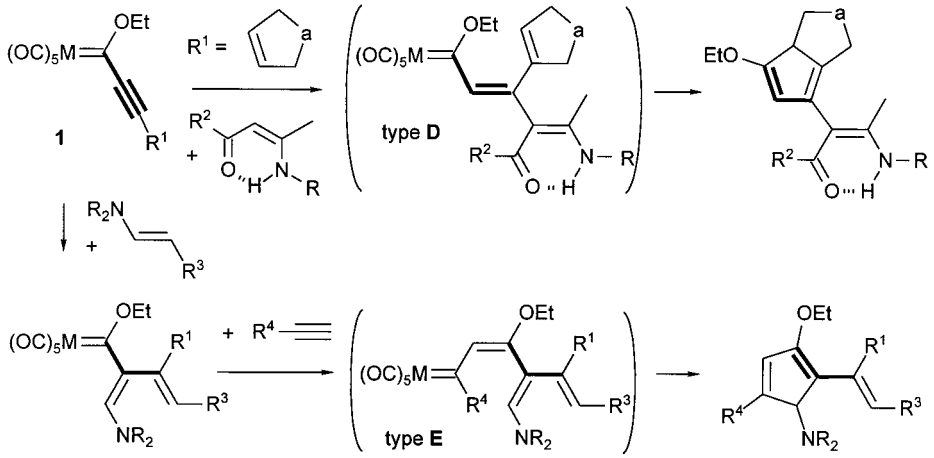
Chart 1. Basic Structures of Conjugated and Cross-Conjugated Metallaoctatetraenes of Types A−H



Scheme 1. Two Regiochemically Different Approaches to the Formation of Vinylcyclopentadienes from (1-Alkynyl)carbene Complexes 1 (M = Cr, W) via π-Cyclization of Metallaoctatetraene Intermediates of Types D and E



alkynyl)carbene derivatives and enamines.[9−11] It was shown, for example, that vinylcyclopentadienes are obtained by π-cyclization of chromaoctatetraenes of type **E**, generated from (1-alkynyl)carbene complexes **1** (R^1 = Ph) by metathesis of certain enamines (Scheme 1, line 2) and subsequent insertion of an alkyne.[8] A quite different approach to the formation of vinylcyclopentadienes involves the π-cyclization of metallaoctatetraenes of type **D**, which are accessible from (1-alkynyl)carbene complexes **1** (R^1 = cycloalkenyl) by Michael addition of *NH*-enaminones (Scheme 1, line 1).[12]

It was suggested that rhodaoctatetraenes of type **E** (structures analogous to those of chromaoctatetraenes of type **E**; Chart 1) would play a key role in the aforementioned rhodium-catalyzed cyclization reactions. The rhodaoctatetraenes of type **E** were assumed to be generated by alkyne insertion into the Rh=C bond of a

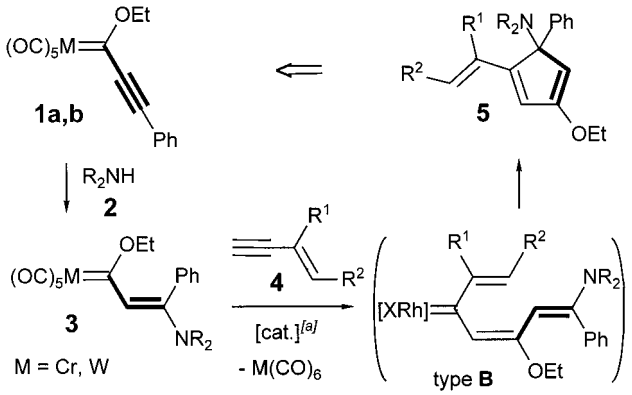
(9) For a recent review on (1-alkynyl)carbene complexes see: Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 161−242.

(10) For a detailed description of this π-cyclization reaction see: (a) Aumann, R.; Heinen, H.; Dartmann, M.; Krebs, B. *Chem. Ber.* **1991**, *124*, 2343−2347. (b) Aumann, R.; Heinen, H.; Hinterding, P.; Sträter, N.; Krebs, B. *Chem. Ber.* **1991**, *124*, 1229−1236.

(11) (a) For a recent review on 1-metalla-1,3,5-hexatrienes see: Aumann, R. *Eur. J. Org. Chem.* **2000**, 17−31. (b) Meyer, A. G.; Aumann, R. *Synlett* **1995**, 1011−1013. (c) Aumann, R.; Meyer, A. G.; Fröhlich, R. *Organometallics* **1996**, *15*, 5018−5027. (d) Aumann, R.; Kössmeier, M.; Zippel, F. *Synlett* **1997**, 621−623. (e) Aumann, R.; Kössmeier, M.; Jäntti, A. *Synlett* **1998**, 1120−1122. (f) Aumann, R.; Heinen, H.; Hinterding, P.; Sträter, N.; Krebs, B. *Chem. Ber.* **1991**, *124*, 2343−2347. (g) Aumann, R.; Heinen, H.; Hinterding, P.; Sträter, N.; Krebs, B. *Chem. Ber.* **1991**, *124*, 1229−1236. (h) Aumann, R.; Fröhlich, R.; Prigge, J.; Meyer, O. *Organometallics* **1999**, *18*, 1369−1380.

(12) Aumann, R.; Göttker-Schnetmann, I.; Fröhlich, R.; Saarenketo, P.; Holst, Ch. *Chem. Eur. J.* in press.

Scheme 2. Vinylcyclopentadienes 5 from (1-Alkynyl)carbene Complexes 1a,b Involving the Formation of Rhodaoctatetraene Intermediates of Type B



[a] [cat.] = 2 mol % $RhCl_3 \cdot 3H_2O$ in THF/MeOH (4:1); 20 °C.

rhodahexatriene precursor derived from the starting carbene complexes **1** (M = Cr, W) by transmetalation (Scheme 2).

Rhodium-Catalyzed Generation of Vinylcyclopentadienes 5 via Rhodaoctatetraenes of Type B (Scheme 2)

It is quite obvious that a π-cyclization of 1-metalla-1,3,5-hexatriene subunits of metallaoctatetraene structures of type **A**−**E** (Chart 1) should highly regioselectively afford vinylcyclopentadienes of complementary substitution patterns with respect to the position of the vinyl group attached to the cyclopentadiene ring. Two different types of such reactions based on the π-cyclization of metallaoctatetraenes of type **D** and type **E**, respectively, are exemplified in Scheme 1. We now wish to report on a third type of reaction, in which vinylcyclopentadienes **5a**−**h** were generated by π-cyclization of a metallaoctatetraene of type **B** involving a rhodium-catalyzed insertion of the C≡C bond of a 1-alken-3-yne **4** into the M=C bond of the 4-amino-1-metalla-1,3-butadiene $(OC)_5M{=}C(OEt)C{=}C(Ph)NR_2$ (**3**; M = Cr, W) (Scheme 2). The latter compounds were obtained from (1-alkynyl)carbene complexes **1** (R^1 = Ph) by addition of a secondary amine **2** and by condensation of methylcarbene complexes with acid amides, respectively.[13]

It was shown by de Meijere et al.[3h] in extensive studies that the thermal (noncatalyzed) condensation of alkynes with 4-amino-1-chroma-1,3-butadienes of structures similar to those of compounds **3** led to formation of cyclopentadienes,[14] methylenecyclopentenones,[15] acylcyclopentenones,[16] or cyclopenta[*b*]pyrans.[17] The reaction course was strongly dependent on substituents and conditions. A marked influence of both the 4-amino- and 4-organyl substituents was found. For example, it was reported that the condensation of the 4-*pyrrolidino* derivative of 4-*phenyl*-1-chroma-1,3-butadiene $(OC)_5Cr{=}(OEt)CH{=}C(Ph)NR_2$ (NR_2 = pyrrolidino) with the alkyne c-PrC≡C-c-Pr in pyridine at 80 °C produced the corresponding cyclopentadiene (supposedly by π-cyclization of a 1-chroma-1,3,5-hexatriene intermediate),[14a] while reaction of the 4-*dimethylamino* derivative of the 4-*phenyl*-1-chroma-1,3-butadiene $(OC)_5Cr{=}(OEt)CH{=}C(Ph)NR_2$ (**3d**; $NR_2 = NMe_2$) with terminal alkynes PhC≡CH (**4c**) (and EtC≡CH) in THF at 52−65 °C did not afford the expected cyclopentadiene **5m** (and the corresponding ethyl derivative, respectively), apparently not even in small yields.[14b] Furthermore, the reaction of the 4-*morpholino* derivative of the 4-*phenyl*-1-chroma-1,3-butadiene $(OC)_5Cr{=}C(OEt)CH{=}C(Ph)NR_2$ (**3e**; NR_2 = morpholino) with terminal alkynes RC≡CH in solvents such as DMF and THF afforded no cyclopentadienes but 2-acyl-3-morpholino-2-cyclopentenones instead by insertion both of the alkyne unit and carbon monoxide.[16]

