Organic Syntheses via Transition-Metal Complexes. 119.[1] α-Methylenation and α-Alkenylation of α,β-Unsaturated Amides by Means of Carbene Tungsten Complexes: A Novel Baylis−Hillman Type Reaction

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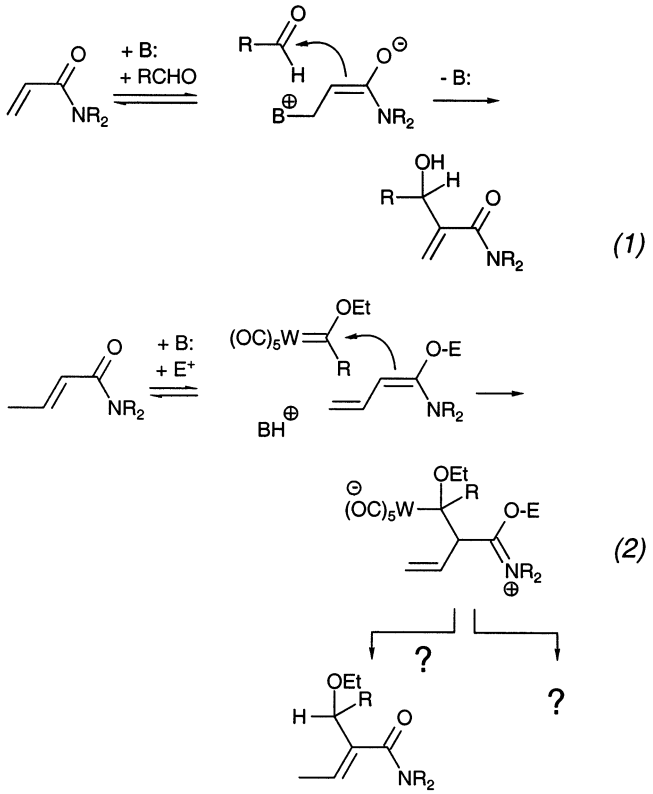
Fischer carbene complexes were found to undergo Baylis−Hillman type additions to α,β-unsaturated acid amides. Reactions of (non-CH-acidic) carbene tungsten complexes **1a**−**c** with (CH-acidic) but-2-enoic acid amides **2** in the presence of $POCl_3/Et_3N$ resulted in an α-addition of the carbene ligand to the amide backbone and formation of cross-conjugated aminocarbene complexes **3**. Reaction of CH-acidic carbene tungsten complexes **1d**−**h** gave the cross-conjugated aminocarbene complexes **9** (which are double-bond isomers of compounds **3**) together with (cyclobutenyl)carbene complexes **10**, by α- and β-addition, respectively, to the but-2-enoic amides **2**. Compounds **9** and **10** are valence isomers, but they do not interconvert thermally.

The α-alkylation of α,β-unsaturated carbonyl compounds by tertiary amine- or phosphine-catalyzed coupling with aldehydes, the so-called Baylis−Hillman reaction, is among the most useful C−C bond-forming reactions in organic synthesis (eq 1 in Scheme 1).[2] Much progress[3] has been achieved since Baylis and Hillman first reported the reaction of acetaldehyde with ethyl acrylate and acrylonitrile in the presence of catalytic amounts of a strong Lewis base such as 1,4-diazabicyclo-[2.2.2]octane in 1972.[4] The hydroxymethylene adducts thus generated contain a structural element that is widely present in products of biological and medicinal interest.[5] The α,β-unsaturated carbonyl compounds which were shown to undergo a Baylis−Hillman reaction include acrylonitrile, acrolein, acrylates, and α,β-unsaturated ketones, but to date, only very few examples are known of acrylamides.[6]

Scheme 1. Baylis−Hillman Reaction of Acid Amides Involving Enolate Intermediates and an "Enol-Approach" to a Corresponding Reaction with Carbene Complexes



We report on Baylis−Hillman type additions of Fischer carbene complexes to the α-position of α,β-unsatur-

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† X-ray structure analysis.

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ated acid amides (eq 2 in Scheme 1). While enolates are typically assumed to be reactive intermediates in Baylis−Hillman reactions, our approach involves the formation of enol intermediates from acid amides under the influence both of a Lewis base and a Lewis acid. To our knowledge, an "enol approach" has not been successfully applied before to such reactions.

Our enol approach is based on the condensation of acid amides with carbene complexes under Vilsmeyer conditions. Reactions of this type have proven most versatile in our hands and have been utilized for the generation of a broad range of interesting compounds from readily available starting components in most straightforward procedures and usually in good yields. Even though seemingly minor structural changes of the amide as well as of the carbene complex are expected to exhibit a strong influence on the overall reaction, it is obvious that the different reaction paths are strictly controlled and are easily distinguished on the basis of mechanistic considerations referring to the specific iminium compounds derived from the amides under Vilsmeyer conditions. Typical reaction paths include the condensation of methylethoxycarbene complexes (M = Cr, Mo, W) with tertiary non-α-CH-acidic amides, such as tertiary arylamides or tertiary formamides, to produce (3*E*)-4-amino-1-metalla-1,3-dienes.[7] Furthermore, condensation of methylethoxycarbene complexes (M = Cr, Mo, W) with secondary arylamides or even secondary alkylamides gave (3*Z*)-4-amino-1-metalla-1,3-dienes, while (in line with expectation) the condensation with secondary formamides took a completely different course and produced ketenimine complexes instead.[8] Condensation of (non-α-CH-acidic) arylethoxycarbene complexes (M = Cr, Mo, W) with (α-CH-acidic) tertiary alkylamides afforded 2-amino-1-metalla-1,3-dienes by insertion of a C,C unit into the M=C bond, which was induced by the elimination of an α-hydrogen atom from the iminium intermediate.[9] A manifold of fascinating products has been derived from α,*β*-unsaturated acid amides. In line with expectation, these reactions were strictly controlled by structural features, such as the presence or absence of acidic hydrogen atoms as well as substituents influencing a 2,1- and 4,1-addition, respectively, in an early reaction stage. Thus, condensation of methylethoxycarbene complexes with tertiary cinnamides produced (3*E*)-4-amino-1-metalla-1,3,5-hexatrienes and aminocyclopentadienes resulting thereof by *π*-cyclization, together with minor amounts of cyclohexanonylcarbene complexes, both resulting from initial 2,1-addition. These products were not obtained from (primary alkyl)ethoxycarbene complexes, since 4,1-addition to the α,*β*-unsaturated amide prevailed with these compounds and resulted in formation of cyclobutenylaminocarbene complexes as the only products.[10] Furthermore, condensation of methylethoxycarbene complexes with secondary cinnamides produced (3*Z*)-amino-1-metalla-1,3,5-hexatrienes, while condensation of (primary alkyl)ethoxycarbene complexes afforded an efficient access to novel (*N*-enamino)carbene complexes.[1] The reaction on which we wish to report in this paper is based on the specific reactivity of tertiary α,*β*-unsaturated acid amides containing a CH-acidic unit (Scheme 2).

Reactions of but-2-enoic acid amides **2a**,**b** with equivalent amounts of phosphorus oxychloride, tungsten carbene complexes **1a**−**c**, and triethylamine in dichloromethane at 25 °C afford the yellow cross-conjugated α-methylenation products **3a**−**e** (Scheme 2). They form 3*E*/3*Z* isomeric mixtures with respect to the 2-amino-3-ethoxy-1-tungstabuta-1,3-diene unit (Scheme 2), in which the 3*E* isomers prevail. Both isomers (3*E*)-**3** and (3*Z*)-**3** exhibit zwitterionic carbiminium carbonylmetalate structures.[11] These are chiral, since they are strongly twisted due to the allyl effect of the ligand backbone (Figure 1).

It is assumed that iminium chlorides **4** and enamines **5** are generated initially and add to the carbene complexes **1**. Interestingly, addition is observed to the carbene carbon atom to give intermediates **6** only, thus providing a good entry to the formation of 1-metallahexa-1,3,5-trienes and 1-metallahexa-1,3-dien-5-ynes. No products arising from *β*-addition to α,*β*-unsaturated carbene complexes **1b**,**c** have been found so far. A typical Baylis−Hillman reaction would involve transformation of an adduct **6** into compound **6′**, but apparently the reaction course is outrun by a 1,3-migration of the $W(CO)_5$ unit to give the zwitterion **7** as precursor to the amino carbene complex **3** (Scheme 2). Compounds **3** undergo hydrolysis of the enol ether unit on extended contact with silica gel to afford the acyl derivatives **8** (eq 1 in Scheme 3), which are considered Baylis−Hillman type products, in which the oxygen atom of the amide moiety is replaced by the isolobal $W(CO)_5$ unit.

While pursuing studies, reactions of the butyl carbene complex **1f** instead of non-CH-acidic compounds **1a**−**c** were found to afford conspicuously small yields of the α-methylenation product **3f**. This observation prompted us to further investigate the influence of CH-acidic groups in compounds **1** on the overall reaction. It was explicitly shown by NMR spectra that the compound (3*E*)-**3f** is smoothly transformed into compound (3*Z*)-**9f** already at 20 °C within 15 h by a (supposedly catalyzed) 1,5-hydrogen transfer (eq 2 in Scheme 3). Metallatrienes **3a**−**e** containing R^1 = aryl, alkynyl, alkenyl instead of R^1 = alkyl proved to be quite stable thermally.

α-CH-Acidic Carbene Complexes 1d−i

Reactions of α-CH-acidic carbene complexes **1d**−**h** with the but-2-enoic acid amides **2a**,**b** in the presence of $POCl_3/Et_3N$ gave three major products: 2-amino-1-tungstapenta-1,3-dienes (3*Z*)-**9**, which are double-bond

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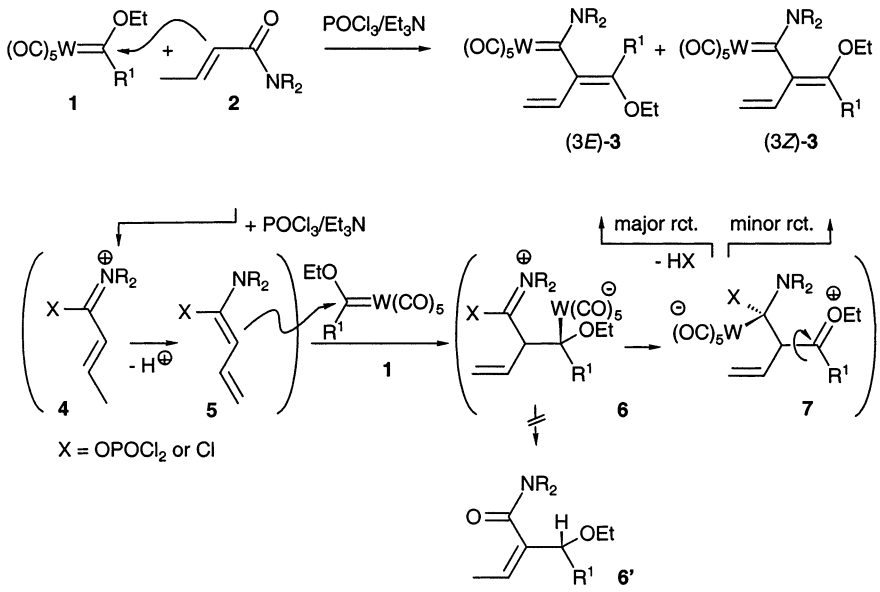
Scheme 2. α-Methylenation of *γ-CH*-Acidic Tertiary Crotyl Amides with Carbene Tungsten Complexes



1	R^1	3,8	R^1	NR_2	3[%]	(*E*/*Z*)-3	8[%]
a	Ph	**a**	Ph	NMe_2	78	4.5/1	12
b	C≡CPh	**b**	Ph	morpholino	65	20/1	12
c	CH=CHPh	**c**	C≡CPh	NMe_2	52	25/1	-
		d	C≡CPh	morpholino	49	20/1	-
2	NR_2	**e**	CH=CHPh	NMe_2	44	12/1	-
a	NMe_2	**f**	*n*-Bu[a]	morpholino	20	20/1	-
b	morpholino						

[a] See Scheme 4 for this reaction.

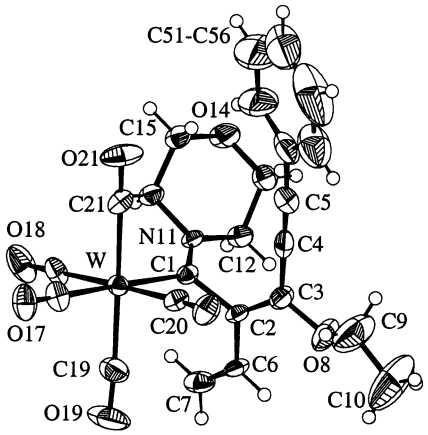
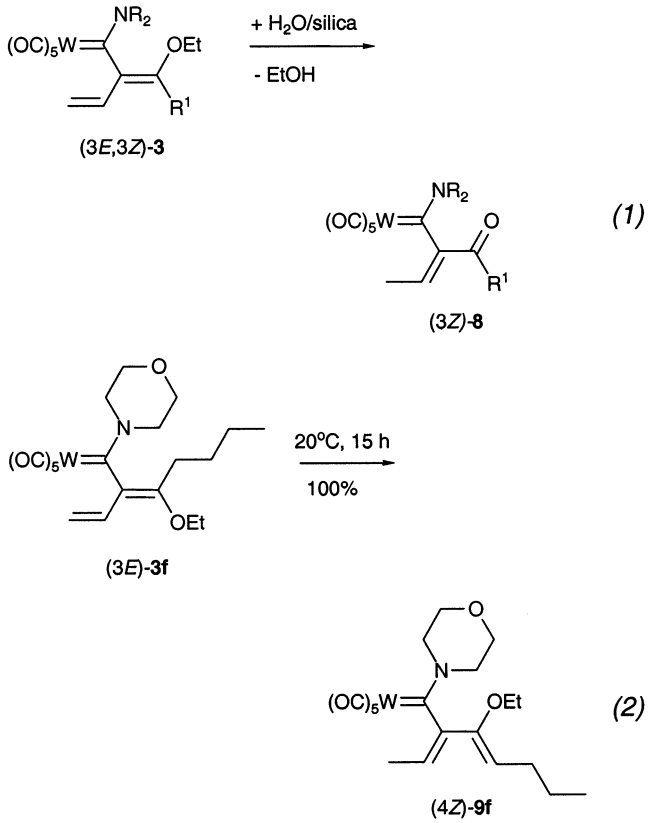


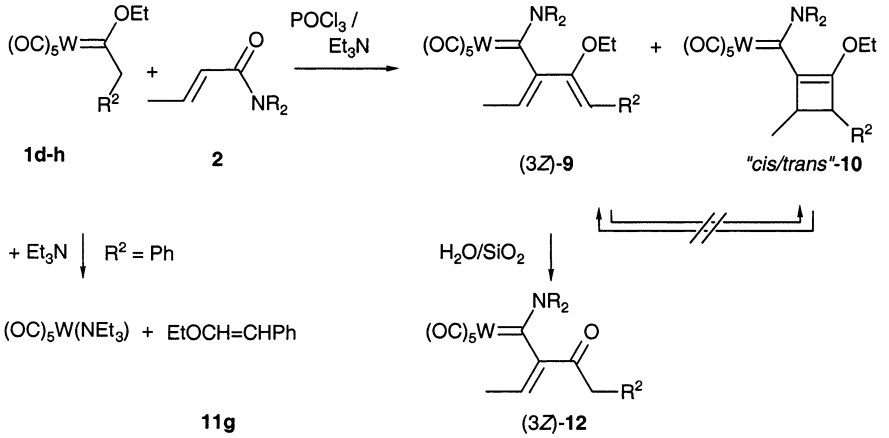
Figure 1. Molecular structure of the 3-ethenyl-1-tungsta-hexa-1,3-dien-5-yne compound (3*E*)-**3d**. Selected bond lengths (Å), valence angles (deg), and dihedral angles (deg): W−C1 = 2.228(8), C1−C2 = 1.514(10), C1−N11 = 1.334(10), C2−C3 = 1.355(12), C2−C6 = 1.454(11), C3−C4 = 1.440(13), C3−O8 = 1.379(10), C4−C5 = 1.208(13), C5−C51 = 1.427(14), C6−C7 = 1.327(13); W−C1−C2 = 115.9(5), W−C1−N11 = 130.6(5), N11−C1−C2 = 113.4(7), C1−C2−C3 = 119.8(7), C1−C2−C6 = 118.9(7), C6−C2−C3 = 121.3(7), C2−C3−C4 = 122.6(8), C2−C3−O8 = 119.0-(7), O8−C3−C4 = 118.4(8), C3−C4−C5 = 177.6(11), C4−C5−C51 = 177.3(11), C2−C6−C7 = 124.4(8); W−C1−C2−C3 = −91.7(8), W−C1−C2−C6 = 89.0(7), C1−C2−C3−C4 = −0.5(13).

isomers of compounds **3**, and acyl derivatives **12**, apparently resulting thereof by hydrolysis (Scheme 4).

Scheme 3. Hydrolysis and Rearrangement of Compounds 3



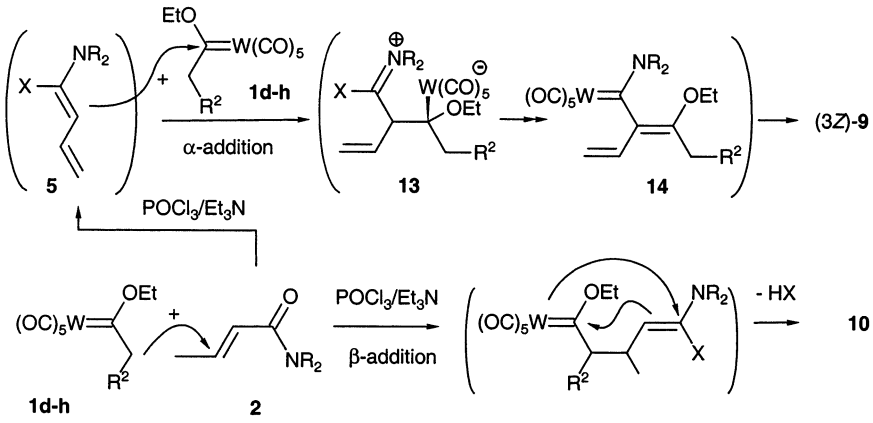
Scheme 4. Aminocarbene Complexes 9 and 10: Stable Valence Isomers Generated from Tertiary Crotyl Amides and CH-Acidic Carbene Complexes 1d−h in Parallel Reactions



1	CH_2R^2	3,9,10,12	R^2	NR_2	3[%][a]	9[%][a]	10[%][a],[b]	12[%][a]
d	Me	**a**	H	NMe_2	-	-	-	66
e	Et	**b**	H	morpholino	-	-	-	59
f	*n*-Bu	**c**	Me	NMe_2	-	22	29 (5:3)	8
g	CH_2Ph	**d**	Me	morpholino	-	17	20 (5:1)	15
h	$CH_2C_7H_7$	**e**	*n*-Pr	NMe_2	-	20	32 (4:1)	6
i	ETHF[c]	**f**	*n*-Pr	morpholino	20[d]	20[d]	18 (20:1)	11
		g	Ph	NMe_2	-	-	13[e] (3:4)	-
		h	Ph	morpholino	-	-	12[e] (3:4)	-
2	NR_2	**i**	C_7H_7	NMe_2	-	-	44 (7:2)	2
a	NMe_2	**j**	C_7H_7	morpholino	-	-	46 (12:1)	2
b	morpholino	**k**	2-HOBu[f]	NMe_2	-	-	-	40

[a] Isolated chemical yields. [b]Molar ratio "*cis*"-**10**/"*trans*"-**10** is shown in parentheses. [c]ETHF = 5-ethyltetrahydrofuran-2-ylidene−$W(CO)_5$. [d]Compound **3f** was isolated instead, if short reaction times were applied (see footnote *a* in Scheme 2), but compound **9f** has been obtained on extension of the reaction time (see Scheme 3), resulting from rearrangement of compound **3f**. [e]1-Ethoxy-2-phenylethene (**11g**) was obtained as major product by a competing base-induced elimination of the carbene ligand. [f]2-Hydroxybutan-1-yl.

Scheme 5. Reaction Paths Initiated by α- and *β*-Addition of CH-Acidic Carbene Complexes 1d−h to α,*β*-Unsaturated Amides 2

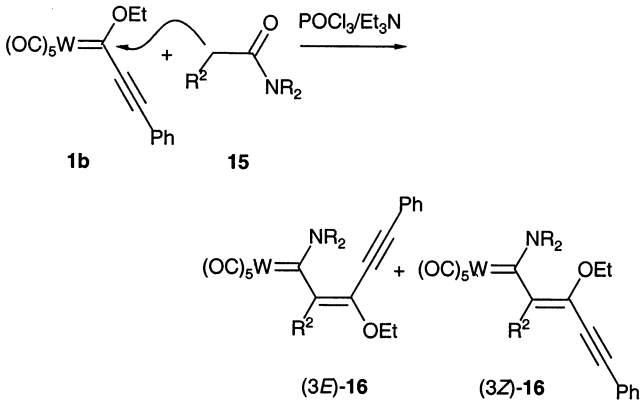


Furthermore, (2-ethoxycyclobutenyl)carbene complexes **10** were obtained, which are valence isomers of compounds **9**.

Side reactions included a base-induced elimination of enol ethers from carbene complexes **1d**−**h**. Formation of the enol ether **11g** was the major reaction of the benzyl carbene complex **1g**, since the α-position of this compound is activated by two neighboring π systems. Reaction of the carbocyclic carbene complex **1i** was shown to afford the open-chain system **12k**, presumably resulting from hydrolysis of its precursor **9k**.

Formation of compounds **9** seems to involve precursors **13** and **14** (Scheme 5). Compounds **14** readily afford isomers **9** by double-bond isomerization (see Scheme 3), particularly since the W=CC=C(OEt) skeleton is not stabilized by π conjugation due to its gauche conformation (see Figure 1). The migration of the C=C bonds is highly stereoselective and yields compounds (3*Z*)-**9** as the only detected organometallic product. Compounds **9** are thermally quite stable but prove to be quite sensitive to hydrolysis on silica gel to give acyl derivatives (3*Z*)-**12** even on fast chromatography.

Scheme 6. α-Methylenation of Aliphatic Amides 15 with the (1-Alkynyl)carbene Complex 1b



15,16	R	R^2	16 [%][a]	(*E*/*Z*)-16
a	Me	H	39	8:1
b	Me	CH_2CH_3	74	14:1

[a] Isolated chemical yields.

Even though (butadien-2-yl)carbene complexes (3*Z*)-**9** and (cyclobutenyl)carbene complexes **10** are valence isomers, it was not possible to induce an interconversion of these compounds. According to NMR measurements, both compounds **9c** and **10c** were stable in C_6D_6 even at 70 °C for at least 2 h and did not undergo an electrocyclic process. It therefore is obvious that these compounds were not generated by isomerization but in parallel reactions (Scheme 5). While the compound (3*Z*)-**9** seems to be obtained by an α-addition similar to that outlined in Scheme 2, compounds **10** are assumed to be obtained by the *β*-addition of a carbene complex **1d**−**h** to the amide **2** in a process which has been recently described in more detail (Scheme 5).[10]

α-Methylenation of Aliphatic Acid Amides

Vilsmeyer conditions with $POCl_3/Et_3N$, which were applied in the enol approach to the Baylis−Hillman reaction, had already previously been found to be superior in condensation reactions of saturated acid amides with Fischer carbene complexes.[7−9] To point out its outstanding performance in the regioselective generation also of highly unsaturated aminocarbene complexes, we wish to report on the formation of 1-tungstahexa-1,3-dien-5-ynes **16a**,**b** (Scheme 6).

Structure Elucidation

The aminocarbene complexes **3**, **8**−**10**, **12**, and **16** were characterized by ^1H and ^{13}C NMR spectra, including $^1J(C,H)$ and $^{2,3}J(C,H)$ correlation experiments. The configuration of the cross-conjugated metallatrienes **3**, **8**, **9**, and **12** were routinely determined by NOE measurements.

Structural details of the compound (3*E*)-**3d** were collected by a crystal structure analysis (Figure 1). The 2-ethoxybut-1-en-3-yne moiety of the compound (3*E*)-**3d** is planar (C1−C2−C3−C4 = 0.5(13)°) and strongly twisted against the plane defined by the bonds to the carbene carbon atom (W−C1−C2−C3 = 91.7(8)°). All bond distances are within expectation.

The molecular structure of the acyl derivative (3*Z*)-**12a** shows an s-trans configuration of the C═CC═O unit, which is arranged perpendicular to the plane defined by the bonds to the carbene carbon atom (W−C1−C2−C3 = 91.6(3)°) (Figure 2).

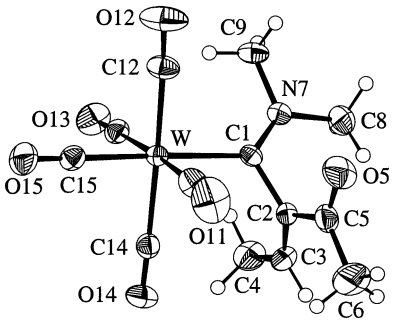


Figure 2. Molecular structure of the acyl derivative (3*Z*)-**12a**. Selected bond lengths (Å), valence angles (deg), and dihedral angles (deg): W−C1 = 2.249(3), C1−C2 = 1.504(4), C1−N7 = 1.304(4), C2−C5 = 1.496(5), C2−C3 = 1.331(5), C3−C4 = 1.490(5), C5−O5 = 1.214(4), C5−C6 = 1.498(5); W−C1−C2 = 114.9(2), W−C1−N7 = 130.8(2), N7−C1−C2 = 114.3(3), C1−C2−C5 = 114.8(3), C1−C2−C3 = 122.9(3), C5−C2−C3 = 122.3(3), C2−C3−C4 = 125.6(3), C2−C5−O5 = 119.5(3), C2−C5−C6 = 119.7(3), O5−C5−C6 = 120.8(3); W−C1−C2−C3 = 91.6(3), W−C1−C2−C5 = −89.0(3), C1−C2−C3−C4 = 4.7(5), C1−C2−C5−O5 = −16.9(5).

Conclusion

Since α,*β*-unsaturated aminocarbene complexes find wide application in organic synthesis, regio- and stereoselective generation of such compounds from readily available starting materiald has become a recent focus in research. Condensation reactions of Fischer carbene complexes with acid amides under Vilsmeyer conditions were shown to provide an efficient entry to the selective formation of very different types of aminocarbene complexes. We are currently unraveling the structural prerequisites of these condensation reactions. In the present paper it was shown that the condensation of non-CH-acidic Fischer carbene complexes **1a**−**c** with (CH-acidic) α,*β*-unsaturated acid amides **2** affords the aminocarbene complexes **3** by α-methylenation of the amide skeleton. Corresponding reactions of CH-acidic compounds **1d**−**h** are different and give compounds **9**, which are double-bond isomers of compounds **3**, together with (cyclobutenyl)carbene complexes **10**.

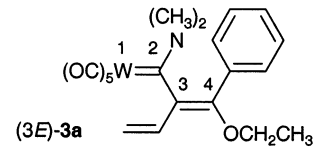
Experimental Section

General Considerations. NMR: Bruker AM 360, Bruker AMX 400, and Varian U 600 instruments. All new compounds were routinely analyzed by ^1H, ^{13}C, DEPT, (^1H,^1H)COSY, (^1H,^{13}C)GHSQC, and (^1H,^{13}C)GHMBC experiments on a Bruker AMX 400 instrument. IR: FT-IR Bio-Rad Digilab Division FTS-45 instrument. MS: Finnigan MAT8200 instrument. Elemental analyses: Heraeus CHN-O Rapid instrument. Column chromatography: Merck silica gel 60F. Flash chromatography was performed under an argon atmosphere. TLC: Merck silica gel $60F_{254}$. R_f values refer to TLC tests.

(2-(Dimethylamino)-3-ethenyl-4-ethoxy-4-phenyl)-1-(pentacarbonyltungsta)-1,3-butadiene ((3*E*)-3a and (3*Z*)-3a) and (3-Benzoyl-2-(dimethylamino)-1-(pentacarbonyltungsta)-1,3-pentadiene ((3*Z*)-8a). To but-2-enoic acid dimethylamide (**2a**; 226 mg, 2.00 mmol) and 2 mL of dry dichloromethane in a 5 mL screw-top vessel was added

phosphorus oxychloride (306 mg, 2.00 mmol) with stirring at 0 °C. Pentacarbonyl(1-ethoxybenzylidene)tungsten (**1a**; 458 mg, 1.00 mmol) and triethylamine (404 mg, 4.00 mmol) in 2 mL of dry dichloromethane was added after ca. 30 min at 0 °C, and the mixture was warmed to 25 °C. Workup after 24 h at 25 °C by flash column chromatography on silica gel with *n*-pentane/dichloromethane (3:1) afforded the compounds (3*Z*)-**3a** (80 mg, 14%, R_f = 0.5 in 2/1 *n*-pentane/dichloromethane), (3*E*)-**3a** (354 mg, 64%, R_f = 0.3 in 2/1 *n*-pentane/dichloromethane, yellow crystals from *n*-pentane at −20 °C, mp 97−98 °C), and **8a** (65 mg, 12%, R_f = 0.5 in 1/2 *n*-pentane/dichloromethane).

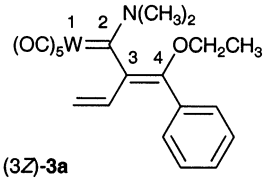
(3*E*)-3a.



(3*E*)-**3a**

^{1}H NMR ($CDCl_3$, 25 °C): δ 7.36−7.28 (5 H, m, Ph), 6.99 (1 H, dd, ^3J = 10.8 Hz and 18.0, H_2C=C*H*), 5.31 (1 H, dd, ^3J = 10.8 Hz, ^2J = 1.2, *cis*-H H_2C=), 4.81 (1 H, dd, ^3J = 18.0 Hz, ^2J = 1.2, *trans*-H H_2C=), 3.87 and 3.27 (3 H each, s each, 2 NCH_3), 3.82 and 3.27 (1 H each, m each, diastereotopic OCH_2), 1.31 (3 H, t, ^3J = 7 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 256.2 (C_q, W=C), 202.6 and 198.2 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 142.9 (C_q, C4), 137.9 (C_q, C3), 134.7 (C_q, *i*-C Ph); 128.8, 128.2, and 128.0 (2:1:2, CH each, Ph), 128.5 (CH, H_2C=H), 116.5 (CH_2, H_2C=CH), 67.6 (OCH_2), 53.1 and 44.1 (NCH_3 each), 15.2 (OCH_2CH_3). IR (*n*-hexane; cm^{-1} (%)): 2061.9 (18), 1970.3 (5), 1926.9 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 553 (35) [M^+], 525 (20) [M^+ − CO], 497 (40) [M^+ − 2 CO], 469 (95) [M^+ − 3 CO], 441 (20) [M^+ − 4 CO], 413 (100) [M^+ − 5 CO]. Anal. Calcd for $C_{20}H_{19}NO_6W$ (553.2): C, 43.42; H, 3.46; N, 2.53. Found: C, 43.41; H, 3.29; N, 2.42.

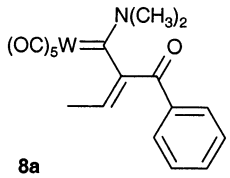
(3*Z*)-3a.



(3*Z*)-**3a**

^{1}H NMR ($CDCl_3$, 25 °C): δ 7.40−7.35 (5 H, m, Ph), 6.01 (1 H, dd, ^3J = 10.8 and 17.7 Hz, H_2C=C*H*), 4.92 (1 H, dd, ^3J = 10.8 Hz, ^2J = 1.2, *cis*-H H_2C=), 4.59 (1 H, dd, ^3J = 17.7 Hz, ^2J = 1.2, *trans*-H H_2C=), 3.90 and 3.32 (3 H each, s each, 2 NCH_3), 3.56 (2 H, q, ^3J = 7 Hz, OCH_2), 1.17 (3 H, t, ^3J = 7 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 254.6 (C_q, W=C), 203.5 and 198.7 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 146.7 (C_q, C4), 144.3 (C_q, C3), 135.7 (C_q, *i*-C Ph); 130.1, 128.4, and 127.1 (1:2:2, CH each, Ph), 128.4 (CH, H_2C=*C*H), 113.6 (CH_2, H_2C=CH), 64.8 (OCH_2), 53.1 and 43.9 (1:1, NCH_3 each), 15.4 (OCH_2CH_3). IR (*n*-hexane; cm^{-1} (%)): 2060.9 (20), 1966.0 (5), 1925.6 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 553 (20) [M^+], 525 (15) [M^+ − CO], 497 (20) [M^+ − 2 CO], 469 (30) [M^+ − 3 CO], 441 (45) [M^+ − 4 CO], 413 (30) [M^+ − 5 CO].

(3*Z*)-8a.



8a

^{1}H NMR ($CDCl_3$, 25 °C): δ 7.85 (2 H, m, *o*-H Ph), 7.58 (1 H, m, *p*-H Ph), 7.49 (2 H, m, *m*-H Ph), 5.79 (1 H, q, ^3J = 7 Hz, =CH), 3.95 and 3.32 (3 H each, s each, 2 NCH_3), 1.76 (3 H, d, ^3J = 7 Hz, C−CH_3). ^{13}C NMR ($CDCl_3$): δ 252.0 (C_q, W=C), 202.7 and 198.0 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 191.7 (C_q, C=O), 151.8 (C_q, *C*=CH), 137.0 (C_q, *i*-C Ph); 132.5, 129.7, and 128.4 (1:2:2, CH each, Ph), 128.7 (CH, =CH), 53.4 and 43.7 (NCH_3 each), 15.0 (C-CH_3). IR (*n*-hexane; cm^{-1} (%)): 2064.1 (25), 1983.8 (3), 1971.8 (8), 1937.8 (100) (ν(C≡O)), 1652.6 (5). MS (70 eV; ^{184}W, *m*/*e* (%)): 497 (60) [M^+ − CO], 469 (40) [M^+ − 2 CO], 441 (55) [M^+ − 3 CO], 413 (70) [M^+ − 4 CO], 385 (90) [M^+ − 5 CO]. Anal. Calcd for $C_{18}H_{15}NO_6W$ (525.2): C, 41.17; H, 2.88; N, 2.67. Found: C, 41.22; H, 3.11; N, 2.54.

(3-Ethenyl-4-ethoxy-2-morpholino-4-phenyl)-1-(pentacarbonyltungsta)-1,3-butadiene ((*3E*)-3b and (3*Z*)-3b) and (3-Benzoyl-2-morpholino-1-(pentacarbonyltungsta)-1,3-pentadiene ((3*Z*)-8b). 1-(Morpholin-4-yl)but-2-en-1-one (**2b**; 310 mg, 2.00 mmol) was reacted with phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxybenzylidene)tungsten (**1a**; 458 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) as described above. Workup after 24 h at 25 °C by flash column chromatography on silica gel with *n*-pentane/dichloromethane (3/1) afforded a 20/1 mixture of compounds (3*E*)-**3b** and (3*Z*)-**3b** (384 mg, 65%, R_f = 0.6 in 2/1 *n*-pentane/dichloromethane, yellow oil) and compound **8b** (65 mg, 12%, R_f = 0.6 in 1/4 *n*-pentane/dichloromethane, yellow oil).

(3*E*)-3b. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.46−7.28 (5 H, m, Ph), 7.04 (1 H, dd, ^3J = 11.1 and 18.3 Hz, H_2C=C*H*), 5.36 (1 H, d, ^3J = 11.1 Hz, *cis*-H H_2C=), 4.88 (1 H, dd, ^3J = 18.3 Hz, ^2J = 1.2, *trans*-H H_2C=); 4.61, 4.24, 3.77, and 3.50 (1 H each, m each, diastereotopic NCH_2); 3.93, 3.88, 3.49, and 3.37 (1 H each, m each, O*C*H_2CH_2N), 3.80 (2 H, m, diastereotopic O*C*H_2-CH_3), 1.34 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 253.7 (C_q, W=C), 202.3 and 198.3 (C_q each, 1:4, *trans*- and *cis*-CO W-$(CO)_5$), 142.5 (C_q, C4), 136.2 (C_q, C3), 134.4 (C_q, *i*-C Ph); 129.4, 128.5, and 128.3 (1:2:2, CH each, Ph), 128.8 (CH, H_2C=*C*H), 117.3 (CH_2, H_2C=CH), 67.8 (O*C*H_2CH_3), 66.9 and 66.5 (O*C*H_2-CH_2 each), 62.2 and 53.6 (NCH_2 each), 15.3 (OCH_2CH_3). IR, MS, and CHN analytical data of a 20/1 mixture of compounds (3*E*)-**3b** and (3*Z*)-**3b** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2062.9 (25), 1971.5 (5), 1935.5 (15), 1926.0 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 595 (30) [M^+], 567 (20) [M^+ − CO], 539 (55) [M^+ − 2 CO], 511 (100) [M^+ − 3 CO], 483 (20) [M^+ − 4 CO], 455 (45) [M^+ −5 CO]. Anal. Calcd for $C_{22}H_{21}NO_7W$ (595.3): C, 44.39; H, 3.56; N, 2.35. Found: C, 43.96; H, 3.59; N, 2.34.

(3*Z*)-3b. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.46−7.28 (5 H, m, Ph), 6.04 (1 H, dd, ^3J = 11.2 and 18.3 Hz, H_2C=C*H*), 4.93 (1 H, d, ^3J = 11.2 Hz, *cis*-H H_2C=), 4.51 (1 H, dd, ^3J = 18.3 Hz, *trans*-H H_2C=), 3.18 (2 H, m, diastereotopic OCH_2), morpholino,[12] 0.98 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ (C_q, W=C),[12] 202.3 and 198.8 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 144.8 (C_q, C4), 135.2 (C_q, *i*-C Ph), 132.7 (C_q, C3); 129.9, 129.5, and 129.1 (1:2:2, CH each, Ph), 127.9 (CH, H_2C=*C*H), 114.0 (CH_2, H_2C=CH); 67.9, 67.3, and 64.9 (OCH_2 each), 64.8 and 53.1 (NCH_2 each), 15.1 (OCH_2CH_3).

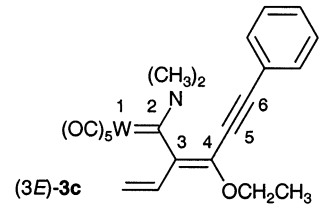
(3*Z*)-8b. ^{1}H NMR ($CDCl_3$): δ 7.87 (2 H, m, *o*-H Ph), 7.59 (1 H, *p*-H Ph), 7.51 (2 H, m, *m*-H Ph), 5.79 (1 H, q, ^3J = 6.9 Hz, =CH), 4.70, 4.30, 3.88, and 3.63 (1 H each, m each, 2 NCH_2), 4.05, 3.99, 3.98, and 3.81 (1 H each, m each, 2 OCH_2CH_2N), 1.78 (3 H, d, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 252.4 (C_q, W=C), 202.4 and 197.7 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 191.6 (C_q, C=O), 150.8 (C_q, C3), 136.6 (C_q, *i*-C Ph), 132.8, 129.7, and 128.5 (1:2:2, CH each, Ph), 128.4 (CH, *C*H=C), 67.7 and 67.6 (2 O*C*H_2CH_2N), 62.7 and 54.2 (2 NCH_2), 15.1 (CH_3). IR (*n*-hexane; cm^{-1} (%)): 2064.1 (20), 1983.8 (6), 1971.6 (5), 1938.6 (80), 1925.6 (16) (ν(C≡O)); 1648.6 (6) (ν(C=O)), 1462.6 (100). MS (70 eV; ^{184}W, *m*/*e* (%)): 539 (80) [M^+ − CO], 511 (50) [M^+ − 2 CO], 483 (55) [M^+ − 3 CO], 455 (70) [M^+ − 4 CO], 427 (100) [M^+ − 5 CO].

(2-(Dimethylamino)-3-ethenyl-4-ethoxy-6-phenyl)-1-(pentacarbonyltungsta)-1,3-hexadien-5-yne ((*3E*)-3c and

(12) Signals not located due to line broadening.

(3*Z*)-3c). But-2-enoic acid dimethylamide (**2a**; 226 mg, 2.00 mmol) was reacted with phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)-tungsten (**1b**; 482 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) as described above. Workup after 24 h at 25 °C by flash column chromatography on silica gel with *n*-pentane/dichloromethane (3/1) afforded a 25/1 mixture of compounds (3*E*)-**3c** and (3*Z*)-**3c** (299 mg, 52%, R_f = 0.5 in 2/1 *n*-pentane/dichloromethane, crystals from 10/1 *n*-pentane/dichloromethane; mp 71 °C).

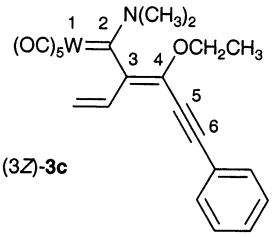
(3*E*)-3c.



(3*E*)-**3c**

^{1}H NMR ($CDCl_3$, 25 °C): δ 7.45−7.33 (5 H, m, Ph), 6.89 (1 H, dd, ^3J = 11.2 and 18.0 Hz, H_2C=C*H*), 5.23 (1 H, dd, ^3J = 11.2, ^2J = 1.2 Hz, *cis*-H H_2C=), 4.79 (1 H, dd, ^3J = 18.0 Hz, ^2J = 1.2, *trans*-H H_2C=), 4.12 (2 H, m, diastereotopic OCH_2), 3.90 and 3.28 (3 H each, s each, 2 NCH_3), 1.35 (3 H, t, ^3J = 7 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 253.1 (C_q, W=C), 203.2 and 198.3 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 139.9 (C_q, C4); 131.3, 129.1, and 128.5 (2:1:2, CH each, Ph), 127.2 (C_q, C3), 126.4 (CH, H_2C=*C*H), 121.7 (C_q, *i*-C Ph), 116.6 (CH_2, H_2C=CH), 102.0 and 82.2 (C_q each, C≡C), 65.7 (OCH_2), 53.3 and 43.2 (NCH_3 each), 15.2 (OCH_2CH_3). IR, MS, and CHN analytical data of a 25/1 mixture of compounds (3*E*)-**3c** and (3*Z*)-**3c** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2062.7 (30), 1972.2 (5), 1935.5 (100) (ν(C≡O)), 1496.7 (5). MS (70 eV; ^{184}W, *m*/*e* (%)): 577 (25) [M^+], 521 (10) [M^+ − 2 CO], 493 (100) [M^+ − 3 CO], 465 (15) [M^+ − 4 CO], 437 (20) [M^+ − 5 CO]. Anal. Calcd for $C_{22}H_{19}NO_6W$ (577.2): C, 45.78; H, 3.32; N, 2.43. Found: C, 45.48; H, 3.25; N, 2.38.

(3*Z*)-3c.



(3*Z*)-**3c**

^{1}H NMR ($CDCl_3$, 25 °C): δ 7.45−7.33 (5 H, m, Ph), 6.20 (1 H, dd, ^3J = 10.8 and 17.7 Hz, H_2C=C*H*), 5.06 (1 H, dd, ^3J = 10.8 Hz, *cis*-H H_2C=CH), 4.66 (1 H, dd, ^3J = 17.7 Hz, *trans*-H H_2C=CH), 3.95 (2 H, q, OCH_2), 3.84 and 3.21 (3 H each, s each, 2 NCH_3), 1.31 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ (C_q, W=C),[12] 202.5 and 198.3 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 139.0 (C_q, C3); 131.4 and 129.4 (2:2, CH each, Ph), 128.1 (C_q, C2), 126.7 (CH, H_2C=*C*H), 124.8 (C_q, *i*-C Ph), 115.1 (CH_2, H_2C=CH), 98.3 and 80.5 (C_q each, C≡C), 65.2 (OCH_2), 52.8 and 43.3 (NCH_3 each), 15.5 (OCH_2CH_3).

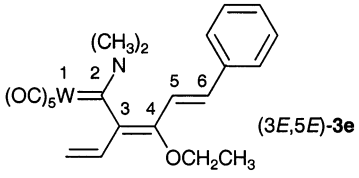
(3-Ethenyl-4-ethoxy-2-morpholino-6-phenyl)-1-(pentacarbonyltungsta)-1,3-hexadien-5-yne ((3*E*)-3d and (3*Z*)-3d). 1-(Morpholin-4-yl)but-2-en-1-one (**2b**; 310 mg, 2.00 mmol) was reacted with phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1b**; 482 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) as described above. Workup after 24 h at 25 °C by flash column chromatography on silica gel with *n*-pentane/dichloromethane (3/1) afforded a 20/1 mixture of compounds (3*E*)-**3d** and (3*Z*)-**3d** (303 mg, 49%, R_f = 0.4 in 2/1 *n*-pentane/dichloromethane, yellow crystals from 10/1 *n*-pentane/dichloromethane; mp 80 °C).

(3*E*)-3d. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.46−7.35 (5 H, m, Ph), 6.89 (1 H, dd, ^3J = 10.8 and 18.0 Hz, H_2C=C*H*), 5.25 (1 H, dd, ^3J = 10.8 Hz, ^2J = 1.2, *cis*-H H_2C=), 4.79 (1 H, dd, ^3J = 18.0 Hz, ^2J = 1.2, *trans*-H H_2C=), 4.59, 4.40, 3.82, and 3.64 (1 H each, m each, 2 NCH_2), 4.17 and 4.09 (1 H each, m each, diastereotopic OCH_2CH_3), 4.02, 3.98, 3.94, and 3.91 (1 H each, m each, 2 OCH_2CH_2N), 1.36 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 252.0 (C_q, W=C), 202.9 and 198.3 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 138.6 (C_q, C4), 131.2, 129.3, and 128.6 (2:1:2, CH each, Ph), 127.5 (C_q, C3), 126.9 (CH, H_2C=*C*H), 121.5 (C_q, *i*-C Ph), 116.7 (CH_2, H_2C=CH), 102.8 and 82.7 (C_q each, C≡C), 67.7 and 67.4 (2 OCH_2CH_2N), 65.9 (OCH_2CH_3), 62.4 and 53.6 (2 NCH_2), 15.2 (OCH_2CH_3). IR (*n*-hexane; cm^{-1} (%)): 2062.7 (30), 1972.3 (5), 1935.5 (100), 1925.9 (11) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 619 (20) [M^+], 563 (10) [M^+ − 2 CO], 535 (100) [M^+ − 3 CO], 507 (15) [M^+ − 4 CO]. Anal. Calcd for $C_{24}H_{21}NO_7W$ (619.3): C, 46.55; H, 3.42; N, 2.26. Found: C, 46.40; H, 3.24; N, 2.11. X-ray crystal structure analysis of compound **3d**: formula $C_{24}H_{21}NO_7W$, M_r = 619.27, yellow crystal, 0.35 × 0.25 × 0.10 mm, a = 18.690(1) Å, b = 9.434(1) Å, c = 15.646(1) Å, β = 101.12(1)°, V = 2706.9(4) Å^3, ρ_{calcd} = 1.520 g cm^{-3}, μ = 43.05 cm^{-1}, empirical absorption correction via SORTAV (0.314 ≤ T ≤ 0.673), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 10 651 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.68 Å^{-1}, 6771 independent (R_{int} = 0.046) and 4916 observed reflections ($I \geq 2\sigma(I)$), 299 refined parameters, R1 = 0.057, wR2 = 0.144, maximum (minimum) residual electron density 4.46 (−1.77) e Å^3, very high remaining electron density around 0, 0, 0 and 0, 0.5, 0.5 that is perhaps disordered petroleum ether, hydrogens calculated and refined as riding atoms.[13]

(3*Z*)-3d. Some typical spectroscopic data which could be collected from the isomer mixture are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.22 (1 H, dd, ^3J = 10.8 and 18.0 Hz, CH), 5.09 (1 H, dd, ^3J = 10.8 Hz, *cis*-H H_2C=), 4.58 (1 H, d, ^3J = 17.7 Hz, *trans*-H H_2C=), 1.31 (3 H, t, ^3J = 7 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): 202.1 and 198.3 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 131.7, 131.5, 129.2, 128.5, 128.1 and 123.9 (alkenyl and phenyl), 67.7, 67.3, 65.2, 62.0 and 53.8 (OCH_2 and NCH_2).

(2-(Dimethylamino)-3-ethenyl-4-ethoxy-6-phenyl)-1-(pentacarbonyltungsta)-1,3,5-hexatrienes ((3*E*,5*E*)-3e and (3*Z*,5*E*)-3e). But-2-enoic acid dimethylamide (**2a**; 226 mg, 2.00 mmol) was reacted with phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propenylidene)-tungsten (**1c**; 484 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) as described above for 2 h. Immediate workup by flash column chromatography on silica gel with *n*-pentane/dichloromethane (3/1) afforded a 12/1 mixture of compounds (3*E*,5*E*)-**3e** and (3*Z*,5*E*)-**3e** (255 mg, 44%, R_f = 0.6 in 2/1 *n*-pentane/dichloromethane, yellow oil).

(3*E*,5*E*)-3e.



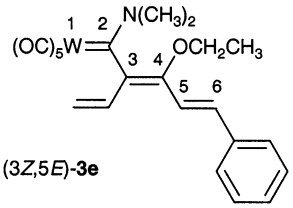
(3*E*,5*E*)-**3e**

^{1}H NMR ($CDCl_3$, 25 °C): δ 7.42−7.25 (5 H, m, Ph), 6.83 (1 H,

(13) Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection COLLECT (Nonius BV, 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, Göttingen, Germany, 1997), graphics DIAMOND (Brandenburg, K. Universität Bonn, Bonn, Germany, 1997).

d, ^3J = 15.6 Hz, 5-H), 6.79 (1 H, dd, ^3J = 10.8 and 18.0 Hz, H_2C=C*H*), 6.35 (1 H, d, ^3J = 15.6 Hz, 6-H), 5.30 and 4.82 (1 H each, dd each, ^3J = 10.8 and 18.0 Hz, ^2J = 0.9, H_2C=CH), 4.01 and 3.88 (1 H each, m each, diastereotopic 4-OCH_2), 3.94 and 3.21 (3 H each, s each, 2 NCH_3), 1.43 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): 255.6 (C_q, W=C), 202.8 and 198.5 (C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 142.6 (C_q, C-4), 139.9 (C_q, C-3), 136.7 (C_q, *i*-C Ph), 130.1 and 121.6 (CH each, HC=CHPh), 128.9, 128.3, and 127.0 (2:1:2, CH each, Ph), 127.7 (H_2C=CH), 117.2 (H_2C=CH), 69.4 (OCH_2), 53.4 and 43.6 (NCH_3 each), 15.6 (OCH_2CH_3). IR and MS data of a 12/1 mixture of (3*E*,5*E*)-**3e** and (3*Z*,5*E*)-**3e** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2062.5 (5), 1983.8 (5), 1935.3 (15), 1927.1 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 579 (5) [M^+], 551 (5) [M^+ − 1 CO], 523 (10) [M^+ − 2 CO], 495 (10) [M^+ − 3 CO], 467 (20) [M^+ − 4 CO], 439 (20) [M^+ − 5 CO], 255 (100).

(3*E*,5*E*)-3e.

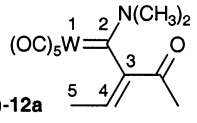


(3*Z*,5*E*)-**3e**

^{1}H NMR ($CDCl_3$, 25 °C): δ 7.42−7.20 (5 H, m, Ph), 6.89 (1 H, d, ^3J = 15.6 Hz, 5-H), 6.60 (1 H, d, ^3J = 15.6 Hz, 6-H), 6.58 (1 H, dd, ^3J = 11.1 and 17.4 Hz, H_2C=C*H*), 5.15 and 4.71 (1 H each, dd each, ^3J = 11.1 and 17.4 Hz, ^2J = 0.9 Hz, H_2C=CH), 3.87 (2 H, m, diastereotopic OCH_2), 3.86 and 3.34 (3 H each, s each, 2 NCH_3), 1.44 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 25 °C; partial assignment only, due to overlapping signals): 251.4 (C_q, W=C), 202.8 and 198.6 (C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 132.2, 131.4, 128.4, 126.8, 126.2, 119.8, 117.5 (*C*=*C* and Ph), 69.2 (OCH_2), 53.4 and 44.3 (NCH_3 each), 14.6 (OCH_2CH_3).

3-Acetyl-2-(dimethylamino)-1-(pentacarbonyltungsta)-1,3-pentadiene ((3*Z*)-12a). But-2-enoic acid dimethylamide (**2a**; 113 mg, 1.00 mmol) was reacted with phosphorus oxychloride (153 mg, 1.00 mmol), pentacarbonyl(1-ethoxy-1-ethylidene)tungsten (**1d**; 198 mg, 0.50 mmol), and triethylamine (202 mg, 2.00 mmol) as described above. Workup after 12 h at 25 °C by flash column chromatography on silica gel with *n*-pentane/dichloromethane (1/2) afforded compound (3*Z*)-**12a** (153 mg, 66%, R_f = 0.4 *n*-pentane/dichloromethane (1/2), yellow crystals from 10/1 *n*-pentane/dichloromethane at −20 °C, mp 121−122 °C).

(3*Z*)-12a.



(3*Z*)-**12a**

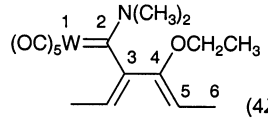
^{1}H NMR ($CDCl_3$, 25 °C): δ 6.10 (1 H, q, ^3J = 6.9 Hz, =CH), 3.87 and 3.18 (3 H each, s each, 2 NCH_3), 2.38 (3 H, s, CH_3-CO), 1.73 (3 H, d, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 253.3 (C_q, W=C), 203.0 and 198.1 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 195.3 (C_q, C=O), 153.8 (C_q, C3), 126.1 (CH, =CH), 53.5 and 43.5 (NCH_3 each), 26.1 (CH_3CO), 15.2 (CH_3). IR (*n*-hexane; cm^{-1} (%)): 2064.1 (20), 1983.8 (10), 1931.5 (100) (ν-(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 463 (5) [M^+], 435 (45) [M^+ − CO], 407 (20) [M^+ − 2 CO], 379 (50) [M^+ − 3 CO], 351 (60) [M^+ − 4 CO], 323 (60) [M^+ − 5 CO]. Anal. Calcd for $C_{13}H_{13}NO_6W$ (463.1): C, 33.72; H, 2.83; N, 3.02. Found: C, 33.67; H, 2.55; N, 2.94. X-ray crystal structure analysis of compound **12a**: formula $C_{13}H_{13}NO_6W$, M_r = 463.09, yellow crystal 0.40 × 0.25 × 0.20 mm, a = 10.603(1) Å, b = 11.790(1) Å, c = 12.614(1) Å, β = 94.36(1)°, V = 1572.3(2) Å^3, ρ_{calcd} = 1.956 g cm^{-3}, μ = 73.71 cm^{-1}, empirical absorption correction via SORTAV (0.157 ≤ T ≤ 0.320), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 298 K, ω and φ scans, 6607 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.66 Å^{-1}, 3723 independent (R_{int} = 0.018) and 3331 observed reflections ($I \geq 2\sigma(I)$), 194 refined parameters, R1 = 0.022, wR2 = 0.048, maximum (minimum) residual electron density 0.60 (−1.06) e Å^{-3}, hydrogens calculated and refined as riding atoms.[13]

3-Acetyl-2-morpholino-1-(pentacarbonyltungsta)-1,3-pentadiene (12b). 1-(Morpholin-4-yl)-but-2-en-1-one (**2b**; 155 mg, 1.00 mmol) was reacted with phosphorus oxychloride (153 mg, 1.00 mmol), pentacarbonyl(1-ethoxy-1-ethylidene)tungsten (**1d**; 198 mg, 0.50 mmol), and triethