Spiro-Fused Cyclopentadienes and Novel Pyridinium Carbonyltungstates from (1-Alkynyl)carbene Tungsten Complexes and *exo*-Methylene *N*-Heterocycles. Competition between 1,4-Addition, 1,2-Addition, and Metathesis[1]

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Reaction of (1-alkynyl)carbene tungsten complexes **1a**−**c** with different *exo*-methylene *N*-heterocycles was found to yield 1,4- and 1,2-adducts as well as metathesis products in ratios depending on structural details. 2-Methyleneindoline **2a** gave conjugated metallahexatrienes **4a**,**c** and cross-conjugated metallahexatrienes **3a**,**c** by 1,4-addition and metathesis, respectively. Cross-conjugated metallahexatrienes were shown to be thermally transformed in conjugated metallahexatrienes by a skeletal rearrangement. 2-Propenylideneindolines **2b**−**d** afforded cross-conjugated metallaoctatetraenes **8** and **9** resulting from metathesis of the *exo*-propenylidene moiety at the 1,2- and the 3,4-double bond position, respectively. 2-Methylene-1,2-dihydropyridines **12a**,**b** and 4-methylene-1,4-dihydropyridines **13c**−**e** yielded conjugated metallaoctatetraenes **14** and **15** in each case by 4-addition, which underwent a π-cyclization to spiro compounds **16** and **17**, respectively. 4-Methylene-1,4-dihydropyridines **13f**,**g** afforded no 4-addition products but novel pyridinium carbonylmetalates **18** by 2-addition.

Introduction

(1-Alkynyl)carbene complexes have been used as stoichiometric reagents in a number of high-yielding reactions of potential use to organic synthesis.[2] For example, addition of (1-alkynyl)carbene complexes to cycloalkenylamines has been shown to provide an efficient entry into the formation of cyclopentadienes. The latter compounds were found to result from π-cyclization of 1-metalla-1,3,5-hexatriene[3] precursors, which were generated by a Michael-type 4-addition of the enamine to the corresponding (1-alkynyl)carbene complex.[4] More detailed information on the course of this transformation was provided more recently. Reactions of (1-alkynyl)carbene tungsten complex **1a** with cycloalkenylamines (Chart 1) were shown to produce both conjugated metallahexatrienes **C** by 4-addition (path b) and cross-conjugated metallahexatrienes **B** by metathesis (path a).[5,6] Evidence for the intermediacy of (aminocyclobutenyl)carbene complexes **A** in this reaction could be

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† X-ray structure analyses.

(1) Part 111 of the series Organic Synthesis via Transition-Metal Complexes. For part 110 see: Wu, H.; Aumann, R.; Fröhlich, R.; Wegelius, E. *Organometallics* **2001**, *20*, in press.

(2) For a review on the chemistry of (1-alkynyl)carbene complexes see: Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163−242.

(3) For a recent review on the chemistry of 1-metalla-1,3,5-hexatrienes see: (a) Aumann, R. *Eur. J. Org. Chem.* **2000**, 17−31. For related chemistry based on the insertion of alkynes into (β-aminoalkenyl)carbene complexes see: (b) de Meijere, A. *Pure Appl. Chem.* **1996**, *68*, 61−72. (c) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem.* **2000**, *112*, 4124−4162; *Angew. Chem., Int. Ed.* **2000**, *39*, 3964−4002. (d) Göttker-Schnetmann, I.; Aumann, R. *Organometallics* **2001**, *20*, 346−354. (e) Flynn, B. L.; Schirmer, H.; Duetsch, M.; de Meijere, A. *J. Org. Chem.* **2001**, *66*, 1747−1754.

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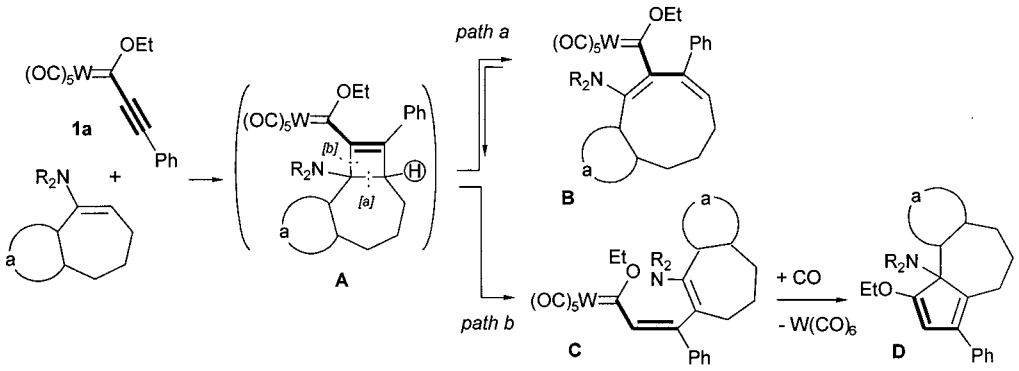
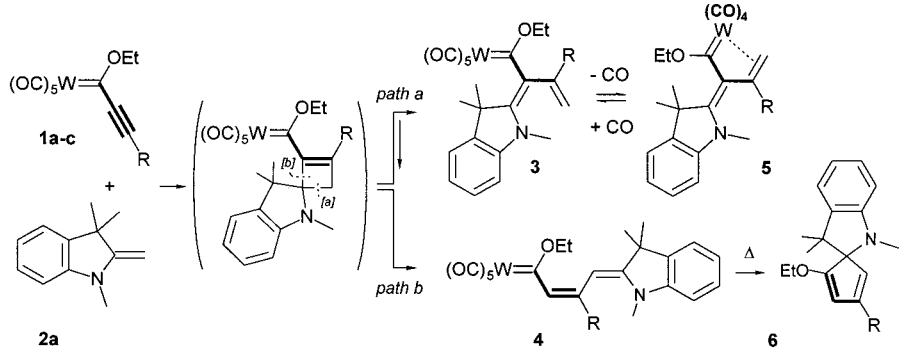
(6) Different results are obtained from reactions of (1-alkynyl)carbene complexes with enol ethers or silylenolethers: Instead of Michael-type adducts, products obtained by a ene-type reaction have been reported in a few cases. However formation of (alkoxy- or siloxycyclobutenyl)carbene complexes which in some cases yielded metathetical products (= cross-conjugated metallatrienes) by cycloreversion reaction has been reported: (a) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727−8729. (b) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miratvitlles, C. *J. Chem Soc., Chem. Commun.* **1989**, 1560−1562. (c) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419−6420. (d) Camps, F.; Llebaría, A, Moretó, J. M.; Ricart, S.; Viñas, J. M. *Tetrahedron Lett.* **1990**, *31*, 2479−2482. (e) de Meijere, A.; Kaufmann, A.; Lackmann, R.; Militzer, H.-Ch.; Reiser, O.; Schömenauer, S.; Weier, A. In *Organometallics in Organic Synthesis II*; Werner, H., Erker, G., Eds.; Springer: Berlin, 1989; pp 255−276. (f) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418−7420. (g) Pipoh, R.; van Eldik, R.; Wang, S. L. B.; Wulff, W. D. *Organometallics* **1992**, *11*, 490−492. (h) Camps, F.; Jordi, L.; Moretó, J. M.; Ricart, S. *J. Organomet. Chem.* **1992**, *436*, 189−198. (i) Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *J. Organomet. Chem.* **1993**, *444*, C28−C30. (j) Jordi, L.; Camps, F.; Ricart, S.; Viñas, J. M.; Moretó, J. M.; Mejias, M.; Molins, E. *J. Organomet. Chem.* **1995**, *494*, 53−64. (k) Wulff, W. D.; Faron, K. L.; Su, J.; Springer, P.; Rheingold, A. L. *J. Chem. Soc., Perkin Trans. 1* **1998**, 197−219. (l) Aumann, R.; Hildmann, B.; Fröhlich, R. *Organometallics* **1998**, *17*, 1197−1202. For the production of "ene" products from reactions of (1-alkynyl)carbene complexes with certain cyclic enamines see: ref 3d; ref 3e; ref 9.

10.1021/om010117b CCC: $20.00
Publication on Web 06/01/2001

Chart 1. Formation of Cross-Conjugated Metallatrienes B and Their Conversion into Conjugated Metallatrienes C According to Ref 5c



Scheme 1. Formation of Cross-Conjugated Metallatrienes 3 and Conjugated Metallatrienes 4 from *exo*-Methyleneindoline 2a and Transformation of Cross-Conjugated into Conjugated Metallatrienes



1	R	3,4	R	[3]%[a]	[4]%[a]	[5]%	[6]%[a]
a	Ph	a	Ph	43[b]	52[b]	49[d]	77[f]/ 72[g]/ 75[h]
b	Me_3Si	b	Me_3Si	0[b]	74[b,c]	-	79[f]/ 78[h]
c	cyclohex-1-enyl	c	cyclohex-1-enyl	86[b]	0[b]	[e]	0[g]/ 0[h]

[a] Isolated yield after chromatography. [b] For reaction conditions see experimtal section. [c] Compound **4b** could not be obtained analytically pure, but contained an impurity of $W(CO)_6$ and it´s demetalation product **6b**. [d] Isolated yield after chromatography and crystallization from diethyl ether. [e] Compound characterized by NMR measurements only. [f] Starting from compounds **4**. [g] Starting from compounds **3**. [h] Starting from compounds **1** and **2a**.

provided by a crystal structure analysis.[7] Most interestingly, it was shown that cross-conjugated metallatrienes **B** could be transformed into conjugated metallatrienes **C**, apparently by (reversible) formation of (aminocyclobutenyl)carbene complexes **A**. Thermolysis of cross-conjugated metallatrienes **B** thus also resulted in formation of cyclopentadienes **D** (Chart 1).[5c,8]

Ring strain had been implied as the driving force for the transformation of cross-conjugated metallatrienes **B** into conjugated metallatrienes **C**.[5c,9] Up to date however, simple rules predicting whether conjugated or cross-conjugated metallatrienes would be obtained in these reactions are still lacking, even though only one isomer of the one or the other kind was observed in most cases.[4,5a,b,d] It appears that the competing reaction paths leading to the formation of metathesis products and Michael-type adducts, respectively, is very sensitive to minor changes of reactant structures as well as reaction conditions. Here we wish to report on reactions of *exo*-methylene *N*-heterocycles with (1-alkynyl)carbene complexes **1** which may be considered borderline cases, since they afford as well 4-addition products as metathesis products of an enamine unit and beyond these also pyridinium carbonylmetalates resulting from an up to date only rarely reported 2-addition to an (1-alkynyl)-carbene complex.

Metathesis of the (N)C=CH_2 Unit of *exo*-Methyleneindoline. The addition of *exo*-**2a** to (1-alkynyl)-carbene complexes **1** in a temperature range −20 to 20 °C affords mixtures of conjugated 1-metalla-1,3,5-trienes **4** (path b) and cross-conjugated metallatrienes **3** (path a) (Scheme 1). From compound **1a** (R = Ph) both types of metallatrienes, **3a** and **4a**, could be isolated. It was shown that the product ratio **3a**:**4a** was dependent not only on the solvent but also on the concentration of the

(7) A ring-opening of a (aminocyclobutenyl)carbene carbene complex to a conjugated 1-metalla-1,3,5-hexatriene is reported by: Aumann, R.; Hildmann, B.; Fröhlich, R. *Organometallics* **1998**, *17*, 1197−1201.

(8) Another example for the interconversion of (cyclic) cross-conjugated into conjugated metallatrienes and subsequent transformation is reported by: Aumann, R.; Kössmeier, M.; Roths, K.; Fröhlich, R. *Tetrahedron* **2000**, *56*, 4935−4949.

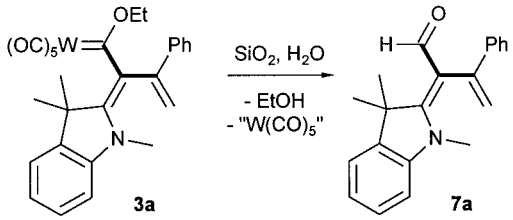
(9) Aumann, R.; Kössmeier, M.; Mück-Lichtenfeld, Ch.; Zippel, F. *Eur. J. Org. Chem.* **2000**, 37−49.

reaction mixture. It was also influenced by the presence of triethylamine. For example, reaction of compound **1a** (R = Ph) in diethyl ether or dichloromethane in a concentration of 0.25 mol/L gave a mixture of compounds **3a** and **4a** in a ratio of ca. 1:1, but in *n*-pentane under otherwise similar conditions this product ratio was changed to ca. 3:2. In more dilute reaction mixtures of 0.01 mol/L in diethyl ether a product ratio of ca. 10:1 could be achieved, if 0.05 mol/L of triethylamine was added. Compound **1b** (R = Me_3Si) under similar conditions afforded only a conjugated metallatriene **4b**, but no cross-conjugated product, while compound **1c** (R = cyclohex-1-enyl) gave only a cross-conjugated metallatriene **3c** but no conjugated metallatriene **4c**, independent of the concentration of the reactants, the solvent, and the presence or absence of triethylamine (Scheme 1).

A thermally induced conversion of a cross-conjugated metallatriene **B** into a conjugated metallatriene **C**, as outlined in Chart 1 for cyclic compounds, was found also for open-chain derivatives **3** and **4**. For example, it was shown by NMR spectra that the conjugated metallatriene **4a** was transformed into the spiro-fused[10] cyclopentadiene **6a** at 55 °C, C_6D_6 (in a sealed NMR tube, 10 h in 77% isolated yield). Interestingly, compound **6a** was also obtained from the corresponding cross-conjugated metallatriene **3a** at 70 °C, C_6D_6 (sealed NMR tube), 60 h in similar yields (Scheme 1). It could be unambiguously shown that the ^{1}H NMR signals of an equilibrium mixture of compound **3a** and its $(CO)_4W$ chelate derivative **5a** were decreasing, while signals of the corresponding cyclopentadiene **6a** were increasing in intensity. It was not possible to directly observe formation of the conjugated metallatriene **4a** from the cross-conjugated compound **3a** in the NMR spectra, in line with the expectation that compound **4a** would undergo a π-cyclization faster than it was generated from compound **3a** by a skeletal rearrangement. The complete transformation of compound **3a** into the cyclopentadiene **6a** requires a constant atmosphere of carbon monoxide, which is provided in a sealed NMR tube. If the thermolysis of the cross-conjugated metallatriene **3a** was performed in an open argon atmosphere at 40 °C, 60 h, it resulted in the loss of 1 equiv of carbon monoxide to give a very stable tetracarbonyl complex **5a**, which was not further transformed into the cyclopentadiene **6a** under these conditions even at 70 °C, 60 h. It should be noted that this is the first report on a skeletal rearrangement of an open-chain cross-conjugated metallatriene into a conjugated metallatriene, thus indicating that ring strain effects imposed in cyclic systems are not essential for this rearrangement to occur. Steric repulsion within the (4-aminocyclobutenyl)-carbene complex seems to favor a proximal ring-opening (path b, Scheme 1).

The ease of the π-cyclization of metallatrienes **4** is strongly influenced by the substituents R. Thus compound **4b** (R = $SiMe_3$), which due to its thermolability could not be isolated analytically pure, afforded the cyclopentadiene **6b** at 30 °C, 6 h. The cross-conjugated metallatriene **3c** (R = cyclohex-1-enyl) was not transformed into the cyclopentadiene **6c** even at 80 °C in toluene-d_8 in a sealed NMR tube after 60 h, but gave a very stable tetracarbonyl chelate complex **5c** instead (Scheme 1).

Scheme 2. Aldehyde 7a by Hydrolysis of Compound 3a



Structure Elucidation of Compounds 3−7. Characteristic of compounds **3** are ^{13}C NMR signals of the $=CH_2$ group at δ 123.0 (**3a**) and 120.1 (**3c**), (broad) signals of $(OC)_5W{=}C(OEt)C(R){=}CN$ at δ 176.8 (**3a**) and 177.4 (**3c**), and (broad) signals of the W=C unit in a range δ 270−266 (**3a**) and 269−266 (**3c**). The connectivty of the ligand backbone of compounds **3a**,**c** is in accordance with GHSQC and GHMBC experiments. Furthermore, it was shown that hydrolysis of compound **3a** on silca gel afforded an aldehyde **7a**, which was identified by a crystal structure analysis (Scheme 2).[5d,11]

Crystals suitable for a crystal structure analysis were not available for cross-conjugated metallatrienes **3** but could be obtained of conjugated metallatriene **4a** from diethyl ether at −40 °C. The molecular structure of compound **4a** revealed a trough-shaped (3*Z*,4-*s*-*cis*)-1-tungsta-1,3,5-hexatriene backbone, which perfectly fits the geometric requirements for the π-cyclization to a cyclopentadiene ring. The pattern of alternating bond distances W−C4 2.267(6), C4−C5 1.411(9), C5−C6 1.393(9), C6−C7 1.436(9), C7−C8 1.361(10), and C8−N9 1.350(9) Å is in accordance with a significant π-conjugation within the 6-amino-1-metalla-1,3,5-hexatriene moiety.

Spectroscopic features characteristic of cyclopentadienes **6** are the ^{13}C NMR signals of the spiro carbon atom at δ 87.6 (**6a**) and 87.9 (**6b**) as well as the ^{1}H NMR signals of the olefinic protons of the cyclopentadiene ring at δ 6.02, 5.22 (**6a**) and δ 6.02, 4.92 (**6b**) [d each, $^4J(^1H,^1H)$ = 1.7 Hz].