The diversity of products obtained by the de Meijere group under thermal conditions could be channeled into generation of cyclopentadienes as the only products, if the condensation was catalyzed by $RhCl_3 \cdot 3H_2O$. Thus, a variety of cyclopentadienes **5a**−**h**,**k**−**n** (including compound **5m**, which could not be obtained by the thermal procedure described above) were shown to be formed from 4-*amino*-4-*phenyl*-1-metalla-1,3-butadienes $(OC)_5M{=}(OEt)CH{=}C(Ph)NR_2$ (**3a**−**g**) in THF/MeOH even at 20 °C in 71−78% yields (Scheme 2, Table 1). It should be noted that our reaction can be applied to both chromium and tungsten compounds, while the procedure reported by de Meijere et al. applies to chromium but not to tungsten complexes. $[(COD)RhCl]_2$, which has

Table 1

3	M	NR_2	**4**	R^1	R^2
a	W	NMe_2	**a**	CH_3	H
b	W	NEt_2	**b**	$-(CH_2)_4-$	
c	W	morpholine	**c**	$-(CH)_4-$	
d	Cr	NMe_2	**d**	*f*	
e	Cr	morpholine			
f	Cr	(+)-prolinole			
g	Cr	(+)-ephedrine			

5	NR_2	R^1	R^2	**[5]**, %[a]	**[5]**, %[b]	**[5]**, %[c]
a	NMe_2	CH_3	H	53	74	78 (76)[d]
b	NEt_2	CH_3	H			74
c	morpholine	CH_3	H	58	75	76 (74)[d]
d	NMe_2	$-(CH_2)_4-$				73 (72)[d]
e	NEt_2	$-(CH_2)_4-$		61		71
f	morpholine	$-(CH_2)_4-$		60		71 (73)[d]
g	(+)-ephedrine	CH_3	H			78[d,e]
h	(+)-prolinole	CH_3	H			75[d,e]
i	NHMe	CH_3	H		0	0
j	NHEt	CH_3	H		0	0
k	NEt_2	*f*		63	77	77
l	morpholine	*f*		61	74	77 (76)[d]
m	NMe_2	$-(CH)_4-$				76 (73)[d]
n	NEt_2	$-(CH)_4-$				77

[a] Isolated yield of reactions with 2.5 mol % of $[(COD)RhCl]_2$ as precatalyst. [b] Isolated yield of reactions with 2.5 mol % of $[(OC)_2RhCl]_2$ as precatalyst. [c] Isolated yields of reaction with 2 mol % of $RhCl_3 \cdot 3H_2O$ in MeOH as precatalyst. [d] Refers to yield from chromium instead of the corresponding tungsten carbene complex. [e] Isolated as a mixture of diastereomers. [f] Methoxymethyl instead of vinyl group $R^2CH{=}CR^1$.

(13) (a) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47−C51. (b) Fischer, E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977**, *131*, 57−64. (c) Aumann, R.; Hinterding, P. *Chem. Ber.* **1990**, *123*, 611−620. (d) de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051−2065.

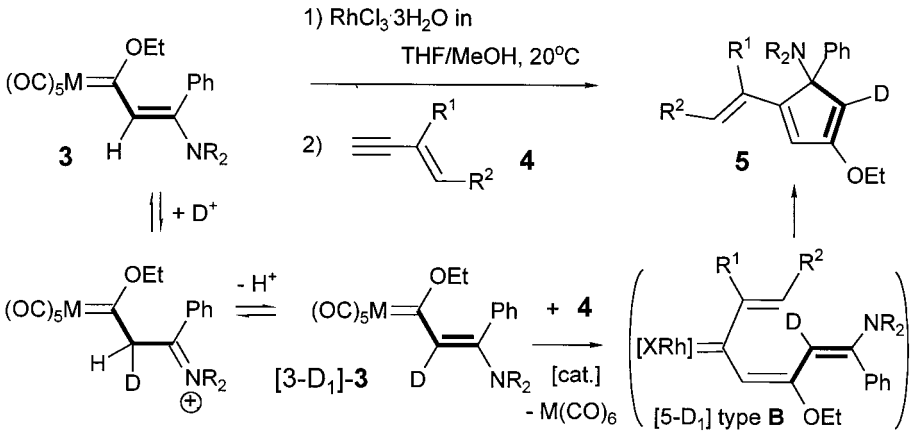
(14) (a) Flynn, B. L.; Funke, F. J.; de Meijere, A. *Synlett* **1995**, 1007−1010. (b) Duetsch, M.; Lackmann, R.; Stein, F.; de Meijere, A. *Synlett* **1991**, 324−326.

(15) Duetsch, M.; Vidoni, S.; Stein, F.; Funke, F. J.; Noltemeyer, M.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1679−1680.

(16) Flynn, B. L.; Funke, F. J.; Noltemeyer, M.; de Meijere, A. *Tetrahedron* **1995**, *51*, 11141−11148.

(17) Stein, F.; Duetsch, M.; Lackmann, R.; Noltemeyer, M.; de Meijere, A. *Angew. Chem.* **1991**, *103*, 1669−1671; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1658−1660.

Scheme 3. Regioselective Incorporation of Deuterium into Vinylcyclopentadienes Supposedly Catalyzed by Acid Generated from the Precatalyst $RhCl_3 \cdot 3H_2O/CH_3OD$



been successfully used for the generation of metallaoctatetraenes of type **E**, was somewhat less efficient in this case and gave cyclopentadienes **5a**−**h** in only 53−63% yields, while $[(OC)_2RhCl]_2$ proved to be almost as good as $RhCl_3 \cdot 3H_2O$ in THF/MeOH (see Table 1). Though a variety of secondary amines was successfully introduced in our system, primary amines such as methylamine or ethylamine were found to be not tolerated (Table 1, entries for **5i**,**j**).[18]

The rhodium-catalyzed condensation of 1-alken-3-ynes **4a**,**b** with 4-amino-1-metalla-1,3-butadienes **3a**−**g** is assumed to involve a transmetalation and an insertion step to finally produce rhodaoctatetraenes of type **B**, which subsequently undergo a π-cyclization to vinylcyclopentadienes **5a**−**h** and a catalytically active rhodium species "[RhX]" (Scheme 2). It should be noted in this context that an induction period of 1−60 min is usually observed prior to a clear-cut change of color from orange to brown, indicating the start of the cyclopentadiene formation. The exact nature of the catalytically active species is currently under investigation. It appears to be a Rh(I) complex, since $[(OC)_2RhCl]_2$ is active in this reaction and the system Rh(III)/CH_3OH is known to generate Rh(I) in the presence of suitable ligands.

3-H/3-D Exchange of 4-Amino-1-metalla-1,3-butadienes 3 Catalyzed by $RhCl_3 \cdot 3H_2O/CH_3OD$

While formation of vinylcyclopentadiene **5a** from compound **3a** in the presence of $RhCl_3 \cdot 3H_2O/CH_3OD$ was monitored by ^1H NMR spectra, it was found that one deuterium atom was selectively incorporated into compound **5a**. On a shorter time scale of a few minutes at 30 °C, an increase in intensity was observed for the hydroxy proton CH_3OH, while the 3-H signal of $(OC)_5W{=}C(OEt)CH{=}C(Ph)NMe_2$ (**3a**) nearly disappeared. Addition of 1.5 equiv of 2-methyl-but-2-ene-3-yne (**4a**) to this solution after a short induction period of 15 min resulted in a complete consumption of the deuterated carbene tungsten complex [3-D]-**3a** within ca. 4 h at 30 °C and the formation of a new set of signals corresponding to the deuterated vinylcyclopentadiene [2-D]-**5a** in a smooth reaction. The H/D ratio of the sample was determined by means of ESI-based mass spectrometry by comparison of the peak intensities of the undeuterated compound **5a** and the partially deuterated compound [2-D]-**5a**.[19] Furthermore, three other monodeuterated cyclopentadienes, [2-D]-**5d**, [2-D]-**5k**, and [2-D]-**5n**, were obtained by reaction of the corresponding alkynes **4** with compounds **3a**,**b** in the presence of $RhCl_3 \cdot 3H_2O/CH_3OD$ as described above (Scheme 3). The H/D ratio observed in each case fits perfectly with the statistically expected one (including six protons of the rhodium precatalyst). However, somewhat higher H/D ratios strongly dependent on minute changes of the reaction conditions were observed, if a mixture of $RhCl_3 \cdot 3H_2O/CH_3OD$ and the alkynes in THF was added to a solution of the carbene complexes **3a**,**b** in THF.

