Organic Synthesis via Transition Metal Complexes. 112.[1] Reactivity Enhancement of Group VI Fischer Carbene Complexes by Copper and Rhodium Catalysts: Experimental Proof of a Carbene Rhodium Complex as an Intermediate

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Rhodium(I) compounds were found to efficiently catalyze reactions of Fischer carbene complexes. It was shown that the thermally quite unreactive tungstaoctatetraenes **14a**−**d** were readily transformed into spiro-fused vinylcyclopentadienes **15a**−**d** in the presence of catalytic amounts of $RhCl_3 \cdot 3H_2O$ in MeOH or $[(COD)RhCl]_2$. A reactivity enhancement was observed also for the transformation of the tungsten complex **8a** into vinylcyclopentadiene **10a**. Experimental proof for the intermediacy of carbene rhodium complexes in these reactions was provided by preparation of the rhodaoctatetraene **16c** from the reaction of the tungsten compound **14c** with a stoichiometric amount of $[(COD)RhCl]_2$. The carbene rhodium compound **16c** was transformed into the vinylcyclopentadiene **15c** thermally in a smooth reaction and showed a catalytic activity similar to $[(COD)RhCl]_2$. Not only rhodium but also copper compounds were found to be good catalysts for the π-cyclization of tungstaoctatetraenes.

Introduction

Application of Fischer carbene complexes[2] to organic synthesis has been amply demonstrated over the past decades.[3] Even though transfer reactions of carbene ligands from one metal to another have been reported, they have not been considered a means to properly adjust the reactivity of carbene complexes to a certain synthetic goal.[4,5] A brand new field of investigations is now directed toward a reactivtiy enhancement of carbene complexes in catalytic processes involving carbene transfer reactions. The investigation was initiated by Sierra et al.[6] and Narasaka et al.,[7] who, independently of each other, reacted Fischer carbene chromium complexes with olefins at ambient temperatures in the presence of catalytic amounts of palladium compounds and obtained coupling products of the carbene ligand with the olefin instead of cyclopropanation products of the olefin, in line with expectation of the chemistry of palladium but not of chromium carbene complexes. It has been shown by us for the first time that rhodium compounds would catalyze an insertion of alkynes into W=C and Cr=C bonds of 4-amino-1-metalla-1,3-butadienes (M = Cr, W)[8] and of 6-amino-1-metalla-1,3,5-hexatrienes[9] to give cyclopentadienes at temperatures as low as 20 °C (Scheme 1). Concerning the mechanism

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(1) For part 111 see: Göttker-Schnetmann, I.; Aumann, R.; Kataeva, O.; Holst, Ch.; Fröhlich, R. *Organometallics* **2001**, *20*, 2889−2904.

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

(3) For recent reviews see: (a) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187−198. (b) Wulff, W. In *Comprehensive Organometallic Chemistry*, Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York 1995; Vol. 12, Chapter 5.3. (c) Doyle, M. P. In *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. (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.

(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.* **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. P. *Organometallics* **1982**, *1*, 148−155. (k) Theopold, 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. *Organometallics* **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) (a) Sierra, M. A.; Mancheño, M. J.; Sáenz, E.; del Amo, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 6812−6813. (b) Sierra, M. A.; del Amo, J. C.; Mancheño, M. J.; Gómez-Gallego, M. *J. Am. Chem. Soc.* **2001**, *123*, 851−861.

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

(8) Göttker-Schnetmann, I.; Aumann, R. *Organometallics* **2001**, *20*, 346−354.

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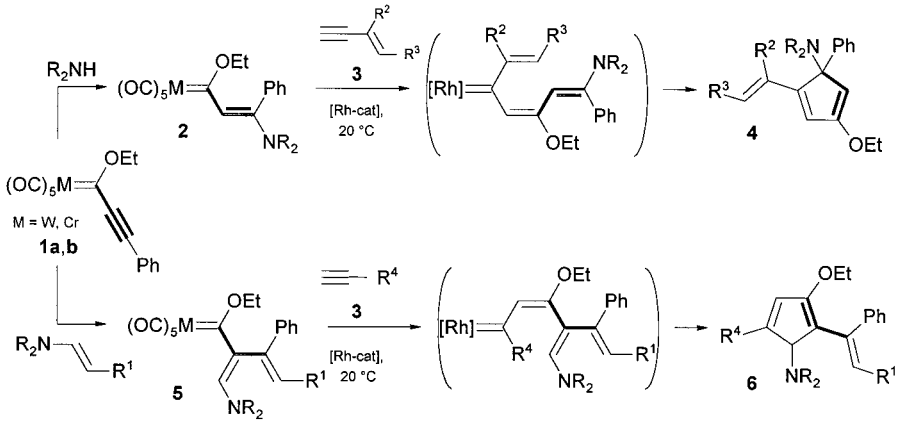
Scheme 1. Rhodium-Catalyzed Insertion of an Alkyne into a M=C Bond Exemplified by Two Different Routes to Vinylcyclopentadienes from (1-Alkynyl)carbene Complexes 1



of such transformation, up to date no experimental evidence could be provided that showed that carbene palladium or carbene rhodium complexes were involved as intermediates. With regard to the formation of vinylcyclopentadienes from group VI carbene complexes and alkynes it was shown that the alkyne insertion step was catalyzed by rhodium(I) species, but it was not obvious that rhodaoctatetraenes thus generated would undergo a π-cyclization to vinylcyclopentadienes **4** and **6** faster than the respective chroma- or tungstaoctatetraenes (Scheme 1).

We present experimental proof that it is not only the insertion of an alkyne into a M=C bond that can be catalyzed by rhodium but also the π-cyclization of the resulting 1-metalla-1,3,5-hexatriene unit to a cyclopentadiene. We now report on the preparation of a rhodaoctatetraene from the reaction of a tungstaoctatetraene with a stoichiometric amount of $[(COD)RhCl]_2$ and its smooth transformation into a vinylcyclopentadiene. It was further demonstrated that the rhodaoctatetraene thus generated was active as catalyst in this reaction. Furthermore, we report on the first example of a copper-catalyzed reaction of a carbene complex.

Vinylcyclopentadiene 10a by a Rhodium-Catalyzed π-Cyclization of 1-Tungsta-1,3,5,7-octatetraenes 8a. In view of our recent finding that the insertion of alkynes **2** into M=C bonds of cross-conjugated 1-metallahexatrienes $(OC)_5M{=}C(OEt)C(=CHNR_2)C{=}CR^1Ph$ **5** (M = W, Cr)[9] as well as 1-metalla-1,3-butadienes $(OC)_5M{=}C(OEt)C{=}C(Ph)NR_2$ **2** (M = W, Cr)[8] could be efficiently catalyzed by rhodium(I) compounds at 20 °C, and the 1-metallaolefins resulting thereby underwent a π-cyclization to vinylcyclopentadienes **4** and **6**, respectively (Scheme 1), we anticipated that it would be not only the insertion of an alkyne into a M=C bond but also the subsequent π-cyclization step of the 1-metallaoctatetraenes **8** to vinylcyclopentadienes **10** that possibly might be catalyzed by rhodium species.[10]