The molecular structure of compound **6a** was established also by a crystal structure analysis (Figure 3). It shows a nearly planar cyclopentadiene ring with C8−C4−C5−C6 1.2(2)°, C4−C5−C6−C7 1.8(2)°, C5−C6−C7−C8 4.1(2)°, which is spiro-fused to the slightly twisted *N*-heterocyclic ring, C8−N9−C110−C115 21.2(1)°, N9−C110−C115−C12 0.2(1)°, C110−C115−C12−C8 19.6(1)°, C10−N9−C110−C115 156.0(1)°. The twisting angle between both rings was found to be α(C8,C4,C5,C6,C7/C8,N9,C110,C115,C12) = 91.0°.

The tetracarbonyl chelate complexes **5a**,**c** were readily distinguished from the corresponding pentacarbonyl complexes **3a**,**c** by a characteristic high-field shift of the signal of the coordinated olefinic group in both the ^{1}H and ^{13}C NMR spectra. For example, compound **5a**:

(10) Formation of spiro-fused cyclopentadienes from (β-aminoalkenyl)carbene complexes and arylalkynes was recently reported by: (a) Schirmer, H.; Duetsch, M.; Stein, F.; Labahn, Th.; Knieriem, B.; de Meijere, A. *Angew. Chem.* **1999**, *111*, 1369−1371; *Angew. Chem., Int. Ed.* **1999**, *35*, 1285−1287. (b) Schirmer, H.; Flynn, B. L.; de Meijere, A. *Tetrahedron* **2000**, *56*, 4977−4984.

(11) (a) Aumann, R.; Hinterding, P.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1993**, *459*, 145−149. (b) Aumann, R.; Schröder, J.; Heinen, H. *Chem. Ber.* **1990**, *123*, 1369−1374.

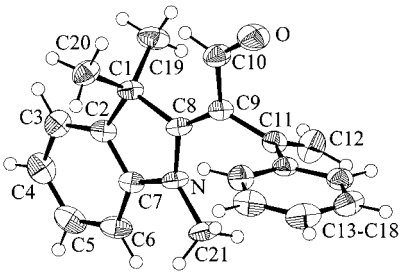


Figure 1. Molecular structure of aldehyde **7a**. Selected bond lengths (Å) and angles (deg): N−C7 1.404(2), N−C8 1.380(2), C8−C1 1.547(2), C8−C9 1.378(3), C9−C10 1.445(3), C10−O 1.223(2), C9−C11 1.498(3), C11−C12 1.323(3), C11−C13 1.490(3); C7−N−C21 120.2(1), C7−N−C8 111.5(1), C21−N−C8 127.5(1), N−C8−C9 125.0(1), C8−C9−C10 120.6(1), C8−C9−C11 124.3(1), C9−C10−O 124.1(1), C10−C9−C11 114.7(1), C9−C11−C12 118.8(1), C9−C11−C13 118.6(1); C7−N−C8−C9 173.3(1), N−C8−C9−C10−171.7(1), N−C8−C9−C11 13.7(3), C8−C9−C10−O 178.0(2), C8−C9−C11−C12 66.3(2), C8−C9−C11−C13 115.3(2).

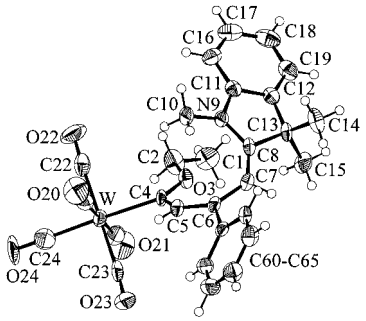


Figure 2. Molecular structure of 1-metalla-1,3,5-hexatriene **4a**. Selected bond lengths (Å) and angles (deg): W−C4 2.267(6), O3−C4 1.323(8), C4−C5 1.411(9), C5−C6 1.393(9), C6−C7 1.436(9), C7−C8 1.361(10), C8−N9 1.350(9), C6−C60 1.498(9), C8−C13 1.537(8); O3−C4−W 128.6(5), C5−C4−W 117.9(5), C6−C5−C4 132.8(6), C5−C6−C60 115.4(6), C5−C6−C7 129.9(6), C8−C7−C6 131.3(6), N9−C8−C7 128.6(6), C7−C8−C13 122.9(6), C8−N9−C10 126.0(6), C8−N9−C11 111.2(5), C11−N9−C10 122.2(6); W−C4−C5−C6 171.3(6), C4−C5−C6−C7 13.9(12), C4−C5−C6−C60 162.3(7), C5−C6−C7−C8 33.4(12), C6−C7−C8−N9 17.9 (13), C6−C7−C8−C13 165.5(7).

$\delta(C{=}CH_2)$ 95.6 (**3a**: 146.5), $(C{=}CH_2)$ 64.9 (**3a**: 123.0), $(C{=}CH_2)$ 4.39 and 4.15 (**3a**: 6.18 and 5.44). The ^{13}C NMR signals of the W=C unit were observed in the expected range at δ 269.6 (**5a**) and 268.5 (**5c**) together with the $(CO)_4$ group for compound **5a** at 218.2, 213.6, 208.6, and 208.3 (**5c**: 216.5, 215.1, 208.6, and 206.6).

Metathesis of the (N)C=CHCH=CH$_2$ Unit of *exo*-Propenylideneindolines Both at the Terminal C=C Bond. Our studies were extended to reactions of (1-alkynyl)carbene complexes **1** with 2-(1-propen-3-ylidene)indolines **2b**−**d** containing a (N)C=CHCH=CH$_2$ unit in order to study its interaction at both the C1=C2 and the C3=C4 bond. The latter compounds were derived from compound **2a** by condensation with isobutyraldehyde, propionaldehyde, and 2-phenylacetaldehyde, respectively. They form mixtures of stereoisomers with respect to the (N)C=CH bond [E/Z = 9:1 (**2b**), 7:3 (**2c**), and 99:1 (**2d**)], while the terminal C=C bond exhibits the *E*-configuration in each case.[12]

Addition of 2-(1-propen-3-ylidene)indolines **2b**−**d** to (1-alkynyl)carbene complexes **1a**,**c** in diethyl ether at 20 °C, 6 h, affords purple-red metallaoctatetraenes **8** [by metathesis of the (N)*C*=*C*HCH=CH unit at the C1=C2 bond, path d] and brown-red metallatetraenes **9** [by metathesis of the (N)C=CH*CH*=*C*H unit at the C3=C4 bond, path c] (Scheme 3). To our knowledge this is the first reported case of a metathesis of a 1-amino butadiene unit at the C3=C4 double bond. It should be noted that Michael adducts (vide supra) were not obtained.

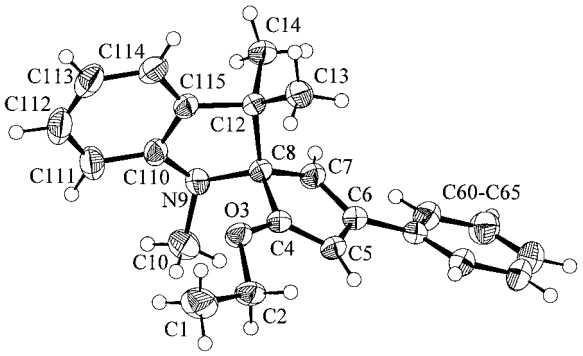


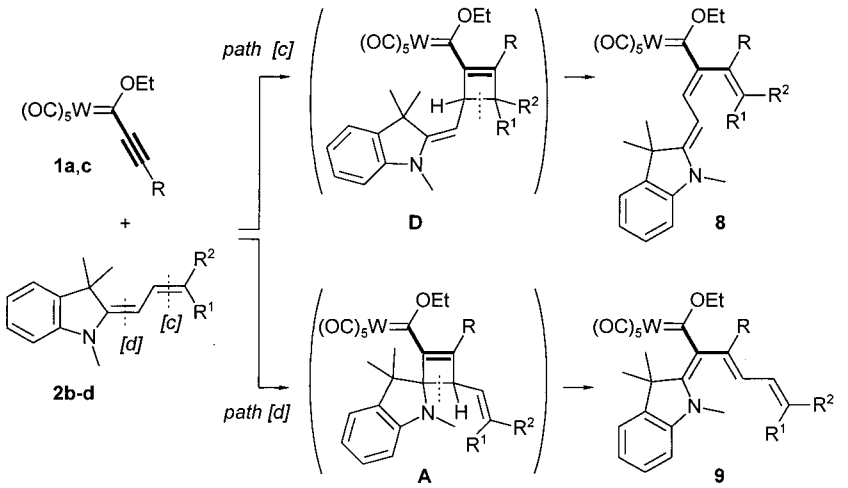
Figure 3. Molecular structure of the *spiro*-cyclopentadiene **6a**. Selected bond lengths (Å) and angles (deg): C8−C4 1.528(2), C4−C5 1.339(2), C5−C6 1.477(2), C6−C7 1.349(2), C7−C8 1.505(2), C8−N9 1.479(2), N9−C110 1.398(2), C110−C115 1.395(2), C115−C12 1.516(2), C12−C8 1.576(2); C4−C5−C6 108.0(1), C7−C6−C5 109.4(1), C6−C7−C8 110.4(1), C7−C8−C4 100.9(1), N9−C8−C4 111.2(1), C4−C8−C12 113.3(1), C7−C8−C12 114.5(1), N9−C8−C7 115.1(1), C115−C12−C8 100.2(1), C110−C115−C12 108.8(1), C115−C110−N9 110.7(1), C110−N9−C8 106.8(1), C10−N9−C8 116.6(1), C110−N9−C10 119.1(1), N9−C8−C12 102.3(1); C8−C4−C5−C6 1.2(2), C4−C5−C6−C7 1.8(2), C5−C6−C7−C8 4.1(2), C8−N9−C110−C115 21.2(1), N9−C110−C115−C12 0.2(1), C110−C115−C12−C8−19.6(1), C10−N9−C110−C115 156.0(1).

The product ratio of compounds **8** and **9** is strongly influenced by steric factors. Generation of metallatetraenes **8b**−**d** was found to be highly favored for compounds **2b**−**d**, which bear only one substituent at the terminal carbon atom of the side-chain. Compounds **9** could not be detected in this case while monitoring the reaction by NMR spectra, even though trace amounts of some red-brown compounds were found by TLC tests, which have an R_f value similiar to that of compound **9a.** Steric hindrance at the terminal C=C bond of compound **2a** by methyl groups resulted in an overall retardation of reaction path c and the generation of noticeable amounts of compound **9a** as a byproduct of the formation of compound **8a** (Scheme 3).

Stereochemical information on the structure of compounds **8** was collected by extensive NMR studies. The ^1H NMR spectrum of compound **8c** in C_6D_6 at 27 °C, 400 MHz, shows two similar sets of signals for its stereoisomers in a molar ratio of ca. 95:5. Most characteristic are the AB systems resulting from protons NC(R)=C*HCH*=C(R), ^3J = 13.0 Hz, δ 9.04 and 6.22 of the major isomer **8c**, and ^3J = 13.0 Hz, δ 9.07 and 6.23 of the minor isomer **8′c**. The signal of the NCH_3 group at δ 2.24 for **8c** is significantly shifted downfield to δ 3.39 for **8′c** by anisotropic effects. The assignment of signals is based on NOE and ROESY experiments (600

(12) Hubschwerlen, Ch.; Fleury, J.-P. *Tetrahedron* **1977**, *33*, 761−765.

Scheme 3. Metalatetraenes 8 and 9 by Metathesis of *exo*-Propenylidene Indolines 2b−d



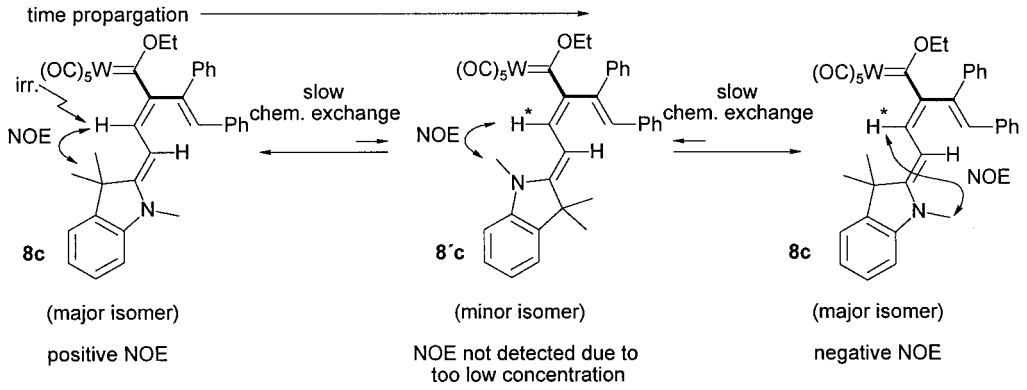
1	R
a	Ph
c	cyclohex-1-enyl

2	R^1	R^2
b	Me	Me
c	H	Me
d	H	Ph

8,9	R	R^1	R^2	[8] %	[9] %
a	Ph	Me	Me	48[a]	33[a]
b	Ph	H	Me	82[b]	trace[c]
c	Ph	H	Ph	86[b]	trace[c]
d	cyclohex-1-enyl	H	Ph	82[b]	trace[c]

[a] Isolated yield after chromatography. [b] Isolated yield after crystallization. [c] Identification based on the R_f value of the brown-red compound only.

Chart 2. NOE Effects Indicating a Slow Chemical Exchange between Isomers 8c and 8′c



MHz), since a severe spin-saturation transfer between the isomers had to be encountered on irradiation of the signals NC(R)=CHC*H*=C(R) and NCH_3. Irradiation of the signal C(CH_3)$_2$ group at δ 1.67 of the major isomer **8c** in a ROESY experiment led to a negative intensity enhancement of a signal at δ 0.87 arising from the minor isomer **8′c** (which due to overlap was not observable in its ^{1}H NMR spectrum). ROESY experiments in this context provided the unambiguous proof for a spin-saturation transfer, since negative ROE effects do not exist.[13] The stereochemistry as well as chemical exchange reaction between compounds **8c** and **8′c** was elucidated by careful studies of spin-saturation transfer, NOE, and ROE experiments. Most importantly, irradiation of the signal NC(R)=CHC*H*=C of compound **8c** in an NOE experiment was causing a negative response of the NCH_3 group and a positive response of the C(CH_3)$_2$ group of **8c**, while irradiation of NCH_3 of compound **8c** showed a negative response of the NC(R)=CHC*H*=C and a positive response of the NC(R)=C*H*−CH=C proton of the same isomer, thus indicating a *cis*/*trans* isomerization of the NC(R)=C*H* bond on the NMR time scale (Chart 2).

Since compounds **8a**−**d** were observed in roughly the same ratio of **8**:**8′** = ca. 95:5 at 300 K in C_6D_6, the stereochemical information introduced by the *E*/*Z* ratio of the NC=CH bond of compounds **2b**−**d** (i.e., for **2b**, 90:10; **2c**, 70:30; **2d**, 99:1) has been lost in the products **8**/**8′** by the exchange phenomena discussed before.

Structural information on the stereochemistry of compounds **8** was further provided by a crystal structure analysis of compound **8a** (Figure 4). The ligand backbone W−C6−C7−C10−C11−C12−N13 of compound **8a** in the solid state fits perfectly with the information derived for the major isomer **8c** from NOE and ROESY experiments.

Spiro-Cyclopentadienes 10 by π-Cyclization of Metallaoctatetraenes 8. It has been previously demonstrated that compounds **8a**−**d** undergo a π-cyclization

(13) (a) Bothner-By, A. A.; Stephens, R. L.; Lee, J. *J. Am. Chem. Soc.* **1984**, *106*, 811−813. (b) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *63*, 207−213.

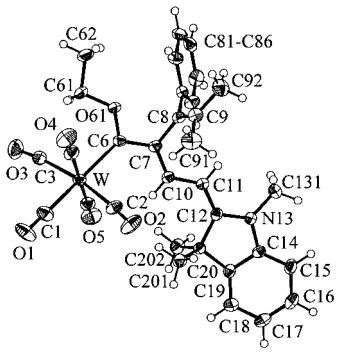
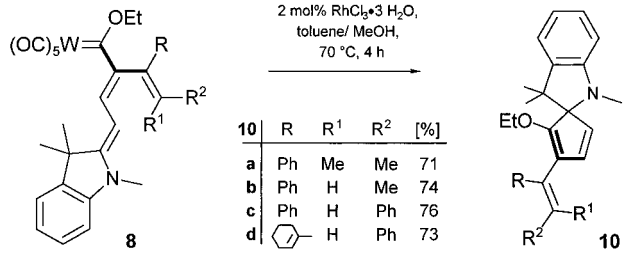


Figure 4. Molecular structure of compound **8a**. Selected bond lengths (Å) and angles (deg): W−C6 2.254(2), O61−C6 1.335(3), C6−C7 1.446(4), C7−C10 1.376(4), C10−C11 1.408(4), C11−C12 1.368(4), C12−N13 1.369(3); W−C6−O61 124.7(1), O61−C6−C7 107.0(2), W−C6−C7 127.3(1), C6−C7−C8 118.8(2), C6−C7−C10 121.5(2), C7−C10−C11 124.7(2), C10−C11−C12 126.7(2), C11−C12−N13 122.6(2); O61−C6−C7−C10 164.3(2), W−C6−C7−C10 26.7(3), W−C6−C7−C8 153.9(1), C6−C7−C10−C11 177.3(2), C6−C7−C8−C9 101.9(3), C7−C10−C11−C12 179.1(2), C10−C11−C12−N13 179.9(2).

Scheme 4. Spiro-Fused Vinylcyclopentadienes 10 by π-Cyclization of the 1-Metalla-1,3,5-hexatriene Moiety of Compounds 8 According to Ref 23



10	R	R^1	R^2	[%]
a	Ph	Me	Me	71
b	Ph	H	Me	74
c	Ph	H	Ph	76
d	⟨⟩	H	Ph	73

of their conjugated 1-metalla-1,3,5-hexatriene unit to spiro-fused vinylcyclopentadienes **10a**−**d** (Scheme 4). This transformation was shown to require catalysis by rhodium.[23] A skeletal rearrangement of the type shown in Scheme 1 was not observed under these conditions.

Single crystals of compound **10c** suitable for a crystal structure analysis were obtained by crystallization from acetonitrile at 0 °C.

Michael Addition of *exo*-Methylene Dihydropyridines 12a,b and 13c−**e.** The reaction of (1-alkynyl)-carbene complex **1a** with 2-methylene-1,2-dihydropyridines **12a**,**b** and 4-methylene-1,4-dihydropyridines **13c**−**e**, respectively (both of which were generated in situ by deprotonation of the respective pyridinium salts **10a**,**b** and **11c**−**e** with triethylamine), yielded spiro-fused cyclopentadienes **16** and **17** in 68−74% yields. The latter compounds were generated by π-cyclization from (very thermolabile) 1-tungsta-1,3,5,7-octatetraene precursors **14** and **15**, obtained by Michael addition of methylene dihydropyridines **12** and **13** to the (1-alkynyl)carbene complex **1a** (Scheme 5). Formation of cross-conjugated products by metathesis of dihydropyridines **12** and **13** and (1-alkynyl)carbene complex **1a** was excluded on the basis that $=CH_2$ signals were not observed in the DEPT spectra (−40 °C) of the reaction mixtures.

Other than compounds **15**, which could not be isolated analytically pure, compound **14a** was readily obtained clean by an elaborate protocol, by which to a (solid) 1:1 mixture of 1,2-dimethylquinolinium iodide (**10a**) and (1-alkynyl)carbene tungsten compound **1a** was added aqueous NaOH and then diethyl ether while vigorously stirring at 20 °C. After 1 min the mixture was cooled to −40 °C to give crystals of an analytically clean sample of compound **14a**. It was shown by ^{1}H and ^{13}C NMR spectra in CD_2Cl_2 at −40 °C, as well as by (^{1}H,^{13}C)-GHSQC, (^{1}H,^{13}C)GHMBC, and ROESY experiments, that only one isomer, namely, (*3Z*,*5E*)-6-amino-1-metalla-1,3,5,7-octatetraene (**14a**) was present in solution. If this sample was allowed to warm to 30 °C while following the reaction by NMR spectra, a smooth conversion into the spiro-fused cyclopentadiene **16a** and hexacarbonyltungsten could be observed within 6 h (Scheme 5).

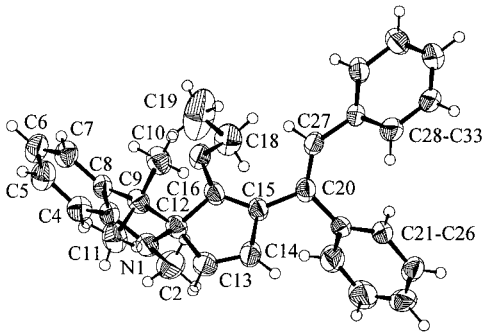
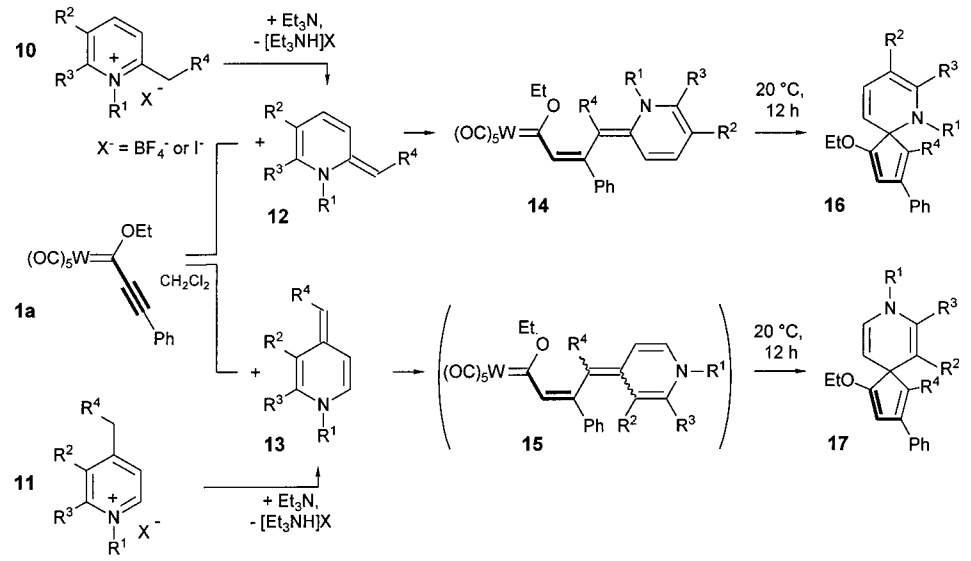


Figure 5. Molecular structure of compound **10c**. Selected bond lengths (Å) and angles (deg): N1−C3 1.391(7), C3−C 81.386(7), C8−C9 1.523(7), C9−C12 1.571(7), C12−N1 1.485(6), C12−C13 1.497(7), C13−C14 1.325(7), C14−C15 1.473(8), C15−C16 1.361(7), C16−C12 1.526(7); C2−N1−C12 119.1(5), C2−N1−C3 119.3(5), C3−N1−C12 107.7(4), N1−C3−C8 110.7(5), C3−C8−C9 108.9(5), C8−C9−C12 100.6(4), C9−C12−C13 115.6(5), C12−C13−C14 108.8(5), C13−C14−C15 112.6(5), C14−C15−C16 105.7(5), C15−C16−C12 110.5(5), C16−C12−C13 102.2(5); C2−N1−C3−C8 159.3(4), N1−C3−C8−C9 1.3(6), C3−C8−C9−C12 19.7(5), C8−C9−C12−N1 29.4(5), C9−C12−N1−C2 170.6(5), C8−C9−C12−C13 152.9(4), C9−C12−C13−C14 124.7(5), C12−C13−C14−C15 2.1(7), C13−C14−C15−C16 2.4(7), C14−C15−C16−C12 1.6(6), C16−C12−C9−C8 89.3(5). α(N1, C3, C8, C9, C12/ C12, C13, C14, C15, C16) = 91.5.

Spectroscopic features most characteristic of compounds **16** are the signals of the spiro carbon atom at δ 75.0 (**16a**) and 75.2 (**16b**) (shifted by ca. 12 ppm to higher field compared to the spiro-fused indolines **6a**,**c**) as well as proton signals of an AB system in the *N*-heterocyclic ring [^3J(^{1}H,^{1}H) = 9.6 Hz (**16a**) and 10.0 (**16b**), respectively] and an AB system of the cyclopentadiene ring [^4J(^{1}H,^{1}H) = 1.7 Hz (**16a**) and 1.8 Hz (**16b**), respectively].

Further structural information could be provided by a crystal structure analysis of compound **16b** (Figure 6). Compound **16b** exhibits two sets of orthogonal π-systems [α(C10,C11,C12,C13,C14/C10,N1,C2,C7,C8,C9) = 90.5°] defined by an almost planar cyclopentadiene ring [C14−C10−C11−C12 3.9(2)°, C10−C11−C12−C13 2.8(2)°, C11−C12−C13−C14 0.3(2)°, C11−C10−C14−C13 3.7(2)°] and the slightly puckered 1,2-dihydropyridine ring [C10−N1−C2−C3 171.6(1)°, C10−N1−C2−C7 9.4(2)°, C2−C7−C8−C9 3.1(2)°, C7−C8−C9−C10 0.6(2)°, C2−N1−C10−C9 12.1(2)°]. A similar situation is observed in compound **17d** (Figure 7), as the angle between the cyclopentadiene and the 1,4-dihydropyri-

Scheme 5. Spiro-Fused Cyclopentadienes 16 and 17 via Michael-type Addition of *exo*-Methylene Dihydropyridines to (1-Alkynyl)carbene Complex 1a



[a]	R^1	R^2,R^3	R^4	**[16]** %*[b]*	**[17]** %*[b]*
10a	Me	$(CH)_4$	H	72	-
10b	Et	$(CH)_4$	H	70	-
11c	Me	$(CH)_4$	H	-	74
11d	Et	$(CH)_4$	H	-	73
11e	Me	H,H	Me	-	68
11f	Me	H,H	H	-	*[c]*
11g	Et	H,H	H	-	*[c]*

[a] Starting material. *[b]* Isolated yield after chromatography. *[c]* Other products are obtained in this case, which will be discussed later in this paper.

dine ring was found to be α(C4, C5, C6, C7, C8/ C4, C3, C2, N1, C14, C9) = 90.3°.

The ^{13}C NMR signals of the spiro carbon atoms of compounds **17** were observed at δ 56.6 (**17c**), 56.7 (both **17d** and **17e**), at higher field than in the *N*-substituted spiro compounds **6** or **16**. The substitution pattern of the cyclopentadiene ring was characterized by an AB-system with ^4J = 1.9 Hz (**17c**) and 1.5 Hz (**17d**), respectively. An AB-system was observed also for the benzannelated 1,4-dihydropyridine rings with ^3J = 8.0 Hz (**17c**,**d**), and an AA′BB′-system was found for the 1,4-dihydropyridine **17e**.

Novel Pyridinium Carbonyltungstates. It has been pointed out above (footnote to table in Scheme 4) that a Michael-type 4-addition as well as a metathesis between 4-methylene dihydropyridines **13** and (1-alkynyl)carbene complex **1a** was completely outrun by a reaction not specified above, which we now identify as resulting from the 2-addition of the methylene carbon to the carbene carbon.[14−16] Reaction of 1,4-dimethyl pyridinium iodide **11f** or 1-ethyl-4-methyl pyridinium tetrafluoroborat **11g** with compound **1a** under conditions identical to those applied for the generation of spiro-fused cyclopentadienes **16** and **17** or metalatetraene **14a** did not afford analogous products, but zwitterionic pyridinium carbonylmetalates **18f**,**g** in 51−53% isolated yield after chromatography. Formation of compounds **18** is suggested to proceed via a nucleophilic attack of the *exo*-methylene carbon atom to the carbene carbon atom to form a zwitterionic adduct, which subsequently rearranges to a novel pyridinium carbonyltungstate **18** by deprotonation/protonation and [1,2]-migration of the pentacarbonyltungstate moiety[17,18] (Scheme 6). The *E*/*Z* ratio of the products **18** and **18′** is in line with the expectation considering the supposed population of the anionic precursors **E**:**E′** based on gauche interactions (Scheme 6).

(14) Nucleophilic 1,2-addition by the nitrogen of 1,4-dihydropyridines to Fischer carbene complexes has been reported by: (a) Cohen, F.; Goumont, R.; Rudler, H. *J. Organomet. Chem.* **1992**, *431*, C6−C10. (b) Rudler, H.; Audouin, M.; Parlier, A.; Martín-Vaca, B.; Goumont, R.; Durand-Réville, T.; Vaissermann, J. *J. Am. Chem. Soc.* **1996**, *118*, 12045−12058. (c) Martín-Vaca, B.; Rudler, H.; Audouin, M.; Nicolas, M.; Durand-Réville, M.; Vissière, B. *J. Organomet. Chem.* **1998**, *567*, 119−126. (d) Rudler, H.; Martín-Vaca, B.; Nicolas, M.; Vaissermann, J. *Organometallics* **1998**, *17*, 361−366.

(15) Nucleophilic 2-addition of 1-aza-1,3-butadienes to (1-alkynyl)-carbene complexes and subsequent [1,2]-migration of the metal has been reported by: (a) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pertierra, P. *J. Am. Chem. Soc.* **1996**, *118*, 695−696. (b) Aumann, R.; Fröhlich, R.; Zippel, F. *Organometallics* **1997**, *16*, 2571−2580. (c) Aumann, R.; Yu, Z.; Fröhlich, R. *J. Organomet Chem.* **1997**, *549*, 311−318. (d) Barluenga, J.; Tómas, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pérez Priede, M. *J. Am. Chem. Soc.* **1999**, *121*, 3065−3071.

(16) Nucleophilic 2-addition of uncharged carbon nucleophiles to (1-alkynyl)carbene complexes has been previously proposed by: (a) See ref 15d. (b) Aumann, R.; Heinen, H.; Hinterding, P.; Sträter, N.; Krebs, B. *Chem. Ber.* **1991**, *124*, 1229−1236. (c) Fischer, H.; Meissner, T.; Hofmann, J. *J. Organomet. Chem.* **1990**, *397*, 41−49. (d) Wu, H.-P.; Aumann, R.; Fröhlich, R.; Saarenketo, P. *Chem. Eur. J.* **2001**, *7*, 700−710.

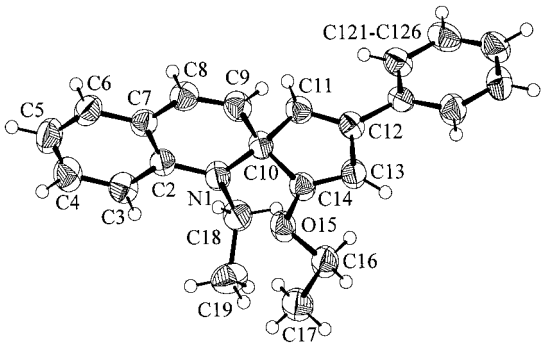


Figure 6. Molecular structure of spiro fused vinyl cyclopentadiene **16b**. Selected bond lengths (Å) and angles (deg): C10−C11 1.519 (2), C11−C12 1.342(2), C12−C13 1.475(2), C13−C14 1.337(2), C14−C10 1.530(2), N1−C2 1.379(2), C2−C7 1.408(2), C7−C8 1.447(2), C8−C9 1.320(2), C9−C10 1.506(2), C10−N1 1.463(2), C12−C121 1.475(2); C2−N1−C18 120.3(1), C10−N1−C18 115.3(1), C2−N1−C10 123.6(1), N1−C10−C9 111.8(1), N1−C10−C11 114.4(1), N1−C10−C14 112.2(2), C9−C10−C11 108.6(1), C12−C11−C10 110.8(1), C11−C12−C13 109.1(1), C12−C13−C14 108.6 (1), C13−C14−C10 111.0(1), C11−C10−C14 100.4(1), N1−C2−C7 120.4(1), C2−C7−C8 118.2(1), C9−C8−C7 121.7(1), C8−C9−C10 123.3(1); C10−N1−C2−C3 171.6(1), C10−N1−C2−C7 9.4(2), C2−C7−C8−C9 3.1(2), C7−C8−C9−C10 0.6(2), C2−N1−C10−C9 12.1(2), C2−N1−C10−C14 134.6(1), C8−C9−C10−C11 119.5(2), C8−C9−C10−C14 132.1(2), N1−C10−C11−C12 124.2(1), C9−C10−C11−C12 110.1(1), C14−C10−C11−C12 3.9(2), C10−C11−C12−C13 2.8(2), C11−C12−C13−C14 0.3(2), N1−C10−C14−C13 125.6(1), C9−C10−C14−C13 110.1(1), C11−C10−C14−C13 3.7(2).

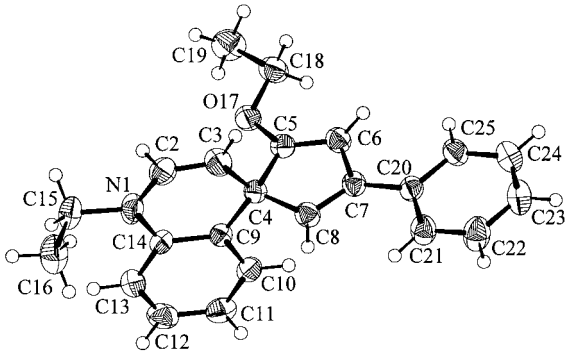
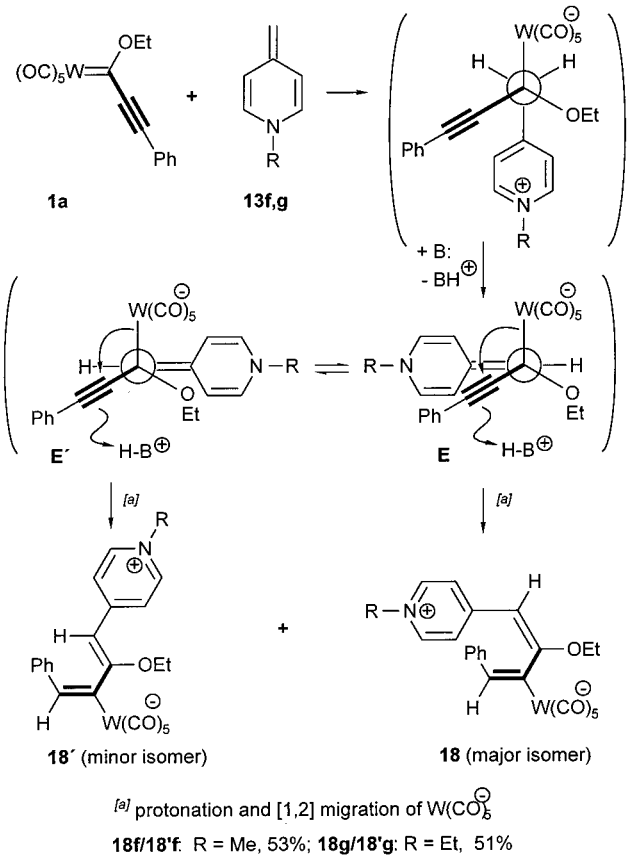


Figure 7. Molecular structure of spiro vinyl cyclopentadiene **17d**. Selected bond lengths (Å) and angles (deg): N1−C2 1.380(5), C2−C3 1.317(6), C3−C4 1.508(5), C4−C9 1.517(5), C9−C14 1.414(5), C4−C5 1.527(5), C5−C6 1.339(5), C6−C7 1.479(5), C6−O17 1.352(4), C7−C8 1.344(5), C8−C4 1.510(5); C2−N1−C14 119.0(3), C2−N1−C15 117.5(3), C14−N1−C15 123.4(3), C3−C2−N1 124.8(4), C2−C3−C4 123.1(3), C3−C4−C9 110.2(3), C14−C9−C4 122.6(3), C9−C14−N1 120.1(3), C6−C5−C4 111.5(3), C5−C6−C7 108.0(3), C8−C7−C6 108.8(3), C7−C8−C4 111.3(3); C2−C3−C4−C5 119.8(4), C2−C3−C4−C8 132.2(4), C3−C4−C5−C6 107.4(3), C3−C4−C8−C7 106.8(4), C9−C4−C5−C6 129.6(3), C9−C4−C8−C7 128.8(3).

The fact that *exo*-methylene dihydropyridines **13f**,**g** exhibit a much higher tendency to form 2-adducts than the corresponding *exo*-methylene (*exo*-prop-2-enylidene)-indolines **2a**−**d** seems to be controlled by the nucleophilicity of the corresponding methylene carbon atoms. It appears that "harder" and also sterically less hindered carbon nucleophiles would rather undergo a 2-addition to (1-alkynyl)carbene complexes **1** than a 4-addition. Up to date, only a few examples of a 1,2-addition of neutral carbon nucleophiles to (1-alkynyl)carbene complexes have been reported.[16] Examples for the addition of anionic carbon nucleophiles are more common.[17a,b,d,e,18]

Compounds **18f**,**g**/**18′f**,**g** are stable in solution at 300 K for several hours. Their structures have been elucidated by spectroscopic techniques and a crystal structure analysis (Figure 8). The ^{1}H and ^{13}C NMR spectra in C_6D_6 showed two sets of signals in a ratio of ca. 3:2 assigned to *E*/*Z* stereoisomers (Scheme 6). In the ^{1}H

Scheme 6. Zwitterionic Pyridinium Carbonylmetalates 18f,g by 2-Addition of Methylene Dihydropyridines 13e,f



NMR spectra at 300 K only two pyridinium protons C*H*-N$^+$(R)=C*H* were detected for the major isomer **18f** at δ 5.77 (5.85 for the minor isomer **18′f**) [**18g**, δ 5.94; **18′g**, 5.98], whereas the other pyridinium protons remained unobserved due to dynamic line-broadening. The proton PhC*H* in each isomer **18f**,**g**/**18′f**,**g** appears as a three-line pattern with a line intensity of ca. 1:12:1 at δ 7.59

(17) [1,2]-Migration of the metal has been previously reported by: (a) Fischer, H.; Meisner, T.; Hofmann, J. *Chem. Ber.* **1990**, *123*, 1799−1804. (b) Dötz, K. H.; Christoffers, C.; Knochel, P. *J. Organomet. Chem.* **1995**, *489*, C84−C86. (c) Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaría, J.; Carbajo, R. J.; López-Ortiz, F.; García-Granda, S.; Pertierra, P. *Chem. Eur. J.* **1996**, *2*, 88−97. (d) Iwasawa, N.; Ochiai, T.; Maeyama, K. *Organometallics* **1997**, *16*, 5137−5139. (e) Iwasawa, N.; Ochiai, T.; Maeyama, K. *J. Org. Chem.* **1998**, *63*, 3164−3165. (f) Barluenga, J.; Rubio, E.; López-Pelegrín, J. A.; Tómas, M. *Angew. Chem.* **1999**, *111*, 1163−1165; *Angew. Chem., Int. Ed.* **1999**, *38*, 1091−1093. (g) Gómez-Gallego, M.; Mancheño, M. J.; Ramírez, P.; Piñar, C.; Sierra, M. A. *Tetrahedron* **2000**, *56*, 4893−4905. And see ref 15.

(18) [1,3]-Migration of the metal is another reaction pathway, which was described by: (a) Barluenga, J.; Trabanco, A. A.; Flórez, J.; García-Granda, S.; Llorca, M.-A. *J. Am. Chem. Soc.* **1998**, *120*, 12129−12130. (b) Caro, B.; Le Poul, P.; Robin-Le Guen, F.; Sénéchal-Tocquer, M.-C.; Saillard, J.-Y.; Kahlal, S.; Ouahab, L.; Gohlen, S. *Eur. J. Org. Chem.* **2000**, 577−581.

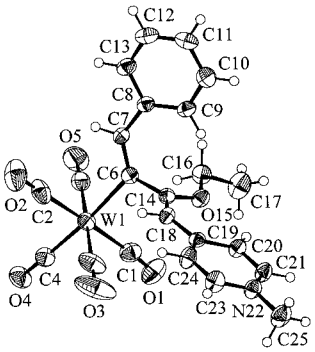


Figure 8. Molecular structure of pyridinium carbonyl tungstate **18f**. Selected bond lengths (Å) and angles (deg): W1−C6 2.306(4), C6−C7 1.338(6), C7−C8 1.483(5), C6−C14 1.464(6), C14−C18 1.372(6), C14−O15 1.347(5), C18−C19 1.407(5), C19−C20 1.418(5), C19−C24 1.405(6), C20−C21 1.354(6), C21−N22 1.344(5), N22−C23 1.351(5), C23−C24 1.351(6), C24−C19 1.405(6), N22−C25 1.474(5); W1−C6−C7 126.0(3), W1−C6−C14 110.5(3), C6−C7−C8 130.8(4), C6−C14−O15 120.8(3), C6−C14−C18 120.6(4), C14−C18−C19 131.5(4), C21−N22−C25 122.0(4), C21−N22−C23 119.2(4), C23−N22−C25 118.8(4); W1−C6−C7−C8 176.8(3), W1−C6−C14−C18 83.9(3), W1−C6−C14−O15 91.9(3), C6−C14−C18−C19 175.8(3), C7−C6−C14−C18 89.9(5), C14−C18−C19−C20 2.2(7).

for compound **18f** (**18′f**: 7.50) [**18g**, δ 7.63; **18′g**, 7.52] resulting from $^3J(^1H,^{183}W) = 6.8$ Hz (**18f/18′f**) and 6.6 Hz (**18g/18′g**).[19,20] ^{1}H NMR spectra of compounds **18f/18′f** in CD_2Cl_2 at 213 K, 600 MHz, exhibit signals of the remaining pyridinium protons with the expected splitting pattern. Spin-saturation transfer experiments indicated a slow chemical exchange between these protons in each isomer, resulting from hindered rotation. Additional NOE as well as GHSQC and GHMBC experiments allowed a complete assignment of the signals to the major and minor isomer of compounds **18f/18′f**. Further structural information was provided by a crystal structure analysis of compound **18f**.

Most characteristic of the molecular structure of compound **18f** in the solid state is the perpendicular distortion of the W1−C6−C7 unit against the plane defined by the atoms C14−C18−C19 [dihedral angles C7−C6−C14−C18 89.9(5)°, W1−C6−C7−C18 83.9(3)°, and C6−C14−C18−C19 175.8(3)°]. Due to an essentially planar arrangement of the C6−C14−C18−C19−C20 chain with dihedral angles C6−C14−C18−C19 175.8(3)° and C14−C18−C19−C20 2.2(7)°, the positive charge is delocalized by π-interaction, resulting in nearly equal bond distances C24−C19 1.405(6)°, C20−C19 1.418(5)°, and C18−C19 1.407(5)°.

Conclusion

Three different reaction pathways were established for reactions of *exo*-methylene *N*-heterocycles **2**, **12**, and **13** with (1-alkynyl)carbene tungsten complexes **1**. They comprise Michael-type 4-additions, metathetical reactions, and 2-additions. The different reaction modes were found to be dependent on the reaction conditions as well as on the nucleophilicity of the carbon nucleophiles. Addition of "soft" 2-methyleneindoline **2a** gave conjugated metallahexatrienes **4a**,**c** and cross-conjugated metallahexatrienes **3a**,**c** by 1,4-addition and metathesis, respectively. Vinylogous compounds, like 2-propenylideneindolines **2b**−**d** afforded cross-conjugated metallaoctatetraenes **8** and **9** resulting from metathesis of the *exo*-propenylidene moiety at the 1,2- and the 3,4-double bond position, respectively. 2-Methylene-1,2-dihydropyridines **12a**,**b** and 4-methylene-1,4-dihydropyridines **13c**−**e** yielded conjugated metallaoctatetraenes **14** and **15** by 4-addition, from which finally spiro compounds **16** and **17** could be obtained. 4-Methylene-1,4-dihydropyridines **13f**,**g**, on the other hand, afforded no 4-addition products but novel pyridinium carbonylmetalates **18** by 2-addition. Thus addition of "hard" and sterically less crowded nucleophiles was found to provide an up to date rarely investigated access to the formation of carbiminium carbonyltungstates by 2-addition.

Experimental Section

NMR: Bruker AM 360, Bruker AMX 400, and Varian U 600. All thermally stable compounds were routinely analyzed by ^{1}H and ^{13}C NMR experiments including (^{1}H,^{1}H)COSY, (^{1}H,^{13}C)-GHSQC, and (^{1}H,^{13}C)GHMBC experiments at a Bruker AMX 400 instrument. NOE and ROESY experiments were performed at a Varian U 600 instrument. Low-temperature experiments were performed either at the Bruker AM 360 or Varian U 600. IR: FT-IR BIO-RAD DIGILAB DIVISION FTS-45. MS: FINNIGAN MAT8200. MALDI-TOF: Lazarus III DE provided by Dr. H. Luftmann, Organisch-Chemisches Institut der Universität Münster. Elemental analyses: HERAEUS CHN-O Rapid. Column chromatography: ICN Alumina N activity IV (10% H_2O) and Merck silica gel 60F. Flash chromatography was performed under an argon pressure of 1.2 bar within ca. 15 min for each compound. Fast chromatographic separation was performed by use of reduced pressure (250 mbar) at the end of the column within 5 min. TLC: Merck silica gel 60F_{254}. R_f values are based on TLC tests and are uncorrected. Melting points are uncorrected. All reactions were performed under argon. CH_2Cl_2 (p.a. quality), diethyl ether, *n*-pentane, C_6D_6, toluene-d_8, $CDCl_3$, and CD_2Cl_2 were used as purchased and not dried prior to use. Compounds **1** were prepared according to refs 2 and 21, and compounds **2b**−**d** according to ref 12. Compounds **8** and **9** were produced in virtual quantitative yield by adding 0.95 equiv of methyl iodide or triethyl oxonium tetrafluoroborate to solutions of lepidine, chinaldine, or the respective alkyl pyridine in CH_2Cl_2, refluxing for several hours, and removal of the solvent and the remaining pyridines together with *n*-pentane. 1,3,3-Trimethyl-2-methylene-indoline **2a** was used as purchased from Fluka.

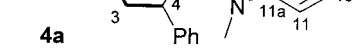
Pentacarbonyl[1-ethoxy-3-phenyl-4-(1,3,3-trimethylindolin-2-ylidene)but-2-enylidene]tungsten (4a), Pentacarbonyl[1-ethoxy-3-phenyl-2-(1,3,3-trimethyl-indolin-2-ylidene)but-3-enylidene]tungsten (3a), 3-Phenyl-2-(1,3,3-trimethylindolin-2-ylidene)but-3-enal (7a), Tetracarbonyl[1-ethoxy-3-phenyl-2-(1,3,3-trimethylindolin-2-ylidene)but-3-enylidene]tungsten (5a), and Spiro[2-ethoxy-4-phenylcyclopenta-2,4-diene-1,2′-*N*-methyl-3′,3′-dimethylindoline] (6a). To pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) in a 4 mL screw-top vessel was added a solution of 1,3,3-trimethyl-2-methyleneindoline **2a** (173 mg, 1.0 mmol) in diethyl ether. Compound **1a** was consumed at 20 °C after stirring for 1 h (TLC). Separation of compounds **3a** and **4a** was achieved by

(19) The natural abundance of ^{183}W is 14.3%. Superposition of a doublet rising from a $^3J(^1H,^{183}W)$ coupling and the singlet of the uncoupled signal is expected to show a pseudotriplet with an intensity ratio of 1:12:1.

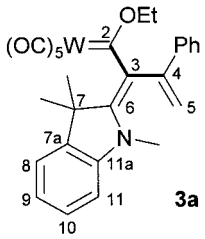
(20) Compound **4b** was found to exhibit the same types of satellites rising from a $^3J(^1H,^{183}W)$ coupling for the proton W=C(OEt)−C*H*; see Experimental Section.

(21) Aumann, R.; Fröhlich, R.; Prigge, J.; Meyer, O. *Organometallics* **1999**, *18*, 1369−1380.

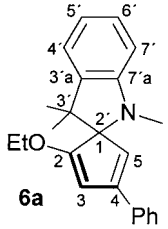
fast chromatography on neutral alumina (activity IV) with *n*-pentane/diethyl ether, 10:1, under reduced pressure. The first colorless fraction contained small amounts of compound **6a** and $W(CO)_6$. Compound **4a** was eluted as a deep purple fraction [340 mg, 52%, mp 112 °C dec, $R_f = 0.8$ on silica gel with *n*-pentane/diethyl ether, 10:1]. A red-brown fraction of compound **3a** containing a small amount of compound **5a** and a colorless fraction of aldehyde **7a** were finally eluted. Slow evaporation of the solvent yielded a single crystal of compound **7a** suitable for a crystal structure analysis. A pure sample of compound **3a** (282 mg, 43%, mp 97 °C, $R_f = 0.6$ on silica gel, *n*-pentane/diethyl ether, 10:1) was obtained from the fraction containing **3a** and traces of **5a** by crystallization from diethyl ether at −40 °C. Compound **6a** was generated by heating a solution of compound **4a** (327 mg, 0.50 mmol) in C_6D_6 at 55 °C for 10 h after chromatography on silica gel (128 mg, 77%, $R_f = 0.9$ on silica gel with *n*-pentane/diethyl ether, 20:1). The same compound was also obtained from compound **3a** (327 mg, 0.50 mmol) in C_6D_6 at 70 °C, 60 h in a sealed NMR tube (119 mg, 72%), and it was also obtained from pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) and 1,3,3-trimethyl-2-methyleneindoline (173 mg, 1.0 mmol) in 4 mL of toluene at 80 °C, 40 h (248 mg, 75%).



4a. ^{1}H NMR (600 MHz, 253 K, $CDCl_3$): δ 7.44 (3H, m, *m*- and *p*-H Ph), 7.38 (1 H, s, 3-H), 7.36 (2 H, m, *o*-H Ph), 7.30 (1 H, m, 8-H), 7.25 (1 H, m, 10-H), 7.11 (1 H, m, 9-H), 6.71 (1 H, m, 11-H), 6.14 (1 H, s, 5-H), 4.71 (2 H, q, $^3J = 7.0$ Hz, OCH_2-CH_3), 2.45 (3 H, s, NCH_3), 1.53 [6 H, s, $C(CH_3)_2$], 1.47 (3 H, t, $^3J = 7.0$ Hz, OCH_2CH_3). ^{13}C NMR (600 MHz, 253 K, $CDCl_3$): δ 280.2 (C_q, W=C), 204.7 and 199.1 [Cq each,1:4, *trans*- und *cis*-CO $W(CO)_5$], 171.4 (C_q, C6), 147.3 and 145.1 (C_q each, *i*-C Ph and C4), 143.9 (C_q, C11a), 138.2 (C_q, C7a), 138.1 (CH, C3), 129.6, 129.3, and 128.8 (CH each, *o*-, *m*-, and *p*-C Ph), 128.1 (CH, C10), 123.0 (CH, C8), 122.1 (CH, C9), 108.7 (CH, C11), 96.7 (CH, C5), 78.1 (OCH_2), 48.6 (C_q, C7), 35.4 (NCH_3), 28.2 [$C(CH_3)_2$], 15.9 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2053 (30), 1966 (6), 1907 (100), 1558 (14), 1460 (18). IR (hexane), cm^{-1} (%): 2057 (27), 1932 (100). MS (^{184}W, 70 eV), *m/e* (%): 599 (9) [$M^+ - 2 \times CO$], 571 (8) [$M^+ - 3 \times CO$], 515 (11) [$M^+ - 5 \times CO$], 485 (13), 331 (64), 302 (100), 272 (71), 258 (25). Anal. Calcd for $C_{28}H_{25}NO_6W$ (655.4): C, 51.32; H, 3.84; N, 2.14. Found: C, 51.47; H, 3.71; N, 2.44. X-ray crystal structure analysis of **4a**:[22] formula $C_{28}H_{25}NO_6W$, $M = 655.34$, red crystal 0.40 × 0.20 × 0.10 mm, $a = 10.104(1)$ Å, $b = 11.408(1)$ Å, $c = 12.796(1)$ Å, $\alpha = 99.66(1)°$, $\beta = 93.66(1)°$, $\gamma = 114.62(1)°$, $V = 1307.0(3)$ Å^3, $\rho_{calc} = 1.665$ g cm^{-3}, $\mu = 44.61$ cm^{-1}, empirical absorption correction via ψ scan data ($0.269 \le T \le 0.664$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 5550 reflections collected ($\pm h$, $-k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 5275 independent ($R_{int} = 0.052$) and 4665 observed reflections [$I \ge 2\sigma(I)$], 329 refined parameters, $R = 0.059$, $wR_2 = 0.146$, max. residual electron density 3.26 (−4.65) e Å^{-3} close to tungsten, hydrogens calculated and refined as riding atoms.



3a. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.56 (2 H, m, *o*-H Ph), 7.18 (2 H, m, *m*-H Ph), 7.06 (1 H, m, *p*-H Ph), 6.98 (1 H, m, 10-H), 6.88 (1 H, m, 9-H), 6.71 (1 H, m, 8-H), 6.47 (1 H, m, 11-H), 6.18 and 5.44 (1:1 H, s each, 5-H_2), 4.52 (2 H, q, $^3J = 7.0$ Hz, OCH_2), 2.94 (3 H, s, NCH_3), 1.09 [6 H, s, br, 7-$(CH_3)_2$], 1.00 (3 H, t, $^3J = 7.0$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 270−266 (C_q, very broad, C2), 204.2 and 201.1 [C_q each, *cis*- and *trans*-CO $W(CO)_5$], 176.8 (C_q, C6), 146.5 (C_q, C4), 142.8 (C_q, C11a), 141.9 (C_q, *i*-C Ph), 141.3 (C_q, C7a), 129.0 (CH, *m*-C Ph), 128.5 (CH, C10), 128.0 (CH, *p*-C Ph), 127.7 (CH, *o*-C Ph), 126.7 (C_q, C3), 125.9 (CH, C9), 123.0 (CH_2, C5), 122.4 (CH, C8), 111.2 (CH, C11), 75.1 (OCH_2), 51.8 (C_q, C7), 37.2 (NCH_3), 27.3 [CH_3, 7-$(CH_3)_2$], 16.0 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2967 (15), 2051 (74), 1955 (51), 1898 (100), 1475 (58), 1365 (47), 1120 (45), 1080 (45). IR (hexane), cm^{-1} (%): 2059 (20), 1975 (8), 1930 (100). MS (^{184}W, 70 eV), *m/e* (%): 627 (16) [$M^+ - CO$], 599 (6) [$M^+ - 2 \times CO$], 571 (100) [$M^+ - 3 \times CO$], 515 (26) [$M^+ - 5 \times CO$], 486 (44), 458 (73), 427 (19), 326 (12). Anal. Calcd for $C_{28}H_{25}NO_6W$ (655.4): C, 51.32; H, 3.84; N, 2.14. Found: C, 51.05; H, 3.79, N 2.33.

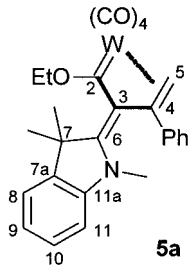


6a. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.47 (2 H, m, *o*-H Ph), 7.21 (2 H, m, *m*-H Ph), 7.16 (1 H, m, 6′-H), 7.13 (1 H, m, *p*-H Ph), 6.98 (1 H, m, 4′-H), 6.82 (1 H, m, 5′-H), 6.47 (1 H, m, 7′-H), 6.03 (1 H, d, $^4J = 1.7$ Hz, 5-H), 5.22 (1 H, d, $^4J = 1.7$ Hz, 3-H), 3.42 (2 H, m, OCH_2), 2.55 (3 H, s, NCH_3), 1.41 and 1.35 [3:3 H, s each, 3′-$(CH_3)_2$], 0.83 (3 H, t, $^3J = 7.2$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 168.7 (C_q, C2), 152.3 (C_q, C7′a), 145.5 (C_q, C4), 140.1 (C_q, C3′a), 135.8 (C_q, *i*-C Ph),128.7 (CH, *m*-C Ph), 128.3 (CH, C6′), 127.7 (CH, *p*-C Ph), 126.2 (CH, *o*-C Ph), 121.0 (CH, C4′), 118.6 (CH, C5), 118.0 (CH, C5′), 107.0 (CH, C7′), 96.8 (CH, C3), 87.6 (C_q, C1), 64.8 (OCH_2), 47.3 (C_q, C3′), 30.5 (NCH_3), 28.8 and 22.1 [CH_3 each, 3′-$(CH_3)_2$], 14.3 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2976 (18), 1620 (70), 1603 (58), 1484 (93), 1297 (41), 740 (100). MS (70 eV), *m/e* (%): 331 (84) [M^+], 316 (43), 302 (100), 272 (67), 258 (21). Anal. Calcd for $C_{23}H_{25}NO$ (331.4): C, 83.34; H, 7.60, N 4.23. Found: C, 83.10; H, 7.73, N 4.36. X-ray crystal structure analysis of **6a**:[22] formula $C_{23}H_{25}NO$, $M = 331.44$, colorless crystal 1.00 × 0.50 × 0.30 mm, $a = 8.443(1)$ Å, $b = 9.047(1)$ Å, $c = 13.215(2)$ Å, $\alpha = 101.79(1)°$, $\beta = 106.43(1)°$, $\gamma = 94.18(1)°$, $V = 938.5(2)$ Å^3, $\rho_{calc} = 1.173$ g cm^{-3}, $\mu = 5.46$ cm^{-1}, empirical absorption correction via ψ scan data ($0.925 \le C \le 0.999$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3993 reflections collected ($\pm h$, $\pm k$, $+l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 3823 independent ($R_{int} = 0.018$) and 3643 observed reflections [$I \ge 2\sigma(I)$], 231 refined parameters, $R =$

(22) X-ray structure analysis: Data sets were collected with Enraf-Nonius CAD4, Nonius MACH3, and KappaCCD diffractometers, the later two equipped with a Nonius FR591 rotating anode generator. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN (K. Fair, Enraf-Nonius B.V., 1990) and Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction for CCD data SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37; Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-86 and SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-93 and SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics DIAMOND (Brandenburg, K. Universität Bonn, 1997).

(23) Göttker-Schnetmann, I.; Aumann, R.; Bergander, K. *Organometallics*, in press.

0.049, $wR_2 = 0.141$, max. residual electron density 0.30 (−0.23) e Å^{-3}, hydrogens calculated and refined as riding atoms.

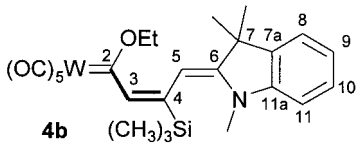


5a

5a. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.32, 7.1−6.94, 6.88, and 6.10 (2:2:4:1 H; s br, s br, m, m; Ph and 8-H-11-H), 4.39 and 4.15 (1:1 H, s each, 5-H_2), 4.32 (2 H, m, OCH_2), 2.63 (3 H, s, NCH_3), 1.55 and 1.44 [3:3 H, s each, 7-$(CH_3)_2$], 1.21 (3 H, t, ^3J = 7.2 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 269.6 (C_q, C2); 218.2, 213.6, 208.6, and 208.3 [C_q each, $W(CO)_4$], 157.7 (C_q, C6), 143.5 (C_q, C7a), 140.9 and 140.8 (C_q each, C11a and *i*-C Ph); 129.6−128.5 (br), 128.0 and 126.3−125.2 (br) (CH each, Ph); 127.6, 124.5, 121.7, and 109.9 (CH each, C8−C11), 117.0 (C_q, C3), 95.6 (C_q, C4), 75.7 (OCH_2), 64.9 (CH_2, C5), 50.5 (C_q, C7), 33.0 (NCH_3), 26.8 and 23.3 [CH_3 each, 7-$(CH_3)_2$], 14.8 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2009 (69), 1976 (8), 1905 (100), 1855 (73), 1478 (46), 1367 (23), 1285 (19). IR (hexane), cm^{-1} (%): 2019 (72), 1983 (69), 1935 (100), 1891 (72).

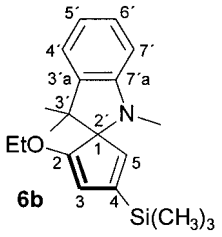
X-ray crystal structure analysis of **7a**:[22] formula $C_{21}H_{21}NO$, M = 303.39, yellow crystal 0.60 × 0.60 × 0.40 mm, a = 11.641(1) Å, b = 8.886(1) Å, c = 16.540(1) Å, β = 103.09(1)°, V = 1666.5(3) Å^3, ρ_{calc} = 1.209 g cm^{-3}, μ = 0.74 cm^{-1}, empirical absorption correction via ψ scan data (0.957 ≤ T ≤ 0.971), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223 K, $\omega/2\theta$ scans, 3536 reflections collected (−h, −k, ±l), [(sin θ)/λ] = 0.62 Å^{-1}, 3369 independent (R_{int} = 0.035) and 2596 observed reflections [$I \geq 2\sigma(I)$], 211 refined parameters, R = 0.066, wR_2 = 0.196, max. residual electron density 0.38 (−0.43) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Pentacarbonyl[1-ethoxy-3-trimethylsilyl-4-(1,3,3-trimethylindolin-2-ylidene)but-2-enylidene]tungsten (4b) and Spiro[2-ethoxy-4-trimethylsilylcyclopenta-2,4-diene-1,2′-*N*-methyl-3′,3′-dimethylindoline] (6b). To pentacarbonyl(1-ethoxy-3-trimethylsilylpropyn-1-ylidene)tungsten (**1b**) (478 mg, 1.00 mmol) in a 4 mL screw-top vessel was added 1,3,3-trimethyl-2-methyleneindoline (**2a**) (173 mg, 1.00 mmol) in 4 mL of toluene. Compound **1c** was consumed after stirring for 30 min at 20 °C (TLC). Additional stirring for 12 h at 50 °C, removal of the solvent, and chromatography on neutral alumina (activity IV) yielded compound **6b** as a colorless oil (254 mg,78%, R_f = 0.8 in *n*-pentane/diethyl ether, 20:1). A sample of compound **4b** containing an impurity of compound **6b** and $W(CO)_6$ was generated from pentacarbonyl(1-ethoxy-3-trimethylsilylpropyn-1-ylidene)tungsten (**1b**) (478 mg, 1.00 mmol) and 1,3,3-trimethyl-2-methyleneindoline (**2a**) (173 mg, 1.00 mmol) in 4 mL of diethyl ether after stirring 30 min at 20 °C and fast chromatography on neutral alumina (activity IV) (482 mg, ca. 74%, R_f = 0.7 with *n*-pentane/diethyl ether, 20:1). This sample was shown by NMR monitoring to produce compound **6b** after 6 h at 30 °C in a smooth reaction (260 mg, 79%).



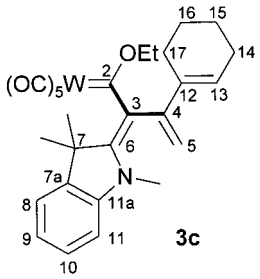
4b

4b. ^{1}H NMR (360 MHz, $CDCl_3$, 243 K): δ 7.70 [1 H, t, 1:12:1, $^3J(^1H,^{183}W)$ = 6.8 Hz, 3-H], 7.35 (1 H, m, 10-H), 7.31 (1 H, m, 8-H), 7.14 (1 H, m, 10-H), 6.97 (1 H, m, 11-H), 5.47 (1 H, s, 5-H), 4.51 and 4.37 (1:1 H, m each, OCH_2), 2.59 (3 H, s, NCH_3), 1.49 and 1.39 [3:3 H, s each, 7-$(CH_3)_2$], 0.83 (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3), 0.28 [9 H, s, $Si(CH_3)_3$]. ^{13}C NMR (90 MHz, $CDCl_3$, 243 K): δ 273.1 (C_q, C2), 204.5 and 199.1 [C_q each, *trans*- and *cis*-CO $W(CO)_5$], 169.1 (C_q, C6), 153.6 (C_q, C4), 146.0 (C_q, C11a), 144.1 (CH, C3), 138.4 (C_q, C7a); 128.3, 123.1 and 122.3 (CH each, C8−C10), 108.6 (CH, C11), 99.3 (CH, C5), 78.3 (OCH_2), 47.9 (C_q, C7), 35.1 (NCH_3), 26.4 [CH_3, 7-$(CH_3)_2$], 15.4 (OCH_2CH_3), −1.3 [CH_3, $Si(CH_3)_3$]. IR (diffuse reflection), cm^{-1} (%): 2961 (18), 2053 (68), 1966 (33), 1915 (100), 1565 (26), 1454 (44). IR (hexane), cm^{-1} (%): 2057 (23), 1970 (6), 1931 (100).

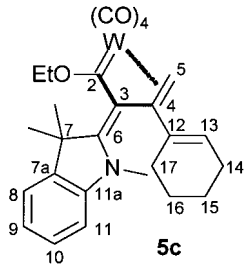


6b. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.22 (1 H, m, 6′-H), 6.94 (1 H, m, 4′-H), 6.74 (1 H, m, 5′-H), 6.45 (1 H, m, 7′H), 6.02 (1 H, d, ^4J = 1.7 Hz, 5-H), 4.92 (1 H, d, ^4J = 1.7 Hz, 3-H), 3.40 (2 H, m OCH_2), 2.52 (3 H, s, NCH_3), 1.37 and 1.32 [3:3 H, s each, 3′-$(CH_3)_2$], 0.84 (3 H, t, ^3J = 7.2 Hz, OCH_2CH_3), 0.20 [9 H, s, $Si(CH_3)_3$]. ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 167.8 (C_q, C2), 152.3 (C_q, C7′a), 148.0 (C_q, C4), 140.1 (C_q, C3′a), 135.7 (CH, C5), 127.6 (CH, C6′), 120.9 (CH, C4′), 117.8 (CH, C5′), 107.0 (CH, C7′), 98.9 (CH, C3), 87.9 (C_q, C1), 64.6 (OCH_2), 46.7 (C_q, C3′), 30.5 (NCH_3), 28.7 and 22.3 [3′-$(CH_3)_2$], 14.4 (OCH_2CH_3), −1.5 [$Si(CH_3)_3$]. IR (diffuse reflection), cm^{-1} (%): 2953 (43), 2802 (10), 1604 (81), 1484 (89), 1312 (50), 1247 (64), 1085 (71), 836 (100). MS (70 eV), *m/e* (%): 327 (37) [M^+], 312 (16), 298 (80), 283 (81), 268 (32), 210 (16), 182 (16). Anal. Calcd for $C_{20}H_{29}NOSi$ (327.5): C, 73.34; H, 8.92; N, 4.28. Found: C, 73.42; H, 9.00; N, 4.11.

Pentacarbonyl[1-ethoxy-3-cyclohex-1-enyl-2-(1,3,3-trimethylindolin-2-ylidene)but-3-enylidene]tungsten (3c) and Tetracarbonyl[1-ethoxy-3-cyclohex-1-enyl-2-(1,3,3-trimethyl- indolin-2-ylidene)but-3-enylidene]tungsten (5c). To pentacarbonyl[1-ethoxy-3-(cyclohex-1-enyl)propyn-1-ylidene]tungsten (**1c**) (486 mg, 1.0 mmol) in a 4 mL screw-top vessel was added 1,3,3-trimethyl-2-methyleneindoline (**2a**) (173 mg, 1.0 mmol) in diethyl ether. Compound **1c** was consumed after stirring 1 h at 20 °C (TLC). After removal of the solvent under reduced pressure (20 mbar, 20 °C) a red oil was obtained, which was extracted carefully with 4 × 4 mL each of *n*-pentane by the aid of ultrasound irradiation, then separated by centrifugation and dried under reduced pressure (20 mbar, then 10^{-3} mbar) to give compound **3c** as a dark red oil (449 mg, 68%, R_f = 0.6 on silica gel with *n*-pentane/diethyl ether, 10:1). An additional 118 mg (18%) of compound **3c** was obtained from the combined organic extracts after 12 h at −40 °C. Generation of tetracarbonyl complex **5c** was monitored by NMR spectra while heating a solution of 137 mg (0.21 mmol) of compound **3c** in 0.7 mL of C_6D_6 for 2 h at 50 °C in a sealed NMR tube. The sample remained essentially unchanged after an additional 60 h, 70 °C.



3c. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.11 (1 H, m, 10-H), 7.03 (1 H, m, 9-H), 6.93 (1 H, m, 8-H), 6.64 (1 H, m, 11-H), 5.99 (1 H, m br, 13-H), 5.62 and 5.16 (1:1 H, s each, 5-H_2), 4.38 (2 H, m, OCH_2), 2.98 (3 H, s, NCH_3); 2.6−2.4, 2.25−1.75, and 1.75−1.4 (1:4:3 H, m br each, 14-H_2-17-H_2), 1.20 [6 H, s, 7-$(CH_3)_2$], 1.01 (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 269−266 (C_q, very broad, C2), 204.4 and 201.1 [C_q each, *cis*- and *trans*-CO $W(CO)_5$], 177.4 (C_q, C6), 148.6 (C_q, C4), 142.7 and 141.5 (C_q, C7a and C11a), 139.8 (C_q, C12), 130.7 (CH, C13), 128.5 (CH, C10), 126.2 (C_q, br, C3), 125.9 (CH, C9), 122.2 (CH, C8), 120.1 (CH_2, C5), 111.1 (CH, C11), 74.0 (OCH_2), 51.6 (C_q, C7), 36.6 (NCH_3); 27.3−26.8, 26.0−25.8, 24.0−23.8, and 23.6−23.2 (CH_2 each, br each, C14−C17), 26.5 [CH_3, 7-$(CH_3)_2$], 15.8 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2929 (10), 2049 (19), 1900 (100), 1474 (22), 1366 (20). IR (hexane), cm^{-1} (%): 2056 (15), 1927 (100). MS (^{184}W, 70 eV), *m/e* (%): 631 [M^+] (20), 605 [M^+ − CO] (23), 575 [M^+ − 2 × CO] (25), 517 [M^+ − 4 × CO] (54), 489 [M^+ − 5 × CO] (55), 460 (86), 458 (95), 425 (28), 378 (22), 171 (81). Anal. Calcd for $C_{28}H_{29}NO_6W$ (659.4): C, 51.00; H, 4.43; N, 2.12. Found: C, 51.05; H, 4.19; N, 2.23.

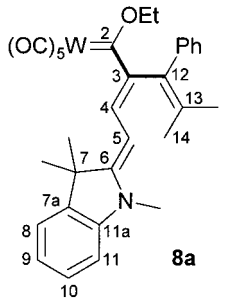


5c

5c. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.11 (1 H, m, 10-H), 6.98 (1 H, m, 9-H), 6.94 (1 H, m, 8-H), 6.57 (1 H, m, 11-H), 5.90 (1 H, m, 13-H), 4.36 (2 H, m, OCH_2), 4.10 and 3.77 (1:1 H, s each, 5-H_2), 3.03 (3 H, s, NCH_3), 2.6−2.4; 2.2−1.5 (1:7 H, m br each, 14-H_2-17-H_2), 1.46 and 1.44 [3:3 H, s each, 7-$(CH_3)_2$], 1.26 (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 268.5 (C_q, C2); 216.5, 215.1, 208.6, and 206.6 [C_q each, $W(CO)_4$], 158.7 (C_q, C6), 143.4 (C_q, C7a), 141.1 (C_q, C11a), 135.8 (C_q, C12), 128.3 (CH, C10), 125.7 (CH, C8), 124.6 (CH, C9), 115.7 (C_q, C3), 104.6 (C_q, C4), 110.9 (CH, C11), 74.0 (OCH_2), 67.7 (CH_2, C5), 50.6 (C_q, C7), 32.7 (NCH_3); 26.6, 25.8, 23.2, and 22.4 (CH_2 each, C14−C17), 26.5 and 23.1 [CH_3 each, 7-$(CH_3)_2$], 14.9 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2008 (51), 1977 (15), 1902 (100), 1853 (57). IR (hexane), cm^{-1} (%): 2015 (68), 1984 (82), 1931 (100), 1885 (70).

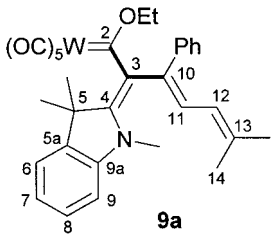
Pentacarbonyl[1-ethoxy-2-(1-phenyl-2-methylprop-1-enyl)-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-1-ylidene]tungsten (8a) and Pentacarbonyl[1-ethoxy-6-methyl-3-phenyl-2-(1,3,3-trimethylindolin-2-ylidene)hepta-3,5-dien-1-ylidene]tungsten (9a). To pentacarbonyl[1-ethoxy-3-phenylproyn-1-ylidene]tungsten (**1a**) (482 mg, 1.00 mmol) in a 4 mL screw-top vessel was added 1,3,3-trimethyl-2-(3-methylbut-2-enylidene)indoline (**2b**) (227 mg, 1.00 mmol) in 3.5 mL of diethyl ether. The mixture was stirred for 6 h at 20 °C until compound **1a** was consumed completely (TLC). The solvent was removed by a stream of argon, and the residue was separated by flash chromatography on silica gel with *n*-pentane/diethyl ether (40:1) to afford a first purple-red fraction containing compound **8a** (342 mg, 0.48 mmol, 48%, mp 116 °C dec, R_f = 0.8 with *n*-pentane/diethyl ether, 10:1) and a second orange-red fraction containing compound **9a** (235 mg, 0.33 mmol, 33%, mp 113 dec, R_f = 0.7 in *n*-pentane/diethyl ether, 10:1).

8a. ^{1}H NMR (600 MHz, C_6D_6, 298 K, major isomer): δ 8.87 (1 H, d, ^3J = 13.0 Hz, 4-H), 7.37 (2 H, m, *o*-H Ph), 7.19 (2 H, m, *m*-H Ph), 7.04 (1 H, m, *p*-H Ph), 6.99 (1 H, m, 10-H), 6.83 (2 H, m, 8-H and 9-H), 6.22 (1 H, m, 11-H), 5.80 (1 H, d, ^3J = 13.0 Hz, 5-H), 4.64 (2 H, m, OCH_2), 2.36 (3 H, s, NCH_3), 1.93 and 1.75 (3:3 H, s each, 13-CH_3 and 14-H_3), 1.64 and 1.58 [3:3 H, s br each, 7-CH_3)$_2$], 1.04 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). ^{13}C NMR (150 MHz, C_6D_6, 298 K): δ 289.1 (C_q, C2), 203.1 and



8a

199.5 [C_q each, *cis*- and *trans*-CO $W(CO)_5$], 169.2 (C_q, C6), 156.3 (CH, C4), 152.7 (C_q, C3), 143.5 (C_q, C11a), 142.6 (C_q, *i*-C Ph), 140.3 (C_q, C7a), 133.9 (C_q, C12), 130.8 (C_q, C13), 129.5 (CH, *o*-C Ph), 127.9 (CH, *m*-C Ph), 127.8 (CH, C10), 126.3 (CH, *p*-C Ph), 122.9 and 122.0 (CH each, C8 and C9), 108.2 (CH, C11), 97.5 (CH, C5), 77.2 (OCH_2), 47.7 (C_q, C7), 28.9 (NCH_3), 28.0 [CH_3, br, 7-$(CH_3)_2$], 23.0 and 21.6 (CH_3 each, 13-CH_3 and C14), 15.2 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2977 (4), 2053 (16), 1964 (9), 1906 (79), 1558 (71), 1157 (83), 1105 (100). IR (hexane), cm^{-1} (%): 2057.7 (10), 1963.2 (3), 1928.8 (100), 1567.4 (14). MS (70 eV), ^{184}W *m/e* (%): 709 [M^+] (1), 653 [M^+ − 2 × CO] (3), 625 [M^+ − 3 × CO] (13), 597 [M^+ − 4 × CO] (6), 569 [M^+ − 5 × CO] (64), 385 [M^+ − $W(CO)_5$] (56), 370 (79), 356 (100). Anal. Calcd for $C_{32}H_{31}NO_6W$ (709.5): C, 54.18; H, 4.40; N, 1.97. Found: C, 54.27; H, 4.55; N, 1.97. X-ray crystal structure analysis of **8a**:[22] formula $C_{32}H_{31}NO_6W$, M = 709.43, red crystal 0.25 × 0.20 × 0.10 mm, a = 10.712(1) Å, b = 10.861(1) Å, c = 14.835(2) Å, α = 79.48(1)°, β = 88.40(1)°, γ = 62.35(1)°, V = 1499.9(2) Å^3, ρ_{calc} = 1.571 g cm^{-3}, μ = 38.94 cm^{-1}, absorption correction via SORTAV (0.443 ≤ T ≤ 0.697), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 9934 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.65 Å^{-1}, 6811 independent (R_{int} = 0.029) and 6448 observed reflections [$I \geq 2\sigma(I)$], 367 refined parameters, R = 0.023, wR_2 = 0.058, max. residual electron density 1.08 (−1.21) e Å^{-3}, hydrogens calculated and refined as riding atoms.

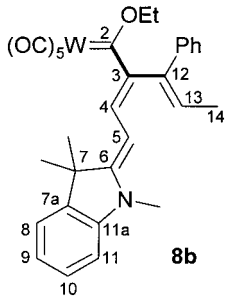


9a

9a. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.65 (2 H, *o*-H Ph), 7.19 (2 H, m, *m*-H Ph), 7.07 (1 H, d, ^3J = 11.5 Hz, 11-H), 7.00 (1 H, m, *p*-H Ph), 6.92 (1 H, m, 8-H), 6.86 (1 H, m, 7-H), 6.67 (2 H, m, 6-H and 12-H), 6.39 (1 H, m, 9-H), 4.37 (2 H, m, OCH_2), 3.02 (3 H, s, NCH_3), 1.87 and 1.70 (3:3 H, s each, 13-CH_3 and 14-H_3), 1.18 [6 H, s br, 5-$(CH_3)_2$], 0.94 (3 H, t, ^3J = 6.9 Hz, OCH_2CH_3). ^{13}C NMR (150 MHz, C_6D_6, 298 K): (C2 not detected due to dynamic line broadening), δ 204.0 and 201.4 [C_q each, *cis*- and *trans*-CO $W(CO)_5$], 181−178.5 (C_q, very br, C4), 142.4 (C_q, C9a), 142.0 (C_q, *i*-C Ph), 141.4 (C_q, C5a), 139.9 (C_q, C13), 137.7 (C_q, br, C3), 135.1 (CH, C11), 130.9 (CH, *o*-C Ph), 128.6 (C_q, br, C10) 128.3 (CH, C8), 128.2 (CH, *m*-C Ph), 127.3 (CH, *p*-C Ph), 126.0 (CH, C7), 123.8 (CH, C12), 122.1 (CH, C6), 111.3 (CH, C9), 74.0 (OCH_2), 51.8 (C_q C5), 36.4 (NCH_3), 26.6 and 18.9 (CH_3 each, 13-CH_3 and C14), 26.4 [CH_3, 5-$(CH_3)_2$], 15.7 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2046 (7), 1951 (4), 1895 (100), 1473 (11), 1381 (8). IR (hexane), cm^{-1} (%): 2057.7 (16), 1926.7 (100). MS (70 eV), ^{184}W *m/e* (%):

681 [$M^+ - CO$] (6), 653 [$M^+ - 2 \times CO$] (16), 625 [$M^+ - 3 \times CO$] (25), 569 [$M^+ - 5 \times CO$] (25), 540 (38), 510 (44), 202 (73), 158 (100). Anal. Calcd for $C_{32}H_{31}NO_6W$ (709.5): C, 54.18; H, 4.40; N, 1.97. Found: C, 54.33; H, 4.64; N, 1.94.

Pentacarbonyl[1-ethoxy-2-(1-phenylprop-1-enyl)-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-1-ylidene]tungsten (8b). Pentacarbonyl[1-ethoxy-3-phenylproyn-1-ylidene]-tungsten (**1a**) (482 mg, 1.00 mmol) in a 4 mL screw-top vessel was reacted with 1,3,3-trimethyl-2-(but-2-enylidene)indoline (**2c**) (275 mg, 1.00 mmol) in 3.5 mL of diethyl ether as described above for 6 h at 20 °C. If compound **8b** was not precipitated at this time, the sample was cooled to −20 °C and irradiated with ultrasound until precipitation took place. The solvent was removed by a stream of argon and the residue washed with 4 × 2 mL each of *n*-pentane, leaving red-brown compound **8a** (573 mg, 0.82 mmol, 82%, mp 110 °C, dec, R_f = 0.8 with *n*-pentane/diethyl ether, 10:1, dark red-brown solid).



8b

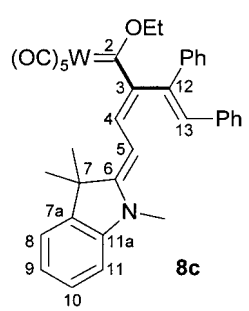
8b. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 8.96 (1 H, d, ^3J = 13.0 Hz, 4-H), 7.38 (2 H, m, *o*-H Ph), 7.19 (2 H, m *m*-H Ph), 7.04 (1 H, m, *p*-H Ph), 6.99 (1 H, m, 10-H), 6.86 (2 H, m, 8-H and 9-H), 6.23 (1 H, m, 11-H), 5.98 (1 H, d, ^3J = 13.0 Hz, 5-H), 5.56 (1 H, q, ^3J = 7.1 Hz, 13-H), 4.58 (2 H, m, OCH_2), 2.33 (3 H, s, NCH_3), 1.89 (3 H, d, ^3J = 7.1 Hz, 14-H_3), 1.66 [6 H, s, 7-$(CH_3)_2$], 0.98 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 289.8 (C_q, C2), 203.0 and 199.6 [C_q each, *cis*- and *trans*-CO $W(CO)_5$], 168.9 (C_q, C6), 156.6 (CH, C4), 154.3 (C_q, C3), 143.6 (C_q, C11a), 140.9 (C_q, *i*-C Ph), 140.4 (C_q, C7a), 139.4 (C_q, C12), 129.1 (CH, *o*-C Ph), 128.1 (CH, *m*-C Ph), 128.0 (CH, C10), 126.8 (CH, *p*-C Ph), 126.3 (CH, C13), 122.8 and 122.0 (CH each, C8 and C9), 108.1 (CH, C11), 97.8 (CH, C5), 77.3 (OCH_2), 47.6 (C_q, C7), 28.9 (NCH_3), 28.1 [CH_3, 7-$(CH_3)_2$], 15.4 (CH_3, C14), 14.9 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2053 (11), 1965 (5), 1905 (100), 1558 (29), 1154 (25), 1106 (31). IR (hexane), cm^{-1} (%): 2058.1 (9), 1959.5 (4), 1929.0 (100), 1567.5 (18). MS (70 eV), ^{184}W *m/e* (%): 695 [M^+] (2), 639 [$M^+ - 2 \times CO$] (2), 611 [$M^+ - 3 \times CO$] (11), 583 [$M^+ - 4 \times CO$] (4), 555 [$M^+ - 5 \times CO$] (14), 371 [$M^+ - W(CO)_5$] (31), 356 (81), 342 (100), 312 (25), 284 (19), 268 (19). Anal. Calcd for $C_{31}H_{29}NO_6W$ (695.4): C, 53.54; H, 4.20; N, 2.01. Found: C, 53.29; H, 4.36; N, 1.99.

Pentacarbonyl[1-ethoxy-2-(1,2-diphenylethenyl)-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-1-ylidene]tungsten (8c) and Spiro[2-ethoxy-3-(1,2-diphenylethenyl)-cyclopentadiene-1,2′-*N*-methyl-3′,3′-dimethylindoline] (10c). Pentacarbonyl[1-ethoxy-3-phenylpropyne-1-ylidene]-tungsten (**1a**) (482 mg, 1.00 mmol) in a 4 mL screw-top vessel was reacted with 1,3,3-trimethyl-2-(3-phenylprop-2-enylidene)-indoline (**2d**) (275 mg, 1.00 mmol) in 3.5 mL of diethyl ether as described above for 6 h at 20 °C. In case compound **8c** did not separate spontaneously, the mixture was cooled to −20 °C and irradiated with ultrasound in order to facilitate this process. The solvent was removed by a stream of argon, and compound **8c** was extracted with 4 × 2 mL each of *n*-pentane (653 mg, 0.86 mmol, 86%, mp 133 °C, dec, R_f = 0.8 with *n*-pentane/diethyl ether, 10:1, dark red solid). Compound **8c** was transformed into the spiro-fused cyclopentadiene **10c** by a rhodium-catalyzed fragmentation.[1] Single crystals of the latter compound were obtained from acetonitrile.

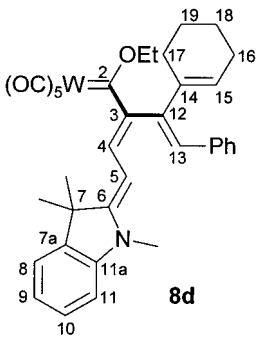
8c. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 9.04 (1 H, d, ^3J = 13.0 Hz, 4-H), 7.42 (2 H, m, *o*-H 12-Ph), 7.24 (2 H, m, *o*-H 13-Ph), 7.05 (4 H, m, *m*-H 12-Ph and 13-Ph), 6.97 (3 H, m, 10-H and *p*-H 12-Ph and 13-Ph), 6.85 (2 H, m, 8-H and 9-H), 6.57 (1 H, s, 13-H), 6.22 (1 H, d, ^3J = 13.0 Hz, 5-H), 6.17 (1 H, m, 11-H), 4.59 (2 H, m, OCH_2), 2.24 (3 H, s, NCH_3), 1.67 [6 H, s, 7-$(CH_3)_2$], 0.94 (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 288.8 (C_q, C2), 202.9 and 199.6 [C_q each, *cis*- and *trans*-CO $W(CO)_5$], 169.4 (C_q, C6), 157.0 (CH, C4), 153.7 (C_q, C3), 143.5 (C_q, C11a), 141.0 and 140.8 (C_q each, C12 and *i*-C 12-Ph), 140.4 (C_q, C7a), 138.3 (C_q, *i*-C 13-Ph), 131.1 (CH, C13), 129.6 and 129.5 (CH each, *o*-C 12-Ph and 13-Ph), 128.5 and 128.3 (CH each, *m*-C 12-Ph and 13-Ph), 128.1 (CH, C10), 127.3 and 127.1 (CH each, *p*-C 12-Ph and 13-Ph), 123.0 and 122.0 (CH each C8 and C9), 108.2 (CH, C11), 97.6 (CH, C5), 77.4 (OCH_2), 47.7 (C_q, C7), 28.9 (NCH_3), 28.1 [CH_3, 7-$(CH_3)_2$], 14.9 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2052 (13), 1904 (100), 1556 (25), 1150 (29), 1106 (30). IR (hexane), cm^{-1} (%): 2052.6 (25), 1929.4 (100), 1563.8 (25). MS (70 eV), ^{184}W *m/e* (%): 701 [$M^+ - 2 \times CO$] (2), 673 [$M^+ - 3 \times CO$] (15), 645 [$M^+ - 4 \times CO$] (11), 613 [$M^+ - 5 \times CO$] (100), 419 (46), 404 (43), 215 (43). Anal. Calcd for $C_{36}H_{31}NO_6W$ (757.6): C, 57.08; H, 4.12; N, 1.85. Found: C, 57.15; H, 4.38; N, 1.71.

10c. X-ray crystal structure analysis of **10c**:[22] formula $C_{31}H_{31}NO{\cdot}C_2H_3N$, M = 474.62, yellow crystal 0.25 × 0.15 × 0.05 mm, a = 8.694(3) Å, b = 16.319(4) Å, c = 19.886(4) Å, β = 94.15(2)°, V = 2814.0(13) Å^3, ρ_{calc} = 1.120 g cm^{-3}, μ = 5.17 cm^{-1}, empirical absorption correction via ψ scan data (0.882 ≤ T ≤ 0.975), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 3988 reflections collected ($\pm h$, $-k$, $+l$), [(sin θ)/λ] = 0.55 Å^{-1}, 3859 independent (R_{int} = 0.069) and 1602 observed reflections [$I \geq 2\sigma(I)$], 330 refined parameters, R = 0.066, wR_2 = 0.147, max. residual electron density 0.24 (−0.21) e Å^{-3}, hydrogens calculated and refined as riding atoms; due to the solvate the crystal diffracted poorly.

Pentacarbonyl[1-ethoxy-2-(1-cyclohex-1-enyl-2-phenylethenyl)-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-1-ylidene]tungsten (8d). Pentacarbonyl[1-ethoxy-3-(cyclohex-1-enyl)propyn-1-ylidene]tungsten (**1b**) (486 mg, 1.00 mmol) in a 4 mL screw-top vessel was reacted with 1,3,3-trimethyl-2-(3-phenylprop-2-enylidene)indoline (**2d**) (275 mg, 1.00 mmol) in 3.5 mL of diethyl ether as described above to give compound **8d** as a dark red-brown solid (627 mg, 0.82 mmol, 82%, mp 123 °C, dec, R_f = 0.9 with *n*-pentane/diethyl ether, 10:1).



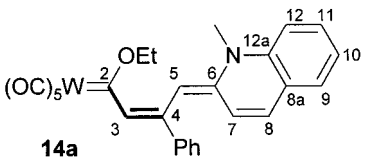
8c



8d

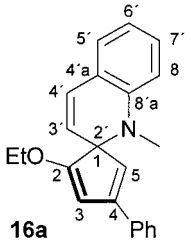
8d. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 8.89 (1 H, d, ^3J = 13.1 Hz, 4-H), 7.48 (2 H, m, *o*-H Ph), 7.22 (2 H, m, *m*-H Ph), 7.07 (1 H, m, *p*-H Ph), 6.97 (1 H, m, 10-H), 6.83 (2 H, m, 8-H and 9-H), 6.33 (1 H, s, 13-H), 6.15 (2 H, m, 5-H and 11-H), 5.93 (1 H, m, 15-H), 4.74 (2 H, m, OCH_2), 2.30 (3 H, s, NCH_3); 2.21, 1.99 and 1.53 (2:2:4 H, m each, 16-H_2-19-H_2), 1.66 [6 H, s, 7-$(CH_3)_2$], 1.15 (OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 291.3 (C_q, C2), 203.1 and 199.6 [C_q each, *cis*- and *trans*-CO W(CO)$_5$], 168.4 (C_q, C6), 156.1 (CH, C4), 154.3 (C_q, C3), 143.6 (C_q, C11a), 143.2 and 138.4 (C_q each, C12 and C14), 140.3 (C_q, C7a), 139.3 (C_q, *i*-C Ph), 129.4 (CH, C13), 129.0 (CH, *o*-C Ph), 128.4 (CH, *m*-C Ph), 128.1 (CH, C10), 126.9 (CH, *p*-C Ph), 122.7 and 122.0 (CH each, C8 and C9), 108.0 (CH, C11), 97.7 (CH, C5), 77.5 (OCH_2), 47.5 (C_q, C7), 28.7 (NCH_3); 28.6, 26.0, 23.5, and 22.6 (CH_2 each, C16−C19), 28.1 [CH_3, 7-$(CH_3)_2$], 15.2 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2926 (4), 2053 (16), 1908 (100), 1559 (34), 1160 (27), 1108 (39). IR (hexane), cm^{-1} (%): 2058.1 (7), 1929.1 (100), 1567.8 (15). MS (70 eV), ^{184}W *m*/*e* (%): 705 [$M^+ - 2 \times CO$] (3), 677 [$M^+ - 3 \times CO$] (18), 649 [$M^+ - 4 \times CO$] (10), 621 [$M^+ - 5 \times CO$] (58), 437 [$M^+ - W(CO)_5$] (44), 422 (75), 408 (88), 301 (14), 283 (20) 171 (100). Anal. Calcd for $C_{36}H_{35}NO_6W$ (761.5): C, 56.78; H, 4.63; N, 1.84. Found: C, 56.38; H, 4.65; N, 1.56.

Pentacarbonyl[1-ethoxy-3-phenyl-4-(1-methylchinaldin-2-ylidene)but-2-enylidene]tungten (14a) and Spiro-[2-ethoxy-4-phenylcyclopenta-2,4-diene-1,2′-*N*-methyl-1′,2′-dihyroquinoline] (16a). To 1,2-dimethylquinolinium iodide (**10a**) (285 mg, 1.0 mmol) and pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) in a 4 mL screw-top vessel was added 0.5 mL of a 4 M aqueous NaOH solution and then 3 mL of diethyl ether. The mixture was vigorously shaken for 1 min, cleared by centrifugation, and stored for 20 h at −40 °C. The sample was then allowed to warm to the melting point of the aqueous phase while centrifugation was continued to afford a dark blue etheral phase (which was discarded) and dark blue crystalline compound **14a** in the aqueous phase. The compound was analytically clean after drying in vacuo (10^{-3} mbar) for 2 h. It was shown by NMR spectra that compound **14a** was quantitatively transformed into compound **16a** at 30 °C within 6 h. A sample of compound **16a** was also obtained by reaction of 1,2-dimethylquinolinium iodide (**10a**) (285 mg, 1.0 mmol) with pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) in a 100 mL flask with 152 mg (1.5 mmol) of triethylamine in 15 mL of dichloromethane. After stirring for 10−20 min at 20 °C a color change from brown to blue was observed and compound **1a** was completely consumed (TLC test). The solvent was removed in vacuo, and the residue was extracted with 2 × 40 mL each of diethyl ether and filtered through Celite. After 12 h at 20 °C the color of the solution had changed from blue to brown and compound **16a** was isolated by chromatography on alumina and removal of the eluant as a colorless oil (227 mg, 72%, R_f = 0.8 on silica gel with *n*-pentane/diethyl ether, 10:1).



14a

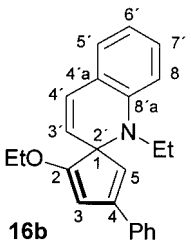
14a. ^{1}H NMR (600 MHz, CD_2Cl_2, 213 K): δ 7.76 (1 H, m, 11-H), 7.68 (1 H, m, 12-H), 7.58 (1 H, m, 9-H), 7.50 (3 H, m, *o*- and *p*-H Ph), 7.43 (3 H, m, *m*-H Ph and 10-H), 7.36 (1 H, s, 5-H), 7.26 (1 H, d, ^3J = 9.6 Hz, 8-H), 6.64 (1 H, s, 3-H), 6.43 (1 H, d, ^3J = 9.6 Hz, 7-H), 4.59 (2 H, m, dyn. br OCH_2), 4.00 (3 h, s, NCH_3), 1.61 (3 H, m, dyn. br OCH_2CH_3). ^{13}C NMR (150 MHz, CD_2Cl_2, 213 K): δ 259.5 (C_q, C2), 204.9 and 199.4 [C_q each, *trans*- and *cis*-CO W(CO)$_5$], 157.3 (C_q, C6), 149.3 (C_q, C3), 142.1 (C_q, *i*-C Ph), 139.1 (C_q, C12a), 132.9 (CH, C8), 132.2 (CH, C3), 131.5 (CH, C11), 129.1 (CH, *o*-C Ph), 128.7 (CH, *p*-C Ph), 128.2 (CH, *m*-C Ph), 128.1 (CH, C9), 124.4 (CH, C10), 124.1 (CH, C7), 123.3 (C_q, C8a), 115.2 (CH, C12), 107.1 (CH, C5), 75.9 (OCH_2), 37.5 (NCH_3), 15.1 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2050 (34), 1968 (10), 1908 (100). MS (70 eV), *m*/*e* (%): 352 (33), 315 (52), 286 (100), 270 (85), 256 (12), 243 (29), 213 (38), 184 (48). Anal. Calcd for $C_{27}H_{21}NO_6W$ (639.3): C, 50.73; H, 3.31; N, 2.19. Found: C, 50.87; H, 3.16; N, 2.12.



16a

16a. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.45 (2 H, m, *o*-H Ph), 7.19 (2 H, m, *m*-H Ph), 7.13 (1 H, m, *p*-H Ph), 7.07 (1 H, m, 7′-H), 6.84 (1 H, m, 5′-H), 6.64 (1 H, m, 6′-H), 6.46 (1 H, m, 8′-H), 6.44 (1 H, d, ^3J = 9.6 Hz, 4′-H), 6.18 (1 H, d, ^4J = 1.7 Hz, 5-H), 5.16 (1 H, d, ^4J = 1.7 Hz, 3-H), 5.15 (1 H, d, ^3J = 9.6 Hz, 3′-H), 3.60 (2 H, m, OCH_2CH_3), 2.58 (3 H, s, NCH_3), 1.00 (3 H, t, ^3J = 7.2 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 173.8 (C_q, C2), 145.5 (C_q, C8′a), 141.1 (C_q, C4), 135.6 (C_q, *i*-C Ph), 129.2 (CH, C7′), 128.8 (CH, *m*-C Ph), 128.3 (CH, *p*-C Ph), 127.9 (CH, C4′), 127.4 (CH, C5′), 126.3 (CH, *o*-C Ph), 125.2 (CH, C5), 122.7 (CH, C3′), 120.6 (C_q, C4′a), 116.6 (CH, C6′), 109.6 (CH, C8′), 95.5 (CH, C3), 75.0 (C_q, C1), 66.0 (OCH_2CH_3), 32.1 (NCH_3), 14.3 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2980 (31), 2891 (26), 1618 (64), 1597 (68), 1488 (100), 1350 (80). MS (70 eV), *m*/*e* (%): 315 (41) [M^+], 286 (100), 270 (24), 256 (12), 243 (31), 167 (15). Anal. Calcd for $C_{22}H_{21}NO$ (315.4): C, 83.78; H, 6.71; N, 4.44. Found: C, 83.65; H, 6.64; N, 4.26.

Spiro[2-ethoxy-4-phenylcyclopenta-2,4-diene-1,2′-*N*-ethyl-1′,2′-dihydroquinoline] (16b). 1,2-Dimethylquinolinium tetrafluoroborate (**10b**) (259 mg, 1.0 mmol) and pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) were reacted in a 100 mL flask with triethylamine (152 mg 1.5 mmol) in 15 mL of dichloremethane as described above to give compound **16b** as a colorless oil (231 mg, 70%, R_f = 0.8 on silica gel with *n*-pentane/diethyl ether, 10:1). A single crystal suitable for X-ray diffraction was obtained from the NMR sample of compound **16b** in C_6D_6 at 20 °C.

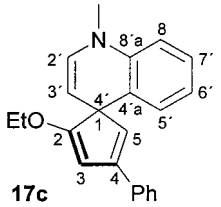


16b

16b. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.46 (2 H, m, *o*-H Ph), 7.21 (2 H, m, *m*-H Ph), 7.13 (1 H, m, *p*-H Ph); 7.07 (1 H, m, 7′-H), 6.85 (1 H, m, 5′-H), 6.63 (1 H, m, 6′-H), 6.50 (1 H, m, d, ^3J = 8.3 Hz, 8′-H), 6.43 (1 H, d ^3J = 10.0 Hz, 4′-H), 6.22 (1 H, d, ^4J = 1.8 Hz, 5-H), 5.15 (1 H, d, ^4J = 1.8 Hz, 3-H), 5.09 (1 H, d, ^3J = 10.0 Hz, 3′-H), 3.57 (2 H, q, ^3J = 7.0 Hz, OCH_2CH_3), 3.03 (2 H, m, NCH_2CH_3), 1.10 (3 H, t, ^3J = 7.0 Hz, NCH_2CH_3), 0.99 (3 H, t, ^3J = 7.0 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 174.6 (C_q, C2), 144.1 (C_q, C8′a), 140.6 (C_q, C4), 135.8 (C_q, *i*-C Ph), 129.4 (CH, C7′), 128.9 (CH, *m*-C Ph), 128.3 (CH, *p*-C Ph), 128.0 (CH, C4′ and C5′), 126.4 (CH, *o*-C Ph), 125.9 (CH, C5), 122.5 (CH, C3′), 120.5 (C_q, C4′a),

116.3 (CH, C6′), 109.7 (CH, C8′), 95.7 (CH, C3), 75.2 (C_q, C1), 66.0 (OCH_2CH_3), 40.4 (NCH_2CH_3), 14.4 (OCH_2CH_3), 13.9 (NCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 29 77 (26), 1615 (24), 1597 (31), 1487 (54), 1342 (48), 1112 (30), 743 (100). MS (70 eV), *m/e* (%): 329 (90) [M^+], 300 (100), 284 (32), 272 (37), 256 (14), 243 (59), 167 (8), 128 (13). Anal. Calcd for $C_{23}H_{23}NO$ (329.4): C, 83.85; H, 7.04; N, 4.25. Found: C, 83.70; H, 7.21; N, 4.03. X-ray crystal structure analysis of **16b**:[22] formula $C_{23}H_{23}NO{\cdot}0.5\ C_6H_6$, $M = 368.48$, yellow crystal 0.45 × 0.30 × 0.20 mm, $a = 11.100(1)$ Å, $b = 16.841(1)$ Å, $c = 11.111(1)$ Å, $\beta = 95.05(1)°$, $V = 2069.0(3)$ Å^3, $\rho_{calc} = 1.183$ g cm^{-3}, $\mu = 0.71$ cm^{-1}, absorption correction via SORTAV ($0.969 \le T \le 0.986$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 293$ K, ω and φ scans, 12 070 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.71 Å^{-1}, 5834 independent ($R_{int} = 0.035$) and 3997 observed reflections [$I \ge 2\sigma(I)$], 255 refined parameters, $R = 0.057$, $wR_2 = 0.136$, max. residual electron density 0.22 (−0.23) e Å^{-3}, hydrogens calculated and refined as riding atoms.

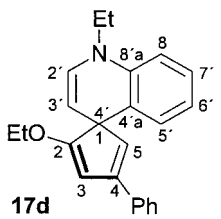
Spiro[2-ethoxy-4-phenylcyclopenta-2,4-diene-1,4′-*N*-methyl-1′,4′-dihydroquinoline] (17c). 1,4-Dimethylquinolinium iodide (**11c**) (285 mg, 1.0 mmol) and pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) in a 100 mL flask were reacted with triethylamine (152 mg, 1.5 mmol) in 15 mL of dichloromethane as described above to give colorless compound **17c** (234 mg, 74%, $R_f = 0.6$ on silica gel with *n*-pentane/diethyl ether, 10:1).



17c

17c. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.57 (2 H, m, *o*-H Ph), 7.20 (2 H, m, *m*-H Ph), 7.16 (1 H, m, 5′-H), 7.12 (1 H, m, *p*-H Ph), 7.05 (1 H, m, 7′-H), 6.79 (1 H, m, 6′-H), 6.55 (1 H, d, $^4J = 1.9$ Hz, 5-H), 6.45 (1 H, d, $^3J = 7.7$ Hz, 8′-H), 5.92 (1 H, d, $^3J = 8.0$ Hz, 2′-H), 5.33 (1 H, d, $^4J = 1.9$ Hz, 3-H), 4.48 (1 H, d, $^3J = 8.0$ Hz, 3′-H), 3.63, (2 H, m, OCH_2CH_3), 2.47 (3 H, s, NCH_3), 0.97 (3 H, t, $^3J = 7.0$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 179.1 (C_q, C2), 141.0 (C_q, C8′a), 139.9 (C_q, C4), 136.5 (C_q, *i*-C Ph), 133.8 (CH, C2′), 132.7 (CH, C5), 128.7 (CH, *o*-C Ph), 128.1 and 127.9 (CH each, *p*-C Ph and C5′), 127.6 (CH, C7′), 126.3 (CH, *o*-C Ph), 121.0 (C_q, C4′a), 120.9 (CH, C6′), 112.3 (CH, C8′), 97.0 (CH, C3′), 95.1 (CH, C3), 65.8 (OCH_2CH_3), 56.6 (C_q, C1), 37.8 (NCH_3), 14.3 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2978 (31), 2908 (32), 1660 (13), 1600 (19), 1481 (39), 1359 (39), 1103 (42), 748 (100). MS (70 eV), *m/e* (%): 315 (60) [M^+], 286 (100), 270 (21), 257 (19), 242 (27), 166 (13), 155 (23). Anal. Calcd for $C_{22}H_{21}NO$ (315.4): C, 83.78; H, 6.71; N, 4.44. Found: C, 83.98; H, 6.96; N, 4.10.

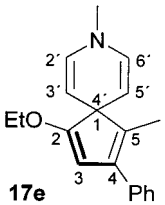
Spiro[2-ethoxy-4-phenylcyclopenta-2,4-diene-1,4′-*N*-ethyl-1′,4′-dihydroquinoline] (17d). 1,4-Dimethylquinolinium tetrafluoroborate (**11d**) (259 mg, 1.0 mmol) and pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) in a 100 mL flask were reacted with triethylamine (152 mg,1.5 mmol) in 15 mL of dichloromethane as described above to give colorless compound **17d** (240 mg, 73%, $R_f = 0.7$ on silica gel with *n*-pentane/diethyl ether, 10:1). A single crystal suitable for X-ray diffraction was obtained from the NMR sample of compound **17d** in C_6D_6 at 20 °C.



17d

17d. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.56 (2 H, m, *o*-H Ph), 7.20 (2 H, m, *m*-H Ph), 7.17 (1 H, m, 5′-H), 7.12 (1 H, m, *p*-H Ph), 7.03 (1 H, m, 7′-H), 6.77 (1 H, m, 6′-H), 6.54 (2 H, m, 8′-H and 5-H), 5.99 (1 H, d, $^3J = 8.0$ Hz, 2′-H), 5.32 (1 H, d, $^4J = 1.5$ Hz, 3-H), 4.44 (1 H, d, $^3J = 8.0$ Hz, 3′-H), 3.63 (2 H, m, OCH_2CH_3), 3.01 (2 H, m, NCH_2CH_3), 0.98 (3 H, t, $^3J = 7.0$ Hz, OCH_2CH_3), 0.94 (3 H, $^3J = 7.2$ Hz, NCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 179.1 (C_q, C2), 140.0 and 139.8 (C_q each, C8′a and C4), 136.5 (C_q, *i*-C Ph), 132.5 and 132.4 (CH each, C2′ and C5), 128.8 and 128.5 (CH each, *m*- and *p*-C Ph), 127.6 (CH, C5′), 126.3 (CH, *o*-C Ph), 121.4 (C_q, C4′a), 120.7 (CH, C6′), 112.4 (CH, C8′), 97.6 (CH, C3′), 95.1 (CH, C3), 65.8 (OCH_2CH_3), 56.7 (C_q, C1), 44.8 (NCH_2CH_3), 14.3 (OCH_2CH_3), 12.8 (NCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2975 (24), 1659 (18), 1599 (25), 1484 (41), 1387 (46), 1110 (30), 748 (100). MS (70 eV), *m/e* (%): 329 (65) [M^+], 300 (100), 284 (17), 272 (40), 254 (13), 242 (41), 215 (12). Anal. Calcd for $C_{23}H_{23}NO$ (329.4): C, 83.85; H, 7.04; N, 4.25. Found: C, 83.54; H, 6.81; N, 4.08. X-ray crystal structure analysis of **17d**:[22] formula $C_{23}H_{23}NO$, $M = 329.42$, light yellow crystal 0.45 × 0.35 × 0.10 mm, $a = 10.812(1)$ Å, $b = 8.533(1)$ Å, $c = 19.789(2)$ Å, $\beta = 96.85(1)°$, $V = 1812.7(3)$ Å^3, $\rho_{calc} = 1.207$ g cm^{-3}, $\mu = 5.65$ cm^{-1}, empirical absorption correction via ψ scan data ($0.785 \le T \le 0.946$), $Z = 4$, monoclinic, space group $P2_1$ (No. 4), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4165 reflections collected ($-h$, $-k$, $\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 3952 independent ($R_{int} = 0.030$) and 3358 observed reflections [$I \ge 2\sigma(I)$], 456 refined parameters, $R = 0.048$, $wR_2 = 0.135$, max. residual electron density 0.22 (−0.20) e Å^{-3}, Flack parameter 0.0(5), two independent molecules in the asymmetric unit, nearly enantiomorphic, difference in the position of the phenyl group C20 to C25, hydrogens calculated and refined as riding atoms.

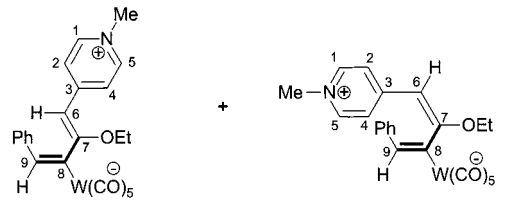
Spiro[2-ethoxy-5-methyl-4-phenylcyclopenta-2,4-diene-1,4′-*N*-methyl-1′,4′-dihydropyridine] (17e). 4-Ethyl-1-methylpyridinium iodide (**11e**) (249 mg, 1.0 mmol) and pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) in a 100 mL flask were reacted with triethylamine (152 mg, 1.5 mmol) in 15 mL of dichloromethane as described above to give colorless compound **17e** (191 mg, 68%, $R_f = 0.5$ on silica gel with *n*-pentane/diethyl ether, 10:1), which turned cherry-red after contact with air.



17e

17e. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 7.56 (2 H, m, *o*-H Ph), 7.28 (2 H, m, *m*-H Ph), 7.17 (1 H, *p*-H Ph), 5.85 (2 H, m, 2′-H and 6′-H), 5.18 (1 H, s, 3-H), 4.24 (2 H, m, 3′-H and 5′-H), 3.71 (2 H, q, $^3J = 7.1$ Hz, OCH_2CH_3), 2.29 (3 H, s, NCH_3), 2.20 (3 H, s, 5-CH_3), 1.16 (3 H, t, $^3J = 7.1$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ 176.1 (C_q, C2); 138.6, 138.5, and 133.9 (C_q each, C4, C5 and *i*-C Ph), 133.0 (CH, C2′ and C6′); 128.5, 128.4, and 126.6 (CH each, *o*-, *m*-, and *p*-C Ph), 99.8 (CH, C3′ and C5′), 98.0 (CH, C3), 65.3 (OCH_2CH_3), 56.7 (C_q, C1), 40.0 (NCH_3), 14.6 (OCH_2CH_3), 12.5 (CH_3, 5-CH_3). IR (diffuse reflection), cm^{-1} (%): 2978 (25), 2906 (29), 1673 (42), 1580 (61), 1374 (56), 1203 (100). MS (70 eV), *m/e* (%): 279 (100) [M^+], 250 (66), 234 (88), 220 (16), 207 (22), 192 (11), 178 (7). Anal. Calcd for $C_{19}H_{21}NO$ (279.4): C, 81.68; H, 7.58; N, 5.01. Found: C, 81.37; H, 7.82; N, 4.91.

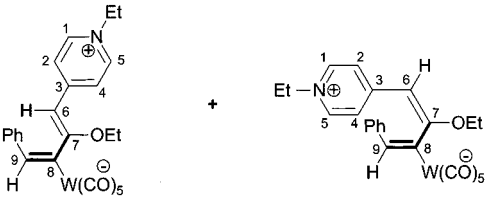
***N*-Methylpyridinium-4-[(*1E/Z,3E*)-(2-ethoxy-4-phenyl-1,3-butadien-3-yl]pentacarbonyltungstate (18f/18′f).** 1,4-Dimethylpyridinium iodide (**11f**) (235 mg, 1.0 mmol) and pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) in a 4 mL screw-top vessel were reacted with triethylamine (152 mg, 1.5 mmol) in 3.5 mL of dichloromethane. Compound **1a** was consumed at 20 °C, 5 min while stirring (TLC test). Flash chromatography on silica gel with diethyl ether/methanol, 20:1, afforded compounds **18f/18′f** as an orange oil (312 mg, 0.53 mmol, 53%, R_f = 0.5 in diethyl ether/methanol, 20:1). An orange powder insoluble in C_6D_6, but soluble in CD_2Cl_2 or $CDCl_3$, was obtained from the NMR sample in C_6D_6 after removal of the solvent. However ^{1}H NMR spectra of this powder in CD_2Cl_2 were found to be identical with that of the orange oil obtained iniatially. Compounds **18f/18′f** were stable in (C_6D_6, $CDCl_3$, or CD_2Cl_2) solution at 300 K for several hours. Single crystals of the major isomer **18f** suitable for an X-ray diffraction analysis were obtained from CH_2Cl_2 after 48 h at 233 K.



18′f (minor isomer) **18f** (major isomer)

18f. ^{1}H NMR (600 MHz, CD_2Cl_2, 213 K; mixture of isomers **18f** and **18′f**, minor isomer **18′f** in brackets): δ 7.99 {8.12} (1 H, "d", br, 4-H), 7.42 {7.49} (1 H, "d", br, 1-H), 7.33 {7.32} (1 H, "d", br, 5-H), 7.21 {7.21} (4 H, m, *o*-H and *m*-H Ph), 7.12 {6.96} (1 H, "t", 1:12:1, $^3J(^1H,^{183}W)$ = 6.8 Hz, 9-H), 7.07 {7.14} (1 H, m, *p*-H Ph), 6.91 {6.72} (1 H, "d", br, 2-H), 5.38 {5.16} (1 H, s, 6-H), 4.35 and 3.82 {4.52 and 3.93} (1:1 H, m each, OCH_2), 3.96 {3.76} (3 H, s, NCH_3), 1.33 {1.47} (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3). ^{13}C NMR (150 MHz, CD_2Cl_2, 213 K; mixture of isomers, minor isomer in brackets): δ 204.2 and 200.7 {205.7 and 200.9} [C_q each, *trans*- and *cis*-CO W(CO)$_5$], 188.3 {189.2} (C_q, C8), 163.2 {163.1} (C_q, C7), 152.1 {152.0} (C_q, C3), 139.6 {138.8} (C_q, *i*-C Ph), 139.5 {139.8} (CH, C1), 138.5 {138.7} (CH, C5), 137.2 {135.6} (CH, C9), 128.3 {128.3} (CH, *m*-C Ph), 126.2 {125.2} (CH, *p*-C Ph), 125.9 {125.5} (CH, *o*-C Ph), 120.8 {120.6} (CH, C2), 118.0 {117.5} (CH, C4), 90.1 {92.0} (CH, C6), 63.0 {64.7} (OCH_2), 44.9 {44.7} (NCH_3), 14.2 {14.7} (OCH_2CH_3). ^{1}H NMR (400 MHz, C_6D_6, 300 K; mixture of isomers, minor isomer in brackets): (2- and 4-H not detected due to dynamical line broadening) δ 7.59 {7.50} (1 H, "t", 1:12:1, $^3J(^1H,^{183}W)$ = 6.8 Hz, 9-H), 7.33 {7.31} (2 H, m, *o*-H Ph), 7.10 {7.13} (2 H, m, *o*-H Ph), 6.92 {6.94} (1 H, m, *p*-H Ph), 5.77 {5.85} (2 H, d, ^3J = 8.0 Hz, 1-and 5-H), 5.42 {5.33} (1 H, s, 6-H), 4.50 and 3.93 {4.68 and 4.04} (1:1 H, m each, OCH_2), 2.04 {2.29} (3 H, s, NCH_3), 1.15 {1.24} (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6, 300 K; mixture of isomers, minor isomer in brackets): δ 204.0 and 202.0 {205.5 and 202.2} (C_q each, *trans*- and *cis*-CO W(CO)$_5$), 190.5 {190.3} (C_q, C8), 164.6 {164.3} (C_q, C7), 152.3 {152.1} (C_q, C3), 141.2 {140.5} (C_q, *i*-C Ph), 138.4 {138.2} (CH, C1 and C5), 137.0 {137.0} (CH, C9), 128.9 {128.8} (CH, *m*-C Ph), 126.7 {127.4} (CH, *o*-C Ph), 126.3 {125.9} (CH, *p*-C Ph), 119.4 {119.4} (C2 and C4, but no cross-peak in the GHSQC and no signal in the DEPT 135 experiment), 93.0 {94.8} (CH, C6), 63.7 {65.6} (OCH_2), 43.1 {43.1} (NCH_3), 14.7 {15.0} (OCH_2CH_3). IR (CH_2Cl_2), cm^{-1} (%): 2051 (15), 1959 (8), 1911 (100), 1870 (26). MS (MALDI-TOF, 337.0 nm, 3 ns, matrix: DCTB[24]): 589 [M^+], 561 [M^+ − CO], 533 [M^+ − 2 × CO]. X-ray crystal structure analysis of **18f**:[22] formula $C_{23}H_{19}NO_6W\cdot CH_2Cl_2$, M = 674.17, orange crystal 0.40 × 0.30 × 0.10 mm, a = 9.880(1) Å, b = 14.654(1) Å, c = 17.779(1) Å, β = 95.20(1)°, V = 2563.5(3) Å^3, ρ_{calc} = 1.747 g cm^{-3}, μ = 47.53 cm^{-1}, absorption correction via SORTAV (0.252 ≤ T ≤ 0.648), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 17 426 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.62 Å^{-1}, 5047 independent (R_{int} = 0.049) and 4122 observed reflections [$I \geq 2\sigma(I)$], 309 refined parameters, R = 0.031, wR_2 = 0.066, max. residual electron density 1.41 (−0.92) e Å^{-3}, hydrogens calculated and refined as riding atoms.

***N*-Ethylpyridinium-4-[(*1E/Z,3E*)-(2-ethoxy-4-phenyl-1,3-butadien-3-yl)]pentacarbonyltungstate (18g/18′g).** 1-Ethyl-4-methylpyridinium tetrafluoroborate (**11g**) (209 mg, 1.0 mmol) and pentacarbonyl(1-ethoxy-3-phenylpropyn-1-ylidene)tungsten (**1a**) (482 mg, 1.0 mmol) in a 4 mL screw-top vessel were reacted with triethylamine (152 mg, 1.5 mmol) in 3.5 mL of dichloromethane as described above to give compounds **18g/18′g** as an orange oil after flash chromatography on silica gel with diethyl ether/methanol, 20:1 (306 mg, 0.51 mmol, 51%, R_f = 0.5 in diethyl ether/methanol, 20:1).



18′g (minor isomer) **18g** (major isomer)

18g. ^{1}H NMR (360 MHz, C_6D_6, 303 K; mixture of isomers **18g** and **18′g**, minor isomer **18′g** in brackets): (2- and 4-H were not detected due to dynamical line broadening) δ 7.63 {7.52} (1 H, "t", $^3J(^1H,^{183}W)$ = 6.6 Hz, 9-H), 7.37 {7.32} (2 H, m, *o*-H Ph), 7.09 {7.12} (2 H, m, *m*-H Ph), 6.92 {6.94} (1 H, m, *p*-H Ph), 5.94 {5.98} (2 H, ^3J = 7.1 Hz, 1- and 5-H), 5.47 {5.37} (1 H, s, 6-H), 4.53 and 3.93 {4.72 and 4.06} (1:1 H, m, each, OCH_2), 2.44 {2.64} (2 H, NCH_2), 1.15 {1.26} (3 H, t, ^3J = 7.1 Hz, OCH_2CH_3), 0.34 {0.52} (3 H, t, ^3J = 7.4 Hz, NCH_2CH_3). ^{13}C NMR (90 MHz, C_6D_6, 303 K; mixture of isomers, minor isomer in brackets): δ 203.9 and 202.0 {205.6 and 202.3} [C_q each, *trans*- and *cis*-CO W(CO)$_5$], 190.5 {190,2} (C_q, C8), 164.8 {164.3} (C_q, C7), 152.6 {152.4} (C_q, C3), 141.2 {140.5} C_q, *i*-C Ph), 138.5 and 136.9 {138.5 and 136.9} CH each, C1, C5 and C9), 129.1 {129.0} (CH, *o*-C Ph), 126.8 {127.5} (CH, *m*-C Ph), 126.5 {126.0} (CH, *p*-C Ph), 119.7 {119.7} (C2 and C4), 93.1 {94.7} (CH, C6), 63.8 {65.7} (OCH_2), 52.3 {52.3} (NCH_2), 15.3 {15.6} (NCH_2CH_3), 14.9 {15.2} (OCH_2CH_3). IR (CH_2Cl_2), cm^{-1} (%): 2051 (13), 1959 (7), 1910 (100), 1871 (25). MS (MALDI-TOF, matrix: DCTB): 603 [M^+], 575 [M^+ − CO], 547 [M^+ − 2 × CO].

Acknowledgment. This investigation was supported by the Deutsche Forschungsgemeinschaft (grant of the Graduiertenkolleg "Hochreaktive Mehrfachbindungssysteme" at Münster to I.G.-S.) and the Fonds der Chemischen Industrie.

Supporting Information Available: Details of the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

(24) DCTB = 1,1-dicyano-3-methyl-4-(4-*tert*-butylphenyl)-1,3-butene.

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