The H/D exchange is reasonably explained on the basis of the acid-catalyzed process outlined in Scheme 3, which has been described already for other compounds **3**.[20] It is assumed that acid is formed by reduction of $RhCl_3 \cdot 3H_2O$ to a catalytically active Rh(I) species. H/D ratios higher than statistically expected are explained on the basis that compounds [3-D]-**3** and [3-H]-**3** compete in reactions with the alkyne to cyclopentadienes **5** already at an early stage of the H/D exchange process. Once cyclopentadienes **5** are formed, the acid-catalyzed H/D exchange is retarded by the inherent basicity of the aminocyclopentadienes **5**.

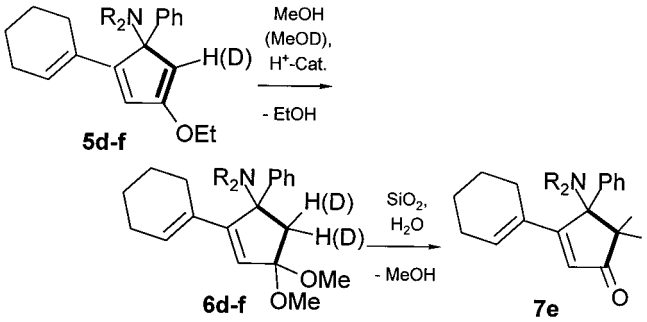
In an attempt to obtain monodeuterated cyclopentadienes [2-D]-**5** in deuteration grades higher than 95%, an excess of CH_3OD was applied to the reaction mixture. It was found that a side reaction was triggered in this case, leading to addition of methanol to the corresponding cyclopentadienes [2-D]-**5** to give 3,3-dimethoxycyclopentenes [5-D_2]-**6** (Scheme 4). The latter reaction was quite smooth in the case of (cyclohex-1-enyl)cyclopentadienes **5d**,**f** and [2-D]-**5f**, especially if the reaction time was extended. Mixed acetals, i.e., 3-ethoxy-3-methoxycyclopentenes, could not be detected in the reaction mixture by NMR measurements. To avoid formation of acetals **6** from cyclopentadienes **5**, it is recommended to isolate the cyclopentadiene within 12 h at 20 °C and furthermore to keep the amount of methanol to a

(18) It should be noted in this context that the reaction of 4-anilino-4-phenyl-1-chroma-1,3-butadiene with phenylacetylene in THF at 80 °C was reported to produce 4(1*H*)-pyridinylidene complexes instead of cyclopentadienes: Aumann, R.; Hinterding, P. *Chem. Ber.* **1992**, *125*, 2765−2772.

(19) With regard to the ESI experiments cone potentials had to be chosen as low as possible in order to avoid fragmentation reactions, which could be discriminated by isotope effects.

(20) Aumann, R.; Hinterding, P. *Chem. Ber.* **1990**, *123*, 2047−2051.

Scheme 4. Formation of Dimethoxycyclopentenes 6 and Cyclopentenones



minimum. It has been verified that cyclopentadienes [2-D]-**5d**,**k**,**n** were obtained in good yields in a solvent mixture of MeOD/THF with a ratio as low as ca. 1:20 (175 mg of CH_3OD in 3.5 mL of THF; see Experimental Section). It should be noted that the presence of methanol is essential for the catalytic reaction to occur. Cyclopentadienes **5** could not be generated if methanol was not present at all. Chromatography of the crude reaction mixture containing compound **6e** (according to NMR spectra) on silica gel (instead of basic alumina) gave cyclopentenone **7e** but no dimethoxycyclopentene **6e**.[21]

Conclusion

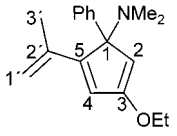
Carbene chromium and tungsten complexes of the Fischer type were shown to undergo a strong reactivity enhancement in the presence of catalytic amounts of $RhCl_3 \cdot 3H_2O$ and MeOH. This new catalytic reaction is exemplified for the generation of isomerically pure vinylcyclopentadienes **5a**−**h** under exceedingly mild conditions at 20 °C from 4-amino-1-metalla-1,3-butadienes **3a**−**g** (M = Cr, W) and alkynes **4a**,**b**. The key step of the reaction is assumed to involve a π-cyclization of 1-rhoda-1,3,5,7-octatetraenes of type **B**, which are generated by transmetalation of the corresponding chromium and tungsten precursors.

Experimental Section

NMR spectra were recorded on Bruker AM 360, Bruker AMX 400, and Varian U 600 instruments. All cyclopentadienes were analyzed by ^1H and ^{13}C spectra, with ^1H,^1H-COSY, GHSQC, and GHMBC experiments being performed with the Bruker AMX 400 instrumentation. Kinetic ^1H NMR experiments were performed with the Bruker AM 360. IR spectra were obtained with a Bio-Rad Digilab Division FTS-45 FT-IR instrument. MS and HRMS spectra were obtained with a Finnigan MAT8200 instrument and ESI measurements with a Micromass Quattro LCZ. Elemental analyses were performed with a Heraeus CHN-O Rapid instrument. Column chromatography was performed with an ICN Alumina B actvity IV column (10% H_2O) for isolation of all cyclopentadienes **5** and acetals **6d**,**f**, and compound **7e** was isolated by chromatography on Merck silica gel $60F_{254}$; flash chromatography was performed under an argon pressure of 1.2 bar within ca. 15 min for each cyclopentadiene. TLC measurements were obtained on Merck silica gel $60F_{254}$ plates; R_f values refer to TLC tests. All reactions were performed under argon. THF and CH_3OH of p.A. quality were used; diethyl ether, *n*-pentane, C_6D_6, CD_3OD, and [D_8]THF were used as purchased. In the case of deuterating experiments THF (p.A.) and CH_3OD were dried by standard procedures prior to use. 4-Amino-1-metalla-1,3-butadienes (**3a**−**g**) were prepared according to ref 13. An induction period of 1−60 min was observed for the catalytic reactions described below.

(3-Ethoxy-5-isopropenyl-1-phenylcyclopenta-2,4-dien-1-yl)dimethylamine (5a) and [2-D]-5a. To pentacarbonyl-[1-ethoxy-3-(dimethylamino)-3-phenylprop-2-en-1-ylidene]tungsten (**3a**; 527 mg, 1.00 mmol) and $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) in a 4 mL screw-top vessel was added a solution of 2-methyl-1-buten-3-yne (**4a**; 99 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1). After the mixture was stirred for 36 h at 20 °C, the solvent was removed under reduced pressure (20 mbar, 20 °C) and the residue was extracted twice with 4 mL of *n*-pentane/diethyl ether (20:1) to leave the major portion of tungsten hexacarbonyl undissolved. Compound **5a** was isolated by flash chromatography on alumina with *n*-pentane/diethyl ether (20:1) at 20 °C (143 mg, 53%, R_f = 0.8 on silica gel, *n*-pentane/diethyl ether (10:1), pale yellow oil). Reaction of compound **3a** (527 mg, 1.00 mmol) with alkyne **4a** (99 mg, 1.5 mmol) in the presence of $[(OC)_2RhCl]_2$ (10 mg, 0.026 mmol) after 12 h at 20 °C gave compound **5a** in better yields (199 mg, 74%). Reaction of compound **3a** (527 mg, 1.00 mmol) with alkyne **4a** (99 mg, 1.5 mmol) and $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) after 12 h at 20 °C afforded optimal yields of cyclopentadiene **5a** (210 mg, 78%). Reaction of the corresponding chromium compound **3d** (395 mg, 1.00 mmol) with alkyne **4a** (99 mg, 1.5 mmol) and $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) gave compound **5a** (204 mg, 76%).

H/D Exchange Experiments. [D_8]THF (0.6 mL) and CD_3OD (64 mg, 1.774 mmol) were added to compound **3a** (158 mg, 0.2998 mmol) in a NMR tube, and a ^1H NMR spectrum was recorded after 5 min, which indicates that no H/D exchange had taken place. After $RhCl_3 \cdot 3H_2O$ (2 mg, 0,008 mmol) was added to the solution and the sample was vigorously shaken, an ^1H NMR spectrum after 5 min indicates a clear increase in intensity of the signal CD_3OH and a concomitant decrease in intensity of the signal 3-H of $(OC)_5W{=}C(OEt)C{H}{=}C(Ph)NMe_2$, in a ratio which remained essentially unchanged within 30 min at 30 °C. 2-Methyl-1-buten-3-yne (**4a**; 32 mg, 0.485 mmol) was added to the solution, and ^1H NMR spectra were recorded in intervals of 30 min after an induction period of ca. 15 min, during which time no change of color was observed. The reaction was complete after 4 h at 30 °C. Workup as described above gave [2-D]-**5a** (60 mg, 74%). The H/D ratio of [2-D]-**5a** was determined by ESI (cone potential 9 V in CH_3OH/CH_3Cl) to be 0.192 in good agreement with 0.189 as calculated on the basis of a statistical distribution.



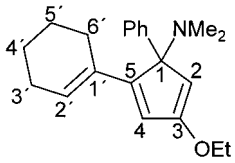
Data for **5a** are as follows. ^1H NMR (400 MHz, C_6D_6, 300 K): δ 7.70 (2 H, m, *o*-H Ph), 7.20 (2 H, m, *m*-H Ph), 7.06 (1 H, m, *p*-H Ph), 6.05 and 4.95 (1:1 H, m each, 1′-H_2), 6.03 (1 H, d, ^4J = 2.0 Hz, 4-H), 5.17 (1 H, d, ^4J = 2.0 Hz, 2-H), 3.65 (2 H, OCH_2), 2.32 [6 H, s, $N(CH_3)_2$], 1.59 (3 H, s, 3′-H_3), 1.17 (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 161.7 (C_q, C3), 156.1 (C_q, C5), 141.9 (C_q, *i*-C Ph), 135.6 (C_q, C2′), 128.2 (CH, *m*-C Ph), 127.7 (CH, *o*-C Ph), 126.6 (CH, *p*-C Ph), 125.2 (CH, C4), 116.2 (CH_2, C1′), 102.1 (CH, C2), 80.9 (C_q, C1), 64.8 (OCH_2), 42.3 [$N(CH_3)_2$], 21.9 (CH_3, C3′), 14.6 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2981 (30), 2940 (29), 2824 (20), 1625 (39), 1605 (100), 1340 (73), 1197 (43). MS (70 eV; *m*/*e* (%)): 269 (31) [M^+], 240 (100), 226 (74), 197 (38), 182 (33), 167 (18), 153 (21). MS (ESI, cone potential 9 V in CH_3OH/CH_3Cl): compound **5a**, 270 [$M + H^+$]; compound [2-D]-**5a**, 271 [$M + H^+$]. Anal. Calcd for $C_{18}H_{23}NO$ (269.4): C, 80.26; H, 8.61; N, 5.20. Found: C, 80.43; H, 8.93; N, 5.11.

(21) Compounds **6** and **7** were identified by ^1H and ^{13}C NMR spectra (including ^1H,^1H-COSY, GHSQC, and GHMBC experiments) as well as by IR and MS spectra.

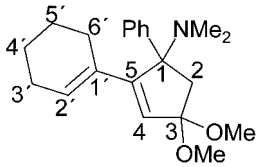
(3-Ethoxy-5-isopropenyl-1-phenylcyclopenta-2,4-dien-1-yl)diethylamine (5b). Reaction of pentacarbonyl[1-ethoxy-3-(diethylamino)-3-phenylprop-2-en-1-ylidene]tungsten (**3b**; 555 mg, 1.00 mmol) and 2-methyl-1-buten-3-yne (**4a**; 99 mg, 1.5 mmol) with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) in 4 mL of THF/MeOH (4:1) as described above gave compound **5b** (219 mg, 74%, $R_f = 0.9$ on silica gel, *n*-pentane/diethyl ether 10:1, pale yellow oil). ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.71 (2 H, m, *o*-H Ph), 7.19 (2 H, m, *m*-H Ph), 7.05 (1 H, m, *p*-H Ph), 6.05 (1 H, d, $^4J = 1.9$ Hz, 4-H), 6.02 and 4.94 (1:1 H, s each, br. each, 1′-H_2), 5.32 (1 H, d, $^4J = 1.9$ Hz, 2-H), 3.67 (2 H, q, $^3J = 7.2$ Hz, OCH_2), 2.82 and 2.69 [2:2 H, m each, $N(CH_2)_2$], 1.60 (3 H, s, 3′-H_3), 1.18 (3 H, t, $^3J = 7.4$ Hz, OCH_2CH_3), 1.14 [6 H, t, $^3J = 7.0$ Hz, $N(CH_2CH_3)_2$]. ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 160.5 (C_q, 3), 155.6 (C_q, C5), 143.0 (C_q, *i*-C Ph), 135.8 (C_q, C2′), 128.3 (CH, *m*-C Ph), 127.5 (CH, *o*-C Ph), 126.5 (CH, *p*-C Ph), 125.8 (CH, C4), 116.8 (CH_2, C1′), 106.6 (CH, C2), 82.4 (C_q, C1), 64.7 (OCH_2), 45.5 [$N(CH_2)_2$], 22.1 (CH_3, C3′), 15.2 [$N(CH_2CH_3)_2$], 14.7 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2974 (54), 2930 (25), 1625 (45), 1605 (100), 1341 (78), 1181 (25). MS (70 eV; *m*/*e* (%)): 297 (17) [M^+], 268 (87), 226 (100), 197 (38), 182 (39), 167 (18), 153 (21). Anal. Calcd for $C_{20}H_{27}NO$ (297.4): C, 80.76; H, 9.15; N, 4.71. Found: C, 80.75; H, 9.67; N, 4.48.

(3-Ethoxy-5-isopropenyl-1-phenylcyclopenta-2,4-dien-1-yl)morpholine (5c). Pentacarbonyl(1-ethoxy-3-morpholino-3-phenylprop-2-en-1-ylidene)tungsten (**3c**; 569 mg, 1.00 mmol) and 2-methyl-1-buten-3-yne (**4a**; 99 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) as described above to give compound **5c** (237 mg, 76%, $R_f = 0.5$ on silica gel, *n*-pentane/diethyl ether 10:1, colorless oil). With $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) as catalyst, compound **5c** was obtained in somewhat lower yield (181 mg, 58%) after 36 h at 20 °C. $[(OC)_2RhCl]_2$ (10 mg, 0.026 mmol) was a more efficient catalyst for the generation of compound **5c** (233 mg, 75%) after 12 h at 20 °C. Compound **5c** (231 mg, 74%) was obtained on reaction of pentacarbonyl[1-ethoxy-3-(diethylamino)-3-phenyl-prop-2-en-1-ylidene]chromium (**3e**; 437 mg, 1.00 mmol) with alkyne **4a** in the presence of $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol). ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.61 (2 H, m, *o*-H Ph), 7.19 (2 H, m, *m*-H Ph), 7.07 (1 H, m, *p*-H Ph), 6.01 (1 H, d, $^4J = 2.1$ Hz, 4-H), 5.97 and 4.88 (1:1 H, s each, br each, 1′-H_2), 5.19 (1 H, d, $^4J = 2.1$ Hz, 2-H), 3.69 [4 H, m, $O(CH_2)_2$], 3.65 (2 H, m, OCH_2), 2.61 and 2.47 [2:2 H, m each, $N(CH_2)_2$], 1.57 (3 H, s, 3′-H_3), 1.18 (3 H, t, $^3J = 7.1$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 161.3 (C_q, C3), 154.7 (C_q, C5), 140.9 (C_q, *i*-C Ph), 135.8 (C_q, C2′), 128.3 (CH, *m*-C Ph), 127.6 (CH, *o*-C Ph), 126.7 (CH, *p*-C Ph), 125.9 (CH, C4), 102.9 (CH, C2), 80.6 (C_q, C1), 67.8 [$O(CH_2)_2$], 64.9 (OCH_2), 49.8 [$N(CH_2)_2$], 22.0 (CH_3, C3′), 14.6 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2958 (45), 2848 (44), 1626 (48), 1605 (97), 1342 (74), 1117 (100). MS (70 eV; *m*/*e* (%)): 311 (17) [M^+], 282 (67), 226 (100), 197 (33), 182 (36), 167 (18), 153 (21). Anal. Calcd for $C_{20}H_{25}NO_2$ (311.4): C, 77.14; H, 8.09; N, 4.50. Found: C, 76.95; H, 8.25; N, 4.43.

[5-(Cyclohexen-1-yl)-3-ethoxy-1-phenylcyclopenta-2,4-dien-1-yl]dimethylamine (5d), [2-D]-5d, and [5-(Cyclohexen-1-yl)-3,3-dimethoxy-1-phenylcyclopent-4-en-1-yl]-dimethylamine (6d). Pentacarbonyl[1-ethoxy-3-(dimethylamino)-3-phenylprop-2-en-1-ylidene]tungsten (**3a**; 517 mg, 1.00 mmol) and 1-ethynylcyclohexene (**4b**; 159 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted as described above with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) to give compound **5d** (226 mg, 73%, $R_f = 0.3$ on silica gel, *n*-pentane/diethyl ether 10:1, pale yellow oil). The corresponding reaction with pentacarbonyl[1-ethoxy-3-(dimethylamino)-3-phenylprop-2-en-1-ylidene]chromium (**3d**; 395 mg, 1.00 mmol) gave compound **5d** (223 mg, 72%). The reaction of **3a** performed in 3.5 mL of THF with CH_3OD (175 mg) and $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) gave compound [2-D]-**5d** (221 mg, 71%). The H/D ratio was found to be 0.221 (ESI, cone potential 9 V, in $MeOH/CH_3Cl$) (calculated H/D ratio 0.210). The reaction of pentacarbonyl-[1-ethoxy-3-(dimethylamino)-3-phenylprop-2-en-1-ylidene]tungsten (**3a**; 517 mg, 1.00 mmol) with 1-ethynylcyclohexene (**4b**; 159 mg, 1.5 mmol) and $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) in 4 mL of THF/MeOH (1:1) gave the acetal **6d** in amounts increasing with the reaction time.



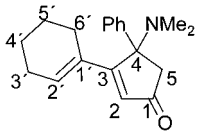
Data for **5d** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.71 (2 H, m, *o*-H Ph), 7.20 (2 H, m, *m*-H Ph), 7.05 (1 H, m *p*-H Ph), 6.84 (1 H, m, 2′-H), 6.03 (1 H, d, $^4J = 1.9$ Hz, 4-H), 5.14 (1 H, d, $^4J = 1.9$ Hz, 2-H), 3.69 (2 H, m, OCH_2), 2.36 [6 H, s, $N(CH_3)_2$], 2.05 and 1.72 (1:1 H, m each, 6′-H_2), 2.05 and 1.95 (1:1 H, m each, 3′-H_2), 1.31 (4 H, m, 4′-H_2 and 5′-H_2), 1.19 (3 H, t, $^3J = 7.2$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 162.0 (C_q, C3), 156.7 (C_q, C5), 142.4 (C_q, *i*-C Ph), 130.1 (C_q, C1′), 128.1 (CH, *m*-C Ph), 127.9 (CH, C2'), 127.7 (CH, *o*-C Ph), 126.4 (CH, *p*-C Ph), 100.7 (CH, C2), 81.0 (C_q, C1), 64.7 (OCH_2), 41.3 [$N(CH_3)_2$], 26.8 (CH_2, C6′), 26.0 (CH_2, C3′), 23.0 and 22.3 (CH_2 each, C4′ and C5′), 14.6 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2931 (79), 2858 (36), 1613 (100), 1341 (90), 1187 (38), 1046 (40). MS (70 eV; *m*/*e* (%)): 326 (42), 309 [M^+] (31), 280 (100), 266 (41), 207 (14), 195 (19), 165 (27). MS (ESI, cone potential 7 V in $MeOH/CH_3Cl$): compound **5d**, 310 [$M + H^+$]; compound [2-D]-**5d**, 311 [$M + H^+$]. Anal. Calcd for $C_{21}H_{27}NO$ (309.5): C, 81.51; H, 8.79; N, 4.53. Found: C, 81.62; H, 8.55; N, 4.51.



Data for **6d** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.91 (2 H, m, *o*-H Ph), 7.22 (2 H, m, *m*-H Ph), 7.03 (1 H, m, *p*-H, Ph), 6.92 (1 H, m, 2′-H), 5.91 (1 H, s, 4-H), 3.29 and 3.26 (3:3 H, s each, 2 × OCH_3), 2.66 and 2.37 (1:1 H, d each, $^2J = 14.5$ Hz, 2-H_2), 2.23 [6 H, s, $N(CH_3)_2$], 2.04 and 1.76 (2 H, m, 3′-H_2), 1.97 and 1.86 (2 H, m, 6′-H_2), 1.37 and 1.30 (2 H, m, 4′-H_2), 1.30 and 1.20 (2 H, m, 5′-H_2). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 153.5 (C_q, C5), 146.9 (C_q, *i*-C Ph), 130.5 (C_q, C1′), 130.1 (CH, C2′), 128.5 (CH, *o*-C Ph), 127.7 (CH, *m*-C Ph), 126.1 (CH, *p*-C Ph), 124.0 (CH, C4), 110.6 (C_q, C3), 78.6 (C_q, C1), 49.3 and 49.2 (2 × OCH_3), 40.4 (CH_2, C2), 40.2 [$N(CH_3)_2$], 27.7 (CH_2, C3′), 26.0 (CH_2, C6′), 23.1 (CH_2, C4′), 22.1 (CH_2, C5′). IR (diffuse reflection; cm^{-1} (%)): 2932 (39), 2826 (19), 1446 (10), 1329 (24), 1116 (100), 1051 (74). MS (70 eV; *m*/*e* (%)): 312 (100) [$M^+ + H$], 296 (14), 283 (17), 252 (23), 238 (12), 209 (16).

[5-(Cyclohexen-1-yl)-3-ethoxy-1-phenylcyclopenta-2,4-dien-1-yl]diethylamine (5e) and 3-(Cyclohexen-1-yl)-4-diethylamino-4-phenylcyclopent-2-enone (7e). Pentacarbonyl[1-ethoxy-3-(diethylamino)-3-phenylprop-2-en-1-ylidene]-tungsten (**3b**; 555 mg, 1.00 mmol) and 1-ethynylcyclohexene (**4b**; 159 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) as described above to give compound **5e** (239 mg, 71%, $R_f = 0.4$ on silica gel, *n*-pentane/diethyl ether 10:1, pale yellow oil). Application of $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) gave compound **5e** (203 mg, 60%). Reaction of compounds **3b** (555 mg, 1.00 mmol), **4b** (159 mg, 1.5 mmol), and $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) in 4 mL of THF/MeOH (1:1) gave cyclopentenone **7e** after chromatography on silica gel, if the reaction time was doubled.

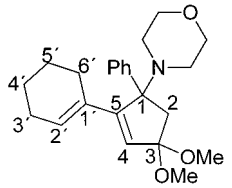
Data for **5e** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.73 (2 H, m, *o*-H Ph), 7.20 (2 H, m, *m*-H Ph), 7.04 (1 H, m, *p*-H Ph), 6.82 (1 H, m, 2′-H), 6.04 (1 H, d, ^4J = 1.9 Hz, 4-H), 5.28 (1 H, d, ^4J = 1.9 Hz), 3.69 (2 H, q, ^3J = 7.1 Hz, OCH_2), 2.77 [4 H, m, $N(CH_2)_2$], 2.07 and 1.83 (1:1 H, m each, 6′-H_2), 2.05 (2 H, m, 3′-H_2), 1.31 (4 H, m, 4′-H_2 and 5′-H_2), 1.18 (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3), 1.16 [6 H, t, ^3J = 6.1 Hz, $N(CH_2CH_3)$]. ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 160.8 (C_q, C3), 156.3 (C_q, C5), 143.4 (C_q, *i*-C Ph), 130.3 (C_q, C1′), 128.5 (CH, C2′), 128.0 (CH, *m*-C Ph), 127.6 (CH, *o*-C Ph), 126.4 (CH, *p*-C Ph), 122.5 (CH, C4), 105.3 (CH, C2), 82.5 (C_q, C1), 64.4 (OCH_2), 45.7 [$N(CH_2)_2$], 26.9 (CH_2, C6′), 25.9 (CH_2, C3′), 23.0 and 22.3 (CH_2 each, C4′and C5′), 15.3 [$N(CH_2CH_3)_2$], 14.7 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2928 (85), 2862 (39), 1615 (100), 1341 (87), 1183 (47), 1046 (50). MS (70 eV; *m*/*e* (%)): 337 [M$^+$] (13), 308 (100), 280 (32), 266 (56), 252 (22), 195 (25), 179 (20), 165 (33). Anal. Calcd for $C_{23}H_{27}NO$ (337.5): C, 81.85; H, 9.26; N, 4.15. Found: C, 81.73; H, 9.13, N; 3.94.



Data for **7e** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.49 (2 H, m, *o*-H Ph), 7.28 (1 H, m, 2′-H), 7.09 (2 H, m, *m*-H Ph), 6.95 (1 H, m, *p*-H Ph), 6.03 (1 H, s, 2-H), 2.90 and 2.64 (1:1 H, d each ^2J = 18.4 Hz, 5-H_2), 2.34 [4 H, m, $N(CH_2)_2$], 1.93 and 1.79 (1:1, m, each, 3′-H_2), 1.79 and 1.63 (1:1 H, m each, 6′-H_2), 1.16 (4 H, m, 4′-H_2 and 5′-H_2), 1.00 [6 H, t, ^3J = 7.1 Hz, $N(CH_2CH_3)_2$]. ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 205.4 (C_q, C1), 176.6 (C_q, C3), 145.6 (C_q, *i*-C Ph), 138.0 (CH, C2'), 131.0 (C_q, C1′), 128.1 (CH, *m*-C Ph), 127.4 (CH, *o*-C Ph), 127.2 (CH, C2), 126.5 (CH, *p*-C Ph), 77.4 (C_q, C4), 47.1 (CH_2, C5), 46.4 [$N(CH_2)_2$], 27.1 (CH_2, C6′), 26.2 (CH_2, C3′), 22.5 and 21.5 (CH_2 each, C4′ and C5′),15.6 [$N(CH_2CH_3)_2$]. IR (diffuse reflection; cm^{-1} (%)): 2927 (19), 1692 (100), 1623 (17), 1563 (20), 1445 (11). MS (70 eV; *m*/*e* (%)): 309 [M$^+$] (40), 292 (63), 281 (24), 266 (20), 252 (23), 237 (100), 174 (90).

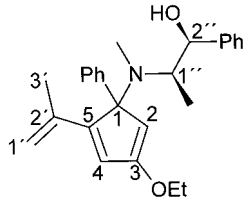
[5-(Cyclohexen-1-yl)-3-ethoxy-1-phenylcyclopenta-2,4-dien-1-yl]morpholine (5f), [5-(Cyclohexen-1-yl)-3,3-dimethoxy-1-phenylcyclopenta-2,4-dien-1-yl]morpholine (6f), and [2-D_2]-6f. Pentacarbonyl(1-ethoxy-3-morpholino-3-phenylprop-2-en-1-ylidene)tungsten (**3c**; 569 mg, 1.00 mmol) and 1-ethynylcyclohexene (**4b**; 159 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) as described above to give compound **5f** (248 mg, 71%, R_f = 0.3 on silica gel, *n*-pentane/diethyl ether 10:1, pale yellow oil). The reaction catalyzed by $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) gave compound **5f** (212 mg, 60%). Pentacarbonyl(1-ethoxy-3-morpholino-3-phenylprop-2-en-1-ylidene)chromium (**3e**; 437 mg, 1.00 mmol) gave compound **5f** (257 mg, 73%). Reaction of compound **3c** (569 mg, 1.00 mmol) with **4b** (159 mg, 1.5 mmol) and $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) in 4 mL of THF/MeOH (1:1) gave the acetal **6f** in amounts increasing with the reaction time. If CH_3OD was used instead of CH_3OH, compound [2-D_2]-**6f** was obtained.

Data for **5f** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.66 (2 H, m, *o*-H Ph), 7.21 (2 H, m, *m*-H Ph), 7.07 (1 H, m, *p*-H Ph), 6.83 (1 H, m, 2′-H), 6.03 (1 H, d, ^4J = 2.0 Hz, 4-H), 5.16 (1 H, d, ^4J = 2.0 Hz, 2′-H), 3.73 [4 H, m, $O(CH_2)_2$], 3.67 (2 H, m, OCH_2CH_3), 2.75 and 2.55 [2:2 H, m each, $N(CH_2)_2$], 2.05 and 1.77 (1:1 H, m each, 6′-H_2), 2.00 (2 H, m, 3′-H_2), 1.28 (4 H, m, 4′-H_2 and 5′-H_2), 1.19 (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 161.6 (C_q, C3), 155.4 (C_q, C5), 141.4 (C_q, *i*-C Ph), 130.4 (C_q, C1′), 128.3 (CH, *m*-C Ph), 127.8 (CH, C2′), 127.7 (CH, *o*-C Ph), 126.6 (CH, *p*-C Ph), 122.7 (CH, C4), 101.5 (CH, C2), 80.8 (C_q, C1), 67.9 [$O(CH_2)_2$], 64.8 (OCH_2CH_3), 49.9 [$N(CH_2)_2$], 26.8 (CH_2, C6′), 26.0 (CH_2, C3′), 22.9 and 22.2 (CH_2 each, C4′and C5′), 14.6 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2926 (100), 2849 (72), 1614 (92), 1341 (86), 1116 (100), 1043 (26). MS (70 eV; *m*/*e* (%)): 368 (39), 351 [M$^+$] (21), 322 (75), 266 (100), 237 (55), 209 (23), 195 (33), 179 (21), 165 (33). ESI (31 V, MeOH/$CHCl_3$) *m*/*e* (%)): 352 [M + H$^+$] (5), 265 [M + H$^+$ − morpholine] (100). Anal. Calcd for $C_{23}H_{29}NO_2$ (351.5): C, 78.59; H, 8.32; N, 3.98. Found: C, 78.66; H, 8.55; N, 3.76.



Data for **6f** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.88 (2 H, m, *o*-H Ph), 7.24 (2 H, m, *m*-H Ph), 7.03 (1 H, m, *p*-H Ph), 6.92 (1 H, m, 2′-H), 5.93 (1 H, s, 4-H), 3.69 [4 H, m, $O(CH_2)_2$], 3.30 and 3.27 (3:3 H, s each, 2 × OCH_3), 2.77 and 2.39 (1:1 H, d each, ^2J = 14.7 Hz, 2-H_2), 2.61 and 2.42 [2:2 H, m each, $N(CH_2)_2$]; 2.00, 1.93, and 1.73 (1:2:1 H, m each, 3′-H_2 and 6′-H_2), 1.27 (4 H, m, 5′-H_2 and 6′-H_2). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 152.2 (C_q, C5), 145.7 (C_q, *i*-C Ph), 130.7 (C_q, C1′), 129.9 (CH, C2′), 128.5 (CH, *o*-C Ph), 127.8 (CH, *m*-C Ph), 126.2 (CH, *p*-C, Ph), 110.5 (C_q, C3), 78.3 (C_q, C1), 67.4 [$O(CH_2)_2$], 49.3 and 48.6 (2 × OCH_3), 41.6 (CH_2, C2), 27.8 and 25.9 (CH_2 each C3′ and C6′), 23.0 and 22.1 (CH_2 each, C4′ and C5′). IR (diffuse reflection; cm^{-1} (%)): 2931 (19), 2830 (15), 1448 (22), 1327 (33), 1110 (100), 1047 (51). MS (70 eV; *m*/*e* (%)): 369 [M$^+$] (8), 354 (100), 322 (20), 283 (35), 252 (41), 209 (29).

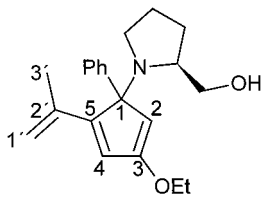
***N*-(3-Ethoxy-5-isopropenyl-1-phenylcyclopenta-2,4-dien-1-yl)-(+)-ephedrine (5g).** Pentacarbonyl{1-ethoxy-3-[methyl-((1*R*,2*S*)-1-hydroxy-1-phenylprop-2-yl)amino]-3-phenylprop-2-en-1-ylidene)}chromium (**3g**; 515 mg, 1.00 mmol) and 2-methyl-1-buten-3-yne (**4a**; 99 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) as described above to give a 3:2 diastereomeric mixture of compound **5g** (304 mg, 78%, R_f = 0.6 on silica gel, *n*-pentane/diethyl ether 4:1, pale yellow oil).



Data for **5g** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K, other diastereomer in braces): δ 7.63 {7.63} (2 H, m, *o*-H 1-Ph), 7.33 {7.37} (2 H, m, *o*-H 2″-Ph), 7.18 {7.18} (4 H, m, *m*-H 1- and 2″-Ph), 7.06 {7.06} (2 H, m, *p*-H 1- and 2″-Ph), 6.12 {6.02} (1 H, d, ^4J = 1.9 Hz, 4-H), 5.78 and 4.90 {5.63 and 4.84} (1:1 H, "d" and m, 1′-H_2), 5.18 {5.47} (1 H, d, ^4J = 1.9 Hz, 2-H), 5.16 {4.98} (1 H, d, ^3J = 3.2 {3.6} Hz, 2″-H), 3.63 {3.63} (2 H, m, OCH_2), 3.30 {3.30} (1 H, m, 1″-H), 2.57 {2.68} (3 H, s, NCH_3), 1.85 {1.85} (1 H, s br, OH), 1.61 {1.58} (3 H, s, 3′-H_3), 1.17 {1.17} (6 H, m, OCH_2CH_3 and 1″-CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 159.7 {159.9} (C_q, C3), 154.8 {154.8} (C_q, C5), 145.4 {145.2} (C_q, *i*-C 1-Ph), 142.3 {142.1} (C_q, *i*-C 2″-Ph), 136.4 {135.6} (C_q, C2′), 128.2 {128.1} (CH, *m*-C 1-Ph), 128.0 and 127.9 {128.0 and 127.9} (CH each, *o*-C 1- and 2″-Ph), 127.0 and 126.4 {127.1 and 126.4} (CH, *p*-C 1- and 2″-Ph), 126.8 {126.7} (CH, C4), 126.4 {126.3} (CH, *o*-C 2″-Ph), 167.6 {116.9} (CH_2, C1′), 106.9 {107.8} (CH, C2), 82.2 {81.8} (C_q, C1), 77.8 {79.4} (CH, C2″), 64.9 {64.8} (OCH_2), 60.0 {60.2} (CH, C1″), 32.4 {33.8} (NCH_3), 22.3 {22.0} (CH_3, C3′), 14.7 {14.7} (OCH_2CH_3), 11.3 {10.1} (CH_3, 1″-CH_3). IR (diffuse reflection; cm^{-1} (%)): 3450 br., 2977 (49), 2877 (22), 1626 (46),

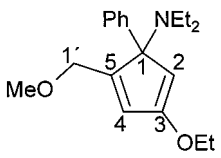
1605 (100), 1341 (76), 1042 (76). MS (70 eV; *m/e* (%)): 282 (53), 225 (75), 197 (100), 182 (54), 167 (21), 153 (31). Anal. Calcd for $C_{26}H_{31}NO_2$ (389.5): C, 80.17; H, 8.02; N, 3.60. Found: C, 80.02; H, 8.36; N, 3.19.

***N*-(3-Ethoxy-5-isopropenyl-1-phenylcyclopenta-2,4-dien-1-yl)-(+)-prolinole (5h).** Pentacarbonyl{1-ethoxy-3-[2*S*-(hydroxymethyl)pyrrolidino]-3-phenylprop-2-en-1-ylidene}-chromium (**3c**; 451 mg, 1.00 mmol) and 2-methyl-1-buten-3-yne (**4a**; 99 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) as described above to give a 5:4 diastereomeric mixture of compound **5h** (245 mg, 75%, $R_f = 0.2$ on silica gel, *n*-pentane/diethyl ether 10:1, pale yellow oil).



Data for **5h** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K, other diastereomer in braces): δ 7.83 {7.50} (2 H, m, *o*-H Ph), 7.17 {7.17} (2 H, m, *m*-H Ph), 7.08 {7.04} (1 H, m, *p*-H Ph), 6.02 {6.04} (1 H, d, $^4J = 2.0$ Hz, 4-H), 5.94 and 5.02 {5.62 and 4.83} (1:1 H, m each, 1′-H_2), 3.63 {3.63} (2 H, m, OCH_2-CH_3), 3.41 {3.36 } (2 H, m, CH_2OH), 2.92 and 2.57 {3.20 and 2.77} (NCH_2), 3.19 {2.77} (1 H, m, NCH), 2.25 {2.25} (1 H, br, OH), 1.73 {1.73} [4 H, m, N(CH_2CH_2)$_2$], 1.63 {1.60} (3 H, s, 3′-H), 1.16 {1.15} (3 H, t, $^3J = 7.3$ {7.3} Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 161.2 {160.6} (C_q, C3), 155.2 {155.0} (C_q, C5), 142.8 {142.6} (C_q, *i*-C Ph), 136.9 {135.9} (C_q, C2′), 128.6 and 128.5 {128.5 and 128.4} (CH each, *o*- and *m*-C Ph), 127.2 {126.2} (CH, *p*-C Ph), 126.8 {126.4} (CH, C4), 116.4 {116.2} (CH_2, C1′), 106.8 {105.2} (CH, C2), 81.1 {80.6} (C_q, C1), 65.7 {64.2} (CH_2OH), 64.8 {64.8} (OCH_2CH_3), 62.7 {61.2} (CH, NCH), 49.8 {54.0} (CH_2, NCH_2), 30.0 and 24.7 {31.1 and 25.8} [CH_2 each, N(CH_2CH_2)$_2$], 22.6 {22.0} (CH_3, C3′), 14.6 {14.6} (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 3450 br., 2956 (44), 2877 (26), 1625 (41), 1605 (100), 1342 (79), 1040 (55). MS (70 eV; *m/e* (%)): 325 [M^+] (15), 294 (30), 226 (55), 197 (51), 182 (33), 153 (23), 69 (58), 57 (100). Anal. Calcd for $C_{21}H_{27}NO_2$ (325.4): C, 77.50; H, 8.36; N, 4.30. Found: C, 77.39; H, 8.28; N, 3.94.

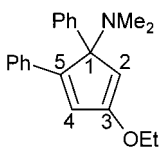
[3-Ethoxy-5-(methoxymethyl)-1-phenylcyclopenta-2,4-dien-1-yl]diethylamine (5k) and [2-D]-5k. Pentacarbonyl-[1-ethoxy-3-(diethylamino)-3-phenyl-prop-2-en-1-ylidene]tungsten (**3b**; 555 mg, 1.00 mmol) and 2-methoxypropyne (**4d**; 105 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) as described above to give compound **5k** (232 mg, 77%, $R_f = 0.8$ on silica gel, *n*-pentane/diethyl ether 10:1, colorless oil). Application of $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) as catalyst afforded compound **5k** (191 mg, 63%) after 36 h at 20 °C. $[(OC)_2RhCl]_2$ (10 mg, 0.026 mmol) generated compound **5k** (233 mg, 77%) after 12 h at 20 °C. In 3.5 mL of THF and CH_3OD (175 mg) with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) compound [2-D]-**5k** (232 mg, 77%) was obtained with a H/D ratio of 0.214 (ESI, cone potential 9 V, in MeOH/CH_3Cl); calculated 0.210).



Data for **5k** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.76 (2 H, m, *o*-H Ph), 7.21 (2 H, m, *m*-H Ph), 7.13 (1 H, m, *p*-H Ph), 6.27 (1 H, "q", 4-H), 5.15 (1 H, d, $^4J = 1.7$ Hz, 2-H), 4.25 and 3.80 (1:1 H, dd each, $^2J = 15.2$ Hz, $^4J = 2.1$ and 2.1 Hz, 1′-H_2), 3.65 (2 H, q, $^3J = 7.1$ Hz, OCH_2), 2.99 (3 H, s, OCH_3), 2.61 [4 H, m, N(CH_2)$_2$], 1.14 (3 H, t, $^3J = 7.1$ Hz, OCH_2CH_3), 1.10 [6 H, t, $^3J = 7.3$ Hz, N(CH_2CH_3)$_2$]. ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 161.1 (C_q, C3), 154.2 (C_q, C5), 143.8 (C_q, *i*-C Ph), 128.6 (CH, *m*-C Ph), 127.2 (CH, *p*-C Ph), 127.1 (CH, *o*-C Ph), 123.9 (CH, C2), 81.2 (C_q, C1), 69.4 (CH_2 C1′), 64.8 (OCH_2CH_3), 58.3 (OCH_3), 45.8 [N(CH_2)$_2$], 16.3 [N(CH_2-CH_3)$_2$], 14.6 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2979 (20), 1625 (72), 1577 (10), 1345 (63), 1195 (47), 763 (100). MS (70 eV; *m/e* (%)): 301 (25) [M^+], 272 (69), 256 (100), 228 (17), 201 (20), 169 (30), 141 (31), 128 (12). MS (ESI, cone potential 9 V in MeOH/CH_3Cl): compound **5k**, 302 [M + H^+]; compound [2-D]-**5k**, 303 [M + H^+]. Anal. Calcd for $C_{19}H_{27}NO_2$ (301.4): C, 75.71; H, 9.03; N, 4.65. Found: C, 76.04; H, 9.33; N, 4.42.

***N*-(3-Ethoxy-5-(methoxymethyl)-1-phenylcyclopenta-2,4-dien-1-yl)morpholine (5l).** Pentacarbonyl(1-ethoxy-3-morpholino-3-phenylprop-2-en-1-ylidene)tungsten (**3c**; 569 mg, 1.00 mmol) and 2-methoxypropyne (**4d**; 105 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) as described above to give compound **5l** (243 mg, 77%, $R_f = 0.6$ on silica gel, *n*-pentane/diethyl ether 7:3, colorless oil). $[(COD)RhCl]_2$ (12 mg, 0.024 mmol) as catalyst produced compound **5l** (192 mg, 61%) after 36 h at 20 °C. $[(OC)_2RhCl]_2$ (10 mg, 0.026 mmol) gave compound **5l** (233 mg, 74%) after 12 h at 20 °C. Compound **5l** (239 mg, 76%) was obtained on reaction of pentacarbonyl(1-ethoxy-3-morpholino-3-phenylprop-2-en-1-ylidene)chromium (**3e**; 437 mg, 1.00 mmol) with alkyne **4d** in the presence of $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol). ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.68 (2 H, m, *o*-H Ph), 7.22 (2 H, m, *o*-H Ph), 7.16 (1 H, m, *p*-H Ph), 6.21 (1 H, m, 4-H), 5.06 (1 H, d, $^4J = 1.8$ Hz, 2-H), 4.06 and 3.73 (1:1 H, dd each, $^2J = 14.9$ Hz, $^4J = 2.0$ and 2.1 Hz, 1′-H_2), 3.65 [6 H, m, O$(CH_2)_2$ and OCH_2], 2.96 (3 H, s, OCH_3), 2.65 and 2.44 [2:2 H, m each, N$(CH_2)_2$], 1.17 (3 H, t, $^3J = 7.1$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 162.2 (C_q, C3), 153.1 (C_q, C5), 141.8 (C_q, *i*-C Ph), 128.8 (CH, *m*-C Ph), 127.4 (CH, *o*-C Ph), 127.3 (CH, *o*-C Ph), 123.8 (CH, C4), 97.9 (CH, C2), 79.5 (C_q, C1), 69.0 (CH_2, C1′), 67.8 [O$(CH_2)_2$], 65.0 (OCH_2CH_3), 58.4 (OCH_3), 48.3 [N$(CH_2)_2$], 14.5 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2954 (16), 2847 (20), 1642 (20), 1589 (42), 1336 (48), 1115 (100). MS (70 eV; *m/e* (%)): 315 (22) [M^+], 286 (43), 270 (100), 242 (13), 201 (14), 169 (24), 141 (31). Anal. Calcd for $C_{19}H_{25}NO_3$ (315.4): C, 72.34; H, 7.99; N, 4.44. Found: C, 72.37; H, 8.16; N, 4.31.

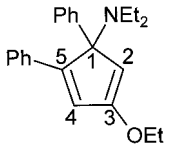
(1,5-Diphenyl-3-ethoxycyclopenta-2,4-dien-1-yl)dimethylamine (5m). Pentacarbonyl[1-ethoxy-3-(dimethylamino)-3-phenylprop-2-en-1-ylidene]tungsten (**3a**; 527 mg, 1.00 mmol) and phenylacetylene (**4c**; 153 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) as described above to give compound **5m** (231 mg, 76%, $R_f = 0.8$ on silica gel, *n*-pentane/diethyl ether 10:1, pale yellow oil, which solidified after standing). Compound **5m** (224 mg, 73%) was obtained on reaction of pentacarbonyl(1-ethoxy-3-morpholino-3-phenylprop-2-en-1-ylidene)chromium (**3d**; 395 mg, 1.00 mmol) with alkyne **4c** in the presence of $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol).



Data for **5m** are as follows. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.79 (4 H, m, 2 × *o*-H, 1- and 5-Ph), 7.09 and 7.05 (2:2 H, meach, 2 × *m*-H, 1- and 5-Ph), 6.95 (2 H, m, 2 × *o*-H, 1- and 5-Ph), 6.37 (1 H, d, $^4J = 2.0$ Hz, 4-H), 5.20 (1 H, d, $^4J = 2.0$ Hz, 2-H), 3.68 (2 H, m, OCH_2), 2.36 [6 H, s, N$(CH_3)_2$], 1.18 (3 H, t, $^3J = 6.9$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 161.8 (C_q, C3), 155.0 (C_q, C5), 141.3 (C_q, *i*-C, 1-Ph),-135.0 (C_q, *i*-C, 5-Ph), 128.3 and 128.2 (CH each, 2 × *m*-C, 1-

and 5-Ph), 127.7 and 126.9 (CH each, 2 × *p*-C, 1- and 5-Ph), 127.6 and 127.2 (CH each, 2 × *o*-C, 1- and 5-Ph), 124.4 (CH, C4), 100.7 (CH, C2), 81.6 (C_q, C1), 64.9 (OCH_2), 41.2 [$N(CH_3)_2$], 14.6 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2973 (66), 2927 (50), 1637 (29), 1587 (53), 1336 (100), 1110 (83). MS (70 eV; *m*/*e* (%)): 305 (48) [M^+], 276 (100), 261 (16), 248 (27), 233 (28), 203 (26). Anal. Calcd for $C_{21}H_{23}NO$ (305.4): C, 82.57; H, 7.60; N, 4.59. Found: C, 82.18; H, 7.60; N, 4.17.

(1,5-Diphenyl-3-ethoxycyclopenta-2,4-dien-1-yl)diethylamine (5n) and [2-D]-5n. Pentacarbonyl[1-ethoxy-3-(dimethylamino)-3-phenylprop-2-en-1-ylidene]tungsten (**3b**; 555 mg, 1.00 mmol) and phenylacetylene (**4c**; 153 mg, 1.5 mmol) in 4 mL of THF/MeOH (4:1) was reacted as described above with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) to give compound **5n** (258 mg, 77%, $R_f = 0.9$ on silica gel, *n*-pentane/diethyl ether 10:1, colorless oil, which solidified after standing). The reaction in 3.5 mL of THF and CH_3OD (175 mg) with $RhCl_3 \cdot 3H_2O$ (5 mg, 0.019 mmol) gave [2-D]-**5n** (254 mg, 76%) with a H/D ratio of 0.217 (ESI, cone potential 9 V, in MeOH/CH_3Cl), calculated H/D ratio 0.210.



Data for **5n** are as follows. ^1H NMR (400 MHz, C_6D_6, 300 K): δ 7.83 (2 H, m, *o*-H 1-Ph), 7.77 (2 H, m, *o*-H 5-Ph), 7.12 (2 H, m, *m*-H 1-Ph), 7.05 (2 H, m, *m*-H 5-Ph), 6.97 (1 H, m, *p*-H 1-Ph), 6.94 (1 H, m, *p*-H 5-Ph), 6.41 (1 H, d, $^4J = 2.0$ Hz, 4-H), 5.21 (1 H, d, $^4J = 2.0$ Hz, 2-H), 3.67 (2 H, q, $^3J = 7.0$ Hz, OCH_2), 2.79 [4 H, m, $N(CH_2)_2$], 1.18 (3 H, t, $^3J = 7.0$ Hz, OCH_2CH_3), 1.12 [6 H, t, $^3J = 7.0$ Hz, $N(CH_2CH_3)_2$]. ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 160.3 (C_q, C3), 154.6 (C_q, C5), 142.4 (C_q, *i*-C 1-Ph), 135.5 (C_q, *i*-C 5-Ph), 128.2 and 128.1 (CH each, *o*-C 1- and 5-Ph), 127.6 (CH, *p*-C 5-Ph), 127.6 and 127.5 (CH each, *m*-C 1- and 5-Ph), 126.9 (CH, *p*-C 1-Ph), 125.2 (CH, C4), 105.6 (CH, C2), 83.1 (C_q, C1), 64.8 (OCH_2), 45.5 [$N(CH_2)_2$], 15.3 [$N(CH_2CH_3)_2$], 14.7 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2973 (30), 1622 (100), 1343 (78), 1195 (40), 1041 (40). MS (70 eV; *m*/*e* (%)): 333 [M^+] (49), 304 (100), 276 (32), 261 (17), 233 (43), 203 (36). MS (ESI, cone potential 9 V in MeOH/CH_3Cl): compound **5n**, 334 [$M + H^+$]; compound [2-D]-**5n**, 335 [$M + H^+$]. Anal. Calcd for $C_{23}H_{27}NO$ (333.5): C, 82.82; H, 8.16; N, 4.20. Found: C, 82.77; H, 7.77; N, 4.24.

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