It was shown in recent studies that an addition of 2-amino-1,3-butadienes **7a**,**b** to (1-alkynyl)carbene complexes **1a**,**b** resulted in formation of conjugated metallaoctatetraenes **8a**−**d** as the major products as well as [4+2]-cycloadduct **9a** as the minor product (Scheme 2).[11] The latter compound underwent a spontaneous cyclization at 20 °C to produce the tetracyclic compound **12a**, while the 1-metallaoctatetraenes **8** exhibited a remarkable thermal stability and even at 65 °C did not undergo a π-cyclization (as anticipated on the basis of earlier studies[12]) to possibly afford vinylcyclopentadienes **10** and cycloheptatrienes **11**, respectively. Heating of compounds **8a**−**d** to 65 °C resulted in formation of untractable mixtures,[13] while 1-tungsta-1,3,5,7-octatetraene **8e** gave the cyclohexadiene derivative in 10% yield, but no cyclopentadiene.[14]

Results and Discussion

While the 1-tungsta-1,3,5,7-octatetraene **8a** did not undergo a π-cyclization at 65 °C (Scheme 2), this compound could be smoothly transformed into the vinylcyclopentadiene **10a** in the presence of the rhodium catalyst $[(COD)RhCl]_2$ (2.5 mol %, 20 °C, 36 h, THF) (Scheme 3). Now, this catalyzed reaction not only provides a synthetically valuable access to the formation of cyclopentadienes from Fischer carbene complexes but also supports the assumption (vide supra) that the π-cyclization of metallaolefins can indeed be catalyzed by rhodium species.

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

(10) The appearance of a 1-rhoda(II)-1,3,5-hexatriene species, obtained from a *o*-dialkynyl-substituted diazoacetophenone and catalytic rhodium(II) octanoate and subsequent π-cyclization to a cyclopentadiene, was postulated by: (a) Padwa, A.; Kassir, J. M.; Xu, S. L. *J. Org. Chem.* **1997**, *62*, 1642−1652. For a general review of (related) rhodium(II)-mediated cyclizations involving carbene rhodium complexes obtained from diazo compounds see: (b) Padwa, A. *J. Organomet. Chem.* **2000**, *610*, 88−101. For further work: (c) Padwa, A.; Weingarten, M. D. *J. Org. Chem.* **2000**, *65*, 3722−3732.

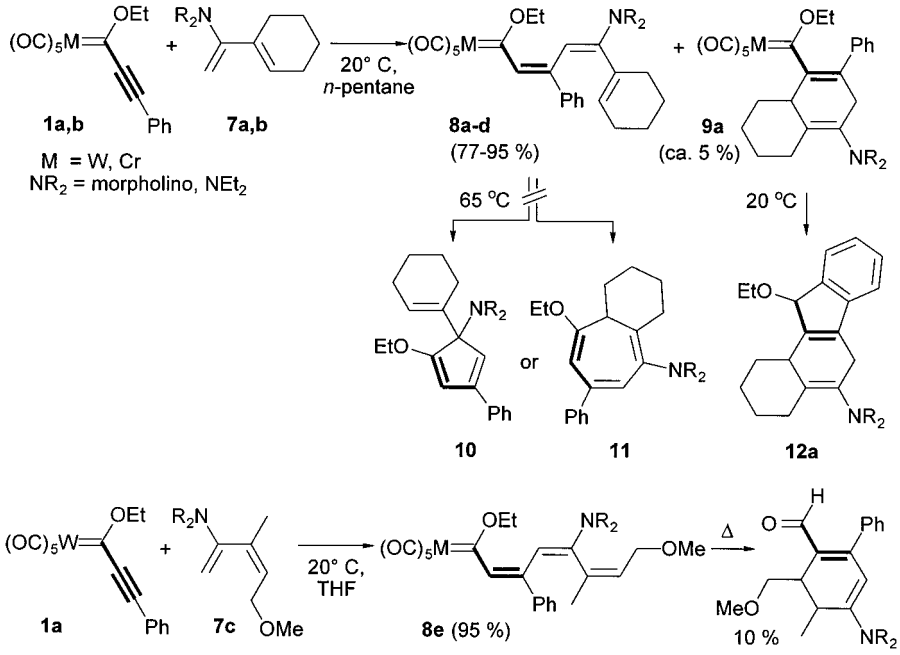
(11) Aumann, R.; Göttker-Schnetmann, I.; Wibbeling, B.; Fröhlich, R. *Tetrahedron Lett.* **1998**, *39*, 795−798.

(12) For the chemistry of 1-metalla-1,3,5-hexatrienes see: (a) 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*, 2343−2343. (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. (i) Wu, H.-P.; Aumann, R.; Fröhlich, R.; Wegelius, E.; Saarenketo, P. *Organometallics* **2000**, *19*, 2373−2381. (j) Wu, H.-P.; Aumann, R.; Venne-Dunker, S.; Saarenketo, P. *Eur. J. Org. Chem.* **2000**, 3463−3473. (k) Aumann, R.; Kössmeier, M.; Mück-Lichtenfeld, Ch.; Zippel, F. *Eur. J. Org. Chem.* **2000**, 37−49. (l) Aumann, R.; Kössmeier, M.; Roths, K.; Fröhlich, R. *Tetrahedron* **2000**, *56*, 4935−4949.

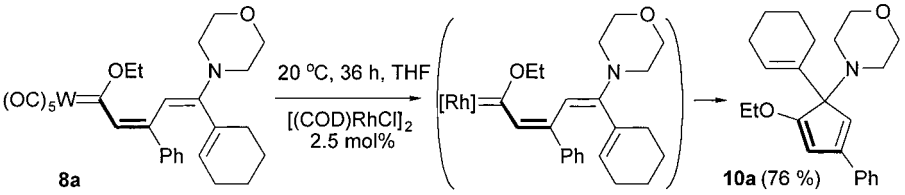
(13) Aumann, R.; Göttker-Schnetmann, I. Unpublished results.

(14) Similar results have been independently reported by: Barluenga, J.; Aznar, F.; Barluenga, S.; Fernández, M.; Martín, A.; García-Granda, S.; Piñera-Nicolás, A. *Chem. Eur. J.* **1998**, *4* (11), 2280−2298.

Scheme 2. Addition of 2-Amino-1,3-butadienes 7 to (1-Alkynyl)carbene Complexes 1 and Thermally Induced Cyclization of Adducts



Scheme 3. Facile Transformation the 1-Tungsta-1,3,5,7-octatetraene 8a into Vinylcyclopentadiene 10a by Means of a Rhodium(I) Catalyst



Spiro-Fused Vinylcyclopentadienes 15 by a Rhodium-Catalyzed π-Cyclization of Cross-Conjugated Tungstaoctatetraenes 14. Further examples of rhodium-catalyzed π-cyclization reactions of metallaolefins are provided in Scheme 4. It was shown, for example, that (rapidly interconverting) tungstaoctatetraenes **14**/**14′**, which are obtained in 48−86% yields[15] by addition of 1,3,3-trimethyl-2-(1-propen-3-ylidene)-indolines **13** to (1-alkynyl)carbene tungsten complexes **1a**,**c** (R = Ph, cyclohexenyl), are quite stable in solution even at 80−100 °C.[1] Even at 110 °C these compounds could be recovered almost completely after 14 h, while a C=C bond isomerization and a subsequent π-cyclization to a cyclopentadiene derivatives **15** were observed to a very minor extent only. However formation of vinylcyclopentadienes **15** from compounds **13** is dramatically improved by rhodium catalysts (Scheme 4).

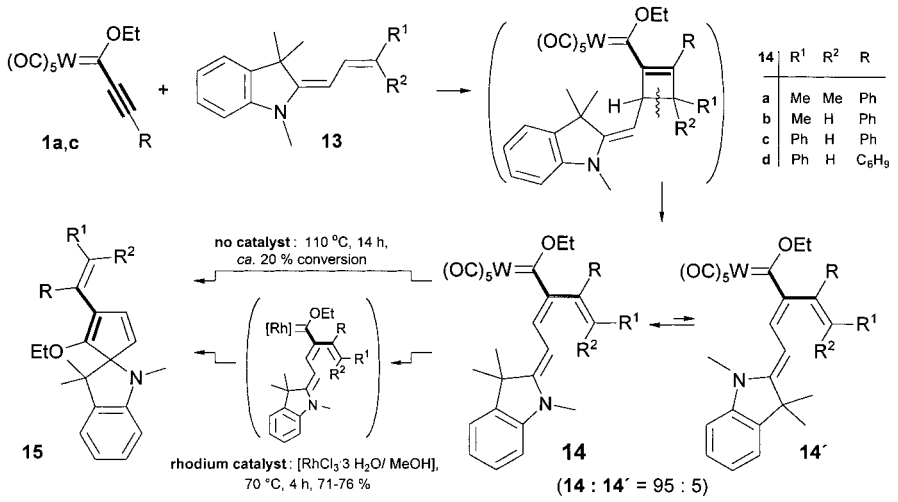
In our initial studies on the reactions shown in Scheme 4 both $[(COD)RhCl]_2$ and $RhCl_3 \cdot 3H_2O$ in MeOH were applied as catalysts in the temperature range from 20 to 70 °C.[16] Addition of 2.5 mol % of $[(COD)RhCl]_2$ to a solution of compound **14c** in THF at 20 °C after 12 h resulted in production of $W(CO)_6$ in trace amounts (identified by TLC), but no organic product could be detected. If 2.0 mol % $RhCl_3 \cdot 3H_2O$ and MeOH were used (instead of $[(COD)RhCl]_2$), compound **15c** was formed in ca. 10% yield at 20 °C after 12 h, but most of the starting material remained unchanged. Optimal yields of compounds **15a**−**d** in the range of 71−76% were obtained in THF or toluene at 70 °C both with $[(COD)RhCl]_2$ (reaction time ca. 12 h) and with $RhCl_3 \cdot 3H_2O$ and MeOH (reaction time of ca. 4 h) (Scheme 4). Since it was anticipated that a transmetalation of the carbene ligand from tungsten to rhodium might possibly be involved in this process, we were aiming for the preparation of such a carbene rhodium complex.

Stable Rhodium Carbene Complex 16c Obtained by Transmetalation. We finally succeeded in providing experimental proof of the intermediacy of rhodium carbene complexes in the catalytic reactions described in Scheme 4 and prepared the carbene rhodium complex **16c** by transmetalation of the carbene ligand of the tungsten complex **14c** with a stoichiometric amount of $[(COD)RhCl]_2$ (Scheme 5). The carbene tungsten compound **14c** was consumed almost completely at 20 °C in 1.5 h to give colorless hexacarbonyltungsten and a new yellow-orange compound. Workup by flash chromatography on silica gel afforded the red rhodaoctatetraene **16c** in 69% yield. On the basis of its ^{13}C NMR spectra (at 150, 100, and 90 MHz), the latter compound was unambiguously identified as a carbene rhodium complex by its doublet at δ 291.1, $^1J(^{103}Rh,^{13}C) = 44 \pm$

(15) Compounds **14b**−**d** were obtained in 82−86% yields, whereas compound **14a** was obtained in 48% yield together with a second isomer in 33% yield. For a detailed discussion see ref 1.

(16) $[(COD)RhCl]_2$ was proven to be an adequate catalyst in acid sensitive systems: see ref 8. $RhCl_3 \cdot (3H_2O)$/MeOH is an more active catalyst but due to formation of HCl only applicable on acid resistant systems: see ref 9.

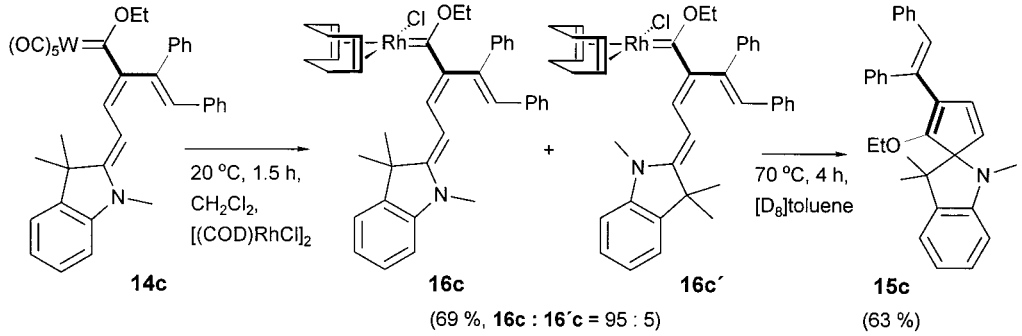
Scheme 4. Influence of Rhodium Catalysts on the π-Cyclization of Cross-Conjugated Tungstaoctatetraenes 14/14′ Generated from (1-Alkynyl)carbene Complexes 1a,c[1]



14,15	R	R^1	R^2	15 [%][a]
a	Ph	Me	Me	71
b	Ph	Me	H	74
c	Ph	Ph	H	76
d	cyclohex-1-enyl	Ph	H	73

[a] Isolated yield after flash chromatography of the reaction mixture obtained from compounds **14** and either 2.5 mol% $[(COD)RhCl]_2$ or 2 mol% $RhCl_3 \cdot (3H_2O)$/MeOH.

Scheme 5. Transmetalation of a Carbene Ligand from the Tungsten Complex 14c to a Rhodium Moiety and Formation of a Vinylcyclopentadiene Derivative 15c by π-Cyclization



1 Hz, typical of a Rh=C unit.[17,18] It should be noted that this is the first example of a transmetalated carbene complex, which has been explicitly shown to be an intermediate in a catalyzed reaction of a Fischer carbene complex.

According to NMR measurements, the COD ligand retains its η^4 coordination throughout the reaction. Two of the four olefinic protons of compound **16c** as well as the carbon atoms of the COD ligand *trans* to chloride are significantly shifted upfield (C*H* of COD: δ 5.76, 5.58, 3.62, and 3.10; *C*H: 103.8 and 103.0 [CH each, d each, $^1J(^{103}Rh,^{13}C) = 4.3$ Hz], 70.3 and 67.2 [CH each, d each, $^1J(^{103}Rh,^{13}C) = 14.3$ Hz]), while the proton signal NC(R)=CHC*H*=C(R) is shifted downfield to δ 10.19 (compound **14c**: δ 9.04) apparently due to an anisotropic deshielding. It was explicitly proven by (^{1}H,^{1}H)COSY, (^{1}H,^{13}C)GHSQC, and (^{1}H,^{13}C)GHMBC experiments that the connectivity of the carbon skeleton of the carbene ligand in compound **14c** and compound **16c** was identical. The ^{1}H NMR spectrum shows two independent sets of signals in a ratio of ca. 95:5 tentatively assigned to stereoisomers **16c** and **16c′** on the basis of NOE and ROESY experiments at 273 K, 600 MHz in [D$_8$]toluene.

(17) Carbene rhodium complexes of the type Rh=C(OR)C are not reported to our knowledge; those of the type Rh=C(OM)C are scarcely reported: (a) Erker, G.; Lecht, R.; Tsay, Y.-H.; Krüger, C. *Chem. Ber.* **1987**, *120*, 1763−1765. (b) Erker, G.; Mena, M.; Hofmann, U.; Menjón, B.; Petersen, J. L. *Organometallics* **1991**, *10*, 291−298. (c) Yeston, J. S.; Bergmann, R. G. *Organometallics* **2000**, *19*, 2947−2949.

(18) For pioniering work on carbene rhodium complexes of the type $Rh=C(NR_2)_2$ see: (a) Cardin, D. J.; Doyle, M. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 927−928. (b) Coleman, A. W.; Hitchcock, P. B.; Lappert, M. F.; Maskell, R. K.; Müller, J. H. *J. Organomet. Chem.* **1985**, *296*, 173−196. (c) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Shaw, D. B.; Spyropoulos, K.; Warhust, N. J. W. *J. Organomet. Chem.* **1993**, *459*, 311−317. Synthetic strategies toward the generation of carbene rhodium complexes of the type $Rh=CR_2$ have been developed by the Werner group: (d) Schwab, P.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem.* **1993**, *105*, 1498−1500; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1480−1482. (e) Schwab, P.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1994**, 3415−3425. (f) Werner, H. *J. Organomet. Chem.* **1995**, *500*, 331−336. (g) Werner, H.; Schwab, P.; Bleuel, E.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1997**, *3* (8), 1375−1384. (h) Bleuel, E.; Gevert, O.; Laubender, M.; Werner, H. *Organometallics* **2000**, *19*, 3109−3114. (i) Werner, H.; Schwab, P.; Bleuel, E.; Mahr, N.; Windmüller, B.; Wolf, J. *Chem. Eur. J.* **2000**, *6* (24), 4461−4470. (j) Bleuel, E.; Weberndörfer, B.; Werner, H. *J. Organomet. Chem.* **2001**, *617*, 502−510.

While an interconversion of the tungsten compounds **14c** and **14c′** could be proven by spin-saturation transfer experiments,[19] this was not the case for the rhodium compounds **16c** and **16c′** within a similar temperature range. A coordination of a carbon monoxide ligand to rhodium is excluded on the basis of ^{13}C NMR and IR measurements. MALDI-TOF experiments show mass peaks at $M^+ - COD$ and $M^+ - Cl$ and a coincidence of the observed and the simulated isotope pattern. The elemental analysis found C, 68.55; H, 6.00; and N, 1.54 is slightly critical with respect to the nitrogen value (calcd C, 68.87; H, 6.37; N, 2.06), if a molecular formula $C_{39}H_{43}ClNORh$ is assumed for compound **16c**.

Structural information obtained from NOE and ROESY experiments (600 MHz, 273 K) comprise a positive signal enhancement of one of the olefinic protons of the COD ligand proton at δ 3.56, which is located *trans* to the chloro ligand, the geminal dimethyl group $C(CH_3)_2$, and the (high-field) proton NC(R)=C*H*CH=C(R) at δ 6.12 on irradiation of the (low-field proton) NC(R)=CHC*H*=C(R). An intensity enhancement was found also for the signals NCH_3 and PhC*H*=C(Ph) on irradiation of NC(R)=C*H*CH=C(R). It was shown by ^1H NMR experiments that the isomers **16c** and **16c′** do not interconvert on the NMR time scale. A spin-saturation transfer between the two olefinic COD protons at the position *trans* to the chloro ligand is not observed, indicating a high rotation barrier of the Rh=C bond. An apparent increase in the back-donation from rhodium atom to the carbene carbon atom[20] is reflected also by a higher isomerization barrier of the enamine double bond N*C*(R)=*C*H in the rhodium compounds **16c** and **16c′** compared to the tungsten compounds **14** and **14′**.[21] On the basis of the ROE enhancements, the plane defined by the square-planar coordination sphere at rhodium appears to be perpendicular toward the plane defined by the carbene unit, in line with earlier reports on *N*-heterocyclic carbene rhodium complexes.[22]

The thermally induced transformation of the rhodaoctatetraene **16c** into the vinylcyclopentadiene **15c** could be monitored by ^1H and ^{13}C NMR spectra in [D_8]-toluene at 70 °C, 4 h. Compound **15c** was obtained in this experiment in a somewhat lower isolated yield of 63% than under conditions of the cataysis with 2 mol % $RhCl_3 \cdot 3H_2O$ (76% isolated yield) (Scheme 5). This drop in chemical yield was attributed to a partial metal-induced polymerization of compound **15c** in more concentrated solution, particularly since additional broad signals were observed in this case both in the aromatic and in the aliphatic region of the ^1H NMR spectra.

It was shown that rhodaoctatetraene **16c** was indeed catalyzing formation of the vinylcylopentadiene **15c** from tungstaoctatetraene **14c**. In the presence of 4 mol % of rhodaoctatetraene **16c**, the tungsten compound **14c** was smoothly transformed into the cyclopentadiene **15c** according to NMR spectra in [D_8]toluene at 70 °C within 10 h (74% isolated yield), while a small signal at δ 10.02, attributed to Rh=C(OEt)C(R)=C*H*CH of compound **16c**, was persistently visible during the reaction time. Some further information on the nature of intermediates was derived from monitoring the stoichiometric transmetalation of the tungstaoctatetraene **14c** with $[(COD)RhCl]_2$ into the rhodaoctatetraene **16c** at 30 °C and its subsequent transformation into the cyclopentadiene **15c** at 70 °C. After ca. 30 min at 70 °C a new carbene rhodium complex, characterized by a carbon signal at δ 267.3 [d, $^1J(^{103}Rh,^{13}C) = 48$ Hz], two CO signals at 208.3 [d, $^1J(^{103}Rh,^{13}C) = 45$ Hz] and 186. 0 [d, $^1J(^{103}Rh,^{13}C) = 91$ Hz], as well as a proton doublet at 10.70, was detected as a transient species. This compound certainly contains a Rh=C(OEt)C(R)=C*H* unit and two CO units replacing the COD ligand (which was detected in metal-free COD in the NMR spectrum). After 4 h at 70 °C the ^1H NMR spectra were essentially identical to those previously obtained on thermolysis of the carbene rhodium complex **16c** at 70 °C, 4 h, including the aforementioned broad signals assigned to formation of polymers and a slight drop in chemical yields of compound **15c**.

First Example of a Copper-Catalyzed Reaction of a Fischer Carbene Complex. On the basis of the finding that reactions of Fischer carbene complexes can be efficiently catalyzed by transmetalation, we are currently investigating different metal systems with respect to their catalytic influence on the reaction course of Fischer carbene complexes. Here we wish to report that also copper(I) compounds might serve as efficient catalysts for the π-cyclization of metallaolefins. It was found, for example, that formation of the vinylcyclopentadiene **15c** from tungstaoctatetraene **14c** is strongly enhanced by CuI in the presence of Et_3N (5 mol % CuI and 8 mol % Et_3N in toluene; 70 °C, 16 h, 74% yield of compound **15c**).

Attempted Stereoinduction of π-Cyclization Induced by Rhodium(I) and Copper(I) Catalysts in the Presence of Chiral Auxiliaries. In view of the fact that rotation of the Rh=C bond in compound **16c** was found to be appreciably hindered (vide supra), we investigated the influence of chiral ligands, like DIOP or BINAP, in the enantioselectivity of the rhodium-catalyzed π-cyclization leading to formation of vinylcyclopentadiene **15c** (Scheme 6). Similar experiments were performed with copper catalysts and chiral amines.

Compound **14c** was reacted with solutions of 2.5 mol % $[(COD)RhCl]_2$ and 7 mol % (−)-DIOP and (−)-BINAP in toluene, respectively. The efficiency of our catalytic system was reduced noticeably by the addition of the phosphorus ligands with respect to the reaction time, which had to be tripled at 70 °C to 36 h for a complete conversion, even though the overall yields remained unchanged. Analysis of the reaction mixture on a chiral HPLC column (ChiraGrom HPLC column, UV detector (210 nm) and *n*-hexane as eluant) showed that a 1:1 mixture of enantiomers **15c** was obtained. Reaction of compound **14c** in the presence of 5 mol % CuI and 7

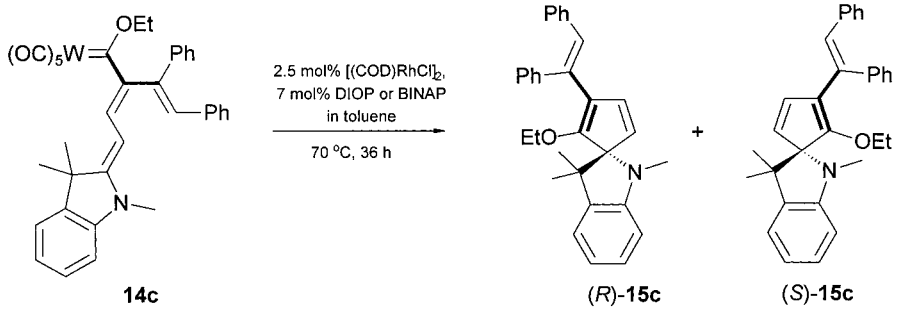
(19) For a detailed discussion of chemical exchange phenomena in compounds **14** see ref 1.

(20) For a discussion of the rotation parameters of the Rh=C bond in N-heterocyclic carbene rhodium complexes see: Doyle, M. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 679−680. While Lappert's carbene rhodium complexes of the $Rh=C(NR_2)_2$ type exhibit a strong σ-donation of the carbene ligand and a weak π-back-donation of the metal, Werner's compounds of type $Rh=CR_2$ as well the compounds studied in this paper show a strong σ-donation and strong π-back-donation according to the ^{13}C chemical shift of the Rh=C bond. X-ray data are provided in refs 18b−f.

(21) A weak back-donation would be equivalent to a more α,ω-zwitterionic carbiminium rhodate structure $^-Rh-C(OEt)=C(R)CH=CHC(R)=N^+$. In fact the zwitterionic character of tungstaoctatetraenes **14** due to the electron-withdrawing CO ligands should be higher than that of compound **16c**.

(22) For examples see: (a) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Boehm, K. *Eur. J. Inorg. Chem.* **1998**, 913−919. (b) References 18b−f.

Scheme 6. Attempted Chiral Induction by a Rhodium-Catalyzed π-Cyclization



14c (*R*)-**15c** (*S*)-**15c**

mol % (−)-sparteine, 14 mol % (+)-methoxyproline, or 14 mol % (+)-1-phenylethylamine in toluene or 1,2-dichloroethane afforded vinylcyclopentadiene **15c** after 12−16 h at 70 °C, but no enantioselectivity was observed in these transformations.

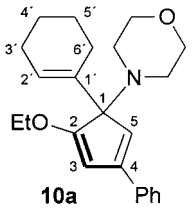
Conclusion

A strong reactivity enhancement of the π-cyclization of tungstaoctatetraenes **8** and **14** to give vinylcyclopentadienes **10a** and **15a**−**d** was achieved in the presence of catalytic amounts of rhodium(I) catalysts. Evidence is presented that the catalysis involves the intermediate formation of rhodium carbene complexes, since the rhodaoctetraene **16c** could be generated and isolated by transmetalation of the carbene ligand from the tungstaoctatetraene **14c** with stoichiometric amounts of $[(COD)RhCl]_2$. The carbene rhodium complex **16c** has been smoothly transformed into the vinylcyclopentadiene **15c**. It was shown for the first time that copper(I) compounds are good catalysts for reactions of Fischer carbene complexes.

Experimental Section

NMR: Bruker AM 360, Bruker AMX 400, and Varian U 600. All new compounds were routineously analyzed by ^{1}H, ^{13}C, DEPT, (^{1}H,^{1}H)COSY, (^{1}H,^{13}C)GHSQC, and (^{1}H,^{13}C)GHMBC experiments on a Bruker AMX 400. NOE-DIFF experiments were performed on a Bruker AM 360. ROESY experiments as well as dynamic NMR experiments were performed on a Varian U 600. IR: FT-IR BIO-RAD DIGILAB DIVISION FTS-45. MS: FINNIGAN MAT8200 and LAZARUS III DE[23] (MALDI). Elemental analyses: HERAEUS CHN-O Rapid. Column chromatography: Merck silica gel 60F. Flash chromatography was performed under an argon pressure of 1.2 bar. TLC: Merck silica gel $60F_{254}$. R_f values are based on TLC tests. All reactions were performed under argon. CH_2Cl_2 (p.a. quality), 1,2-dichloroethane, diethyl ether, *n*-pentane, THF, toluene C_6D_6, and $[D_8]$toluene were used as purchased and not dried. Compounds **1** were prepared according to ref 24, compound **8a** according to ref 11, and compounds **14** according to ref 1.

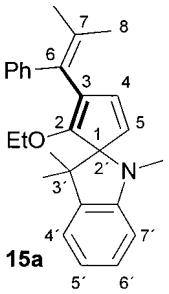
[1-(Cyclohex-1-enyl)-2-ethoxy-4-phenyl-2,4-cyclopentadien-1-yl]morpholine (10a). Pentacarbony[(2*Z*)-5-(cyclohex-1-enyl)-1-ethoxy-3-phenyl-2,4-pentadien-1-ylidene]tungsten (**1a**) (337 mg, 0.50 mmol) and $[(COD)RhCl]_2$ (6 mg, 0.012 mmol) were stirred for 36 h at 20 °C in 3.5 mL of THF until compound **1a** was consumed (TLC test). Chromatography on silica gel with *n*-pentane/diethyl ether (20:1) afforded compound **10a** (133 mg, 0.38 mmol, 76%, R_f = 0.7 in *n*-pentane/diethyl ether, 20:1, pale yellowish oil).



10a

^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.48 (2 H, m, *o*-H Ph), 7.21 (2 H, m, *m*-H Ph), 7.13 (1 H, m, *p*-H Ph), 6.07 (1 H, d, ^4J = 2.0 Hz, 5-H), 6.02 (1 H, m, 2′-H), 5.36 (1 H, d, ^4J = 2.0 Hz, 3-H), 3.72 (4 H, m, 2 OCH_2), 3.60 (2 H, m, OCH_2CH_3), 2.93 and 2.66 (2:2 H, m each, 2 NCH_2), 2.30 and 2.27 (1:1 H, m each, 6′-H_2), 2.00 (2 H, m, 3-H_2), 1.63 (2 H, m, 5′-H_2), 1.52 (2 H, m, 4′-H_2), 1.11 (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 169.7 (C_q, C2), 142.9 (C_q, C4), 136.4 and 136.1 (C_q each, C1′ and *i*-C Ph), 128.7 (CH, *m*-C Ph), 127.7 (CH, *p*-C Ph), 126.0 (CH, *o*-C Ph), 124.1 (CH, C2′), 121.7 (CH, C5), 97.8 (CH, C3), 80.6 (C_q, C1), 68.2 (2 OCH_2), 65.2 (OCH_2CH_3), 48.3 (2 $N(CH_2)$, 26.3 (CH_2, C6′), 61.1 (CH_2, C3′), 23.9 (CH_2, C5′), 23.0 (CH_2, C4′), 14.7 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2926 (56), 2849 (46), 1616 (18), 1568 (25), 1203 (56), 1112 (100). MS (70 eV), *m/e* (%): 351 (3) [M^+], 322 (31), 266 (100), 237 (30), 178 (22), 165 (37), 152 (27). Anal. Calcd for $C_{23}H_{29}NO_2$ (351.5): C, 78.59; H, 8.32; N, 3.98. Found: C, 78.50; H, 8.50; N, 3.80.

Spiro[2-ethoxy-3-(1-phenyl-2-methylprop-1-enyl)cyclopentadiene-1,2′-*N*-methyl-3′,3′-dimethylindoline] (15a). Compound **15a** was obtained from pentacarbonyl[1-ethoxy-2-(1,2-diphenylethenyl)-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-1-ylidene]tungsten (**14a**) (284 mg, 0.40 mmol) and $[(COD)RhCl]_2$ (2 mg, 0.004 mmol) in 3.5 mL of toluene at 70 °C, 12 h by flash chromatography on silica gel (110 mg, 0.28 mmol, 71%, R_f = 0.8 in *n*-pentane/diethyl ether, 20:1, pale yellowish oil). $RhCl_3 \cdot (3H_2O)$ (2.6 mg, 0.01 mmol) and 0.3 mL of MeOH were somewhat more efficient catalysts, which gave compound **14a** at 70 °C, 4 h in 72% yield.



15a

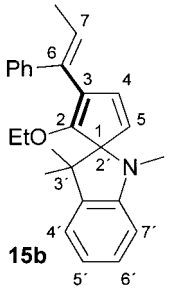
^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.26 (2 H, m, *o*-H Ph), 7.20 (2 H, m, *m*-H Ph), 7.17 (1 H, m, 6′-H), 7.07 (1 H, m, *p*-H

(23) The mass spectrometer LAZARUS III DE was provided by Dr. H. Luftmann, Organisch-Chemisches Institut der Universität Münster. Data sets were collected with LeCroy DSO 9450A instrumentation.

(24) (a) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163−242. (b) Aumann, R.; Fröhlich, R.; Meyer, O.; Prigge, J. *Organometallics* **1999**, *18*, 1369−1380.

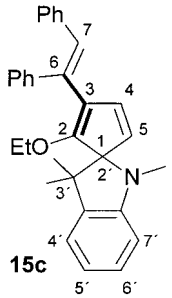
Ph), 6.95 (1 H, m, 4′-H), 6.80 (1 H, m, 5′-H), 6.45 (1 H, m, 7′-H), 6.01 (1 H, d, ^3J = 6.1 Hz, 4-H), 5.65 (1 H, d, ^3J = 6.1 Hz, 5-H), 3.75 (2 H, m, OCH_2), 2.59 (3 H, s, NCH_3), 1.81 and 1.68 (3:3 H, s each, 7-CH_3 and 8-H_3), 1.42 and 1.35 [3:3 H, s each, 3′-$(CH_3)_2$], 0.76 (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 161.4 (C_q, C2), 152.3 (C_q, C7′a), 141.8 (C_q, *i*-C Ph), 140.3 (C_q, C3′a), 138.1 (CH, C4), 132.8 and 131.6 (C_q each, C6 and C7), 130.0 (CH, *o*-C Ph), 128.2 (CH, *m*-C Ph), 127.5 (C_q,C6′), 126.7 (CH, *p*-C Ph), 124.9 (CH, C5), 120.8 (CH, C4′), 117.6 (CH, C5′), 116.2 (C_q, C3) 106.6 (CH, C7′), 88.4 (C_q, C1), 65.1 (OCH_2), 46.9 (C_q, C3′), 30.5 (NCH_3), 29.1 and 22.3 [CH_3, 3′-$(CH_3)_2$], 23.3 and 21.9 (CH_3 each, 7-CH_3 and C8), 15.7 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2924 (57), 2856 (29), 1605 (39), 1557 (16), 1483 (100), 1445 (49), 1363 (26), 1300 (35). MS (70 eV), *m*/*e* (%): 385 (31) [M$^+$], 370 (69), 356 (100), 326 (26), 210 (21), 158 (30). Anal. Calcd for $C_{27}H_{31}NO$ (385.6): C, 84.11; H, 8.10; N, 3.63. Found: C, 84.14; H, 8.07; N, 3.61.

Spiro[2-ethoxy-3-(1-phenylprop-1-enyl)cyclopentadiene-1,2′-*N*-methyl-3′,3′-dimethylindoline] (15b). Compound **15b** was obtained from pentacarbonyl[1-ethoxy-2-(1-phenylprop-1-enyl)-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-1-ylidene]tungsten (**14b**) (348 mg, 0.50 mmol) and [(COD)RhCl]$_2$ (2.5 mg, 0.005 mmol) in 3.5 mL of toluene at 70 °C, 12 h by flash chromatography on silica gel (137 mg, 0.37 mmol, 74%, R_f = 0.9 in *n*-pentane/diethyl ether, 20:1, pale yellowish oil). $RhCl_3 \cdot 3H_2O$ (2.6 mg, 0.01 mmol) and 0.3 mL of MeOH instead of [(COD)RhCl]$_2$ gave compound **15b** in 74% yield at 70 °C, 4 h.



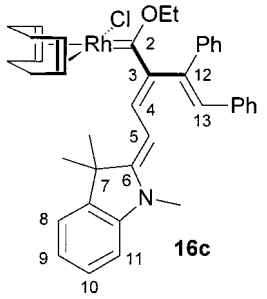
^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.27 (2 H, m, *o*-H Ph), 7.19 (2 H, m, *m*-H Ph), 7.14 (1 H, m, 6′-H), 7.08 (1 H, *p*-H Ph), 6.95 (1 H, m, 4′-H), 6.78 (1 H, m, 4-H), 6.42 (1 H, m, 7′-H), 6.14 (1 H, d, ^3J = 6.1 Hz, 4-H), 5.82 (1 H, q, ^3J = 7.1 Hz, 7-H), 5.66 (1 H, d, ^3J = 6.1 Hz, 5-H), 3.62 (2 H, m, OCH_2), 2.58 (3 H, s, NCH_3), 1.66 (3 H, d, ^3J = 7.1 Hz, 8-H_3), 1.43 and 1.34 [3:3 H, s each, 3′-$(CH_3)_2$], 0.65 (3 H, t, ^3J = 7.2 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 161,7 (C_q, C2), 152.2 (C_q, C7′a), 140.3 (C_q, C3′a), 139.4 (C_q, *i*-C Ph), 137.1 (CH, C4), 136.4 (C_q, C6), 129.7 (CH, *o*-C Ph), 128.3 (CH, *m*-C Ph), 127.5 (CH, C6′), 127.1 (CH, *p*-C Ph), 126.1 (CH, C7), 125.6 (CH, C5), 120.8 (CH, C4′), 118.8 (C_q, C3), 117.6 (CH, C5′), 106.4 (CH, C7′), 88.4 (C_q, C1), 66.5 (OCH_2), 47.2 (C_q, C3′), 30.4 (NCH_3), 29.0 and 22.0 [CH_3 each, 3′-$(CH_3)_2$], 15.5 (OCH_2CH_3), 15.1 (CH_3, C8). IR (diffuse reflection), cm^{-1} (%): 2975 (12), 2861 (10), 1605 (51), 1556 (22), 1483 (100), 1443 (40), 1361 (32), 1300 (55). MS (70 eV), *m*/*e* (%): 371 (37) [M$^+$], 356 (87), 342 (100), 327 (15), 312 (24), 284 (15), 268 (12), 210 (22), 182 (21), 167 (19), 158 (33). Anal. Calcd for $C_{26}H_{29}NO$ (371.5): C, 84.06; H, 7.87; N, 3.77. Found: C, 83.85; H, 7.93; N, 3.63.

Spiro[2-ethoxy-3-(1,2-diphenylethenyl)cyclopentadiene-1,2′-*N*-methyl-3′,3′-dimethylindoline] (15c) and η^4-Cyclooctadiene[1-ethoxy-2-(1,2-diphenylethenyl)-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-1-ylidene]-rhodium Chloride (16c). Compound **15c** was obtained from pentacarbonyl[1-ethoxy-2-(1,2-diphenylethenyl)-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-1-ylidene]tungsten (**14c**) (378 mg, 0.50 mmol) and [(COD)RhCl]$_2$ (2.5 mg, 0.005 mmol) in 3.5 mL of toluene at 70 °C, 12 h by flash chromatography on silica gel (164 mg, 76%, R_f = 0.8 in *n*-pentane/diethyl ether, 10:1, pale yellowish oil). $RhCl_3 \cdot (3H_2O)$ (2.6 mg, 0.01 mmol) and 0.3 mL of MeOH instead of [(COD)RhCl]$_2$ at 70 °C for 12 h gave compound **15c** in 75% yield. Application of the copper catalyst CuI (4.8 mg, 0.025 mmol) and Et_3N (4 mg, 0.04 mmol) at 70 °C for 16 h gave compound **15c** in 75% yield. Experiments toward attempted stereoinduction with different catalysts—(a) 2.5 mol % [(COD)RhCl]$_2$ and 5 mol % (−)-DIOP or (−)-BINAP in toluene, (b) 5 mol % CuI and 7 mol % of (−)-sparteine in 1,2-dichloroethane, (c) 5 mol % CuI and 14 mol % of (+)-methoxyproline in toluene, (d) 5 mol % CuI and 14 mol % of (+)-1-phenylethylamine in toluene—gave compound **15c** in each case as racemic mixtures. The stoichiometric reaction of CuI, 1.5 equiv of Et_3N, and compound **14c** yielded compound **15c** after 60 h at 20 °C, but no isolable copper carbene could be detected. The rhodium compound **16c** was obtained from compound **14c** (378 mg, 0.50 mmol) and [(COD)RhCl]$_2$ (126 mg, 0.26 mmol) in 10 mL of dichloromethane at 20 °C, 1.5 h (compound **14c** was nearly totally consumed according to a TLC test), flash chromatography on silica gel with *n*-pentane/diethyl ether, 1:1 (234 mg, 69%, R_f = 0.4 in *n*-pentane/diethyl ether, 1:1). An analytically pure sample of solid **16c** was obtained from a filtered benzene solution of compound **16c** by careful removal of the solvent at 0 °C. Rearrangement of compound **16c** (103 mg, 0.15 mmol) was studied by monitoring the NMR spectra in [D_8]toluene. Compound **15c** was isolated from this sample after 4 h at 70 °C by flash chromatography on silca gel (41 mg, 63%). Stoichiometric reaction of compound **14c** (179 mg, 0.25 mmol) with [(COD)RhCl]$_2$ (63 mg, 0.13 mmol) in [D_8]toluene at 30 °C was monitored by ^{1}H NMR experiments to give a complete transformation into compound **16c** and $W(CO)_6$ after 1 h. At 70 °C after 4 h compound **15c** (69 mg, 64% after chromatography) was obtained. ^{1}H and ^{13}C NMR spectra after 60, 120, and 240 min at 70 °C showed additional signals of a carbonyl carbene rhodium complex as a transient species. Reaction of compound **14c** (179 mg, 0.25 mmol) in [D_8]toluene and 4 mol % carbene rhodium complex **16c** (7 mg, 0.01 mmol) gave compound **15c** (80 mg, 74%) after 12 h at 70 °C.



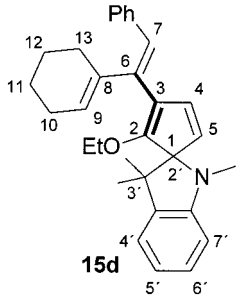
^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.33 (2 H, m, *o*-H 12-Ph), 7.16 (1 H, m, 6′-H), 7.07 (4 H, m, *o*-H 7-Ph and *m*-H 6-Ph), 7.03 (1 H, m, *p*-H 6-Ph), 6.95 (3 H, m, *m*-H 7-Ph and 4′-H), 6.88 (1 H, *p*-H 7-Ph), 6.79 (2 H, m, 5′-H and 7-H), 6.43 (1 H, m, 7′-H), 6.12 (1 H, d, ^3J = 6.2 Hz, 4-H), 5.67 (1 H, d, ^3J = 6.2 Hz, 5-H), 3.75 (2 H, m, OCH_2), 2.61 (3 H, s, NCH_3), 1.47 and 1.36 [3:3 H, s each, 3′-$(CH_3)_2$], 0.63 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 163.9 (C_q, C2), 152.1 (C_q, C7′a), 140.2 (C_q, C3′a), 139.6 (C_q, C6), 137.6 (C_q, *i*-C 7-Ph), 136.6 (CH, C4), 136.5 (C_q, *i*-C 6-Ph), 130.3 (CH, *o*-C 6-Ph), 129.9 (CH, C7), 129.7 and 128.7 (CH each, *m*-C 6-Ph and *o*-C 7-Ph), 128.4 (CH, *m*-C 7-Ph), 127.7 and 127.6 (CH each, C6′ and *p*-C 6-Ph), 127.0 (CH, *p*-C 7-Ph), 125.7 (CH, C5), 120.9 (CH, C4′), 118.9 (C_q, C3), 117.7 (CH, C5′), 106.5 (CH, C7′), 88.7 (C_q, C1), 67.2 (OCH_2), 47.4 (C_q, C3′), 30.4 (NCH_3), 29.1 and 22.0 [CH_3 each, 3′-$(CH_3)_2$], 15.6 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2975 (21), 2863 (14), 1605 (56), 1554 (13), 1484 (100), 1445 (35), 1299 (33). MS (70 eV), *m*/*e* (%): 433 (47) [M$^+$], 418 (100), 404 (99), 372 (24), 284 (13), 268

(19), 215 (34), 178 (24), 159 (37). Anal. Calcd for $C_{31}H_{31}NO$ (433.6): C, 85.87; H, 7.21; N, 3.23. Found: C, 85.63; H, 7.54; N, 3.16.



^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 10.19 (1 H, d, ^3J = 13.4 Hz, 4-H), 7.47 (2 H, m, *o*-H 13-Ph), 7.24 (2 H, *o*-H 12-Ph), 7.08 (2 H, m, *m*-H 13-Ph), 7.02 (2 H, m, *m*-H 12-Ph), 6.97 (4 H, m, 8-H, 10-H, *p*-H 12- and 13-Ph), 6.86 (1 H, m, 9-H), 6.64 (1 H, s, 13-H), 6.24 (1 H, m, 11-H), 6.12 (1 H, d, ^3J = 13.4 Hz, 5-H), 6.00 and 5.26 (1:1 H, m each, OCH_2), 5.76 and 5.58 [1:1 H, m each, COD-C*H cis* to Cl], 3.62 and 3.10 [1:1 H, m, each, COD-CH *trans* to Cl]; 2.67, 2.38, 2.13, 2.07, 1.97, 1.83 and 1.71 (1:2:1:1:1:1:1 H, m each, COD), 2.34 (3 H, s, NCH_3), 2.02 and 1.95 [3:3 H, s each, 7-$(CH_3)_2$], 1.19 (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 291.1 [C_q, d, $^1J(^{13}C,^{103}Rh)$ = 45 Hz, C2], 169.0 (C_q, C6), 162.0 (CH, C4), 144.0 (C_q, C3), 143.8 (C_q, C11a), 141.3 (C_q, *i*-C 13-Ph), 140.4 (C_q, C7a), 138.4 (C_q, C12), 138.2 (C_q, *i*-C 12-Ph), 131.2 (CH, C13), 129.8 and 129.7 (CH each, *o*-C 12- and 13-Ph), 128.4 and 128.3 (CH each, *m*-C 12- and 13-Ph), 128.0 (CH, C8), 127.1 and 127.0 (CH each, *p*-C 12- and 13-Ph), 122.6 and 122.1 (CH each, C9 and C10), 108.0 (CH, C11), 103.8 and 103.0 [CH each, COD-CH *cis* to Cl], 96.1 (CH, C5), 75.2 (OCH_2), 70.3 and 67.2 [CH each, d each, $^1J(^{13}C,^{103}Rh)$ = 15.0 and 14.8 Hz, COD-CH *trans* to Cl], 48.0 (C_q, C7); 34.3, 32.4, 29.6 and 27.8 (CH_2 each, COD); 28.8, 28.8 and 28,7 [CH_3 each, NCH_3 and 7-$(CH_3)_2$], 15.1 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2973 (15), 2871 (13), 1561 (92), 1308 (40), 1189 (90), 1172 (100), 1118 (60). MS (MALDI, DCTB, 337.0 nm, 3 ns): 644 [M^+ − Cl], 571(573) [M^+ − COD]. Anal. Calcd for $C_{39}H_{43}NOClRh$ (680.1): C, 68.87; H, 6.37; N, 2.06. Found: C, 68.55; H, 6.00; N, 1.54.

Spiro[2-ethoxy-3-(1-cyclohex-1-enyl-2-phenylethenyl)-cyclopentadiene-1,2′-*N*-methyl-3′,3′-dimethylindoline] (15d). Compound **15d** was obtained from pentacarbonyl[1-ethoxy-2-(1-cyclohex-1-enyl-2-phenylethenyl)-4-(1,3,3-trimethyl-indolin-2-ylidene)but-2-en-1-ylidene]tungsten (**14d**) (381 mg, 0.50 mmol) and $[(COD)RhCl]_2$ (2.5 mg, 0.005 mmol) in 3.5 mL of toluene at 70 °C after 12 h by flash chromatography on silica gel (160 mg, 73%, R_f = 0.9 in *n*-pentane/diethyl ether, 20:1, yellowish oil). $RhCl_3 \cdot 3H_2O$ (2.6 mg, 0.01 mmol) and 0.3 mL of MeOH instead of $[(COD)RhCl]_2$ gave compound **15d** in 74% yield at 70 °C, 12 h.



^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.38 (2 H, m, *o*-H Ph), 7.15 (3 H, m, *m*-H Ph and 6′-H), 7.01 (1 H, m, *p*-H Ph), 6.97 (1 H, m, 4′-H), 6.79 (1 H, m, 5′-H), 6.56 (1 H, s, 7-H), 6.43 (1 H, m, 7′-H), 6.34 (1 H, d, ^3J = 6.0 Hz, 4-H), 5.76 (1 H, m, 9-H), 5.74 (1 H, d, ^3J = 6.0 Hz, 5-H), 3.94 and 3.73 (1:1 H, m each, OCH_2), 2.58 (3 H, s, NCH_3); 2.20, 2.06, 1.57 and 1.48 (1:1:2:2 H, m each, 10-H_2−13-H_2), 1.46 and 1.38 [3:3 H, s each, 3′-$(CH_3)_2$], 0.75 (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 163.3 (C_q, C2), 152.2 (C_q, C7′a), 140.3 (C_q, C3′a), 139.1 (C_q, C8), 138.4 (C_q, *i*-C Ph), 136.8 (C_q, C6), 136.4 (CH, C4), 129.2 (CH, *o*-C Ph), 128.7 (CH, C9), 128.5 (CH, C7), 128.4 (CH, *m*-C Ph), 127.6 (CH, C6′), 126.8 (CH, *p*-C Ph), 125.6 (CH, C5), 120.9 (CH, C4′), 118.9 (C_q, C3), 117.7 (CH, C5′), 106.5 (CH, C7′), 88.7 (C_q, C1), 67.0 (OCH_2), 47.2 (C_q, C3′) 30.4 (NCH_3), 29.0 and 22.0 [3′-$(CH_3)_2$]; 28.7, 25.9, 23.3 and 22.4 (CH_2 each, C10−C13), 15.7 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2929 (30), 1604 (73), 1556 (25), 1484 (100), 1360 (32), 1338 (38), 1298 (54). MS (70 eV), *m/e* (%): 437 [M^+] (43), 422 (87), 408 (100), 302 (14), 283 (18), 171 (54), 158 (22). Anal. Calcd for $C_{31}H_{35}NO$ (437.6): C, 85.08; H, 8.06; N, 3.20, Found: C, 85.26; H, 8.31; N, 3.01.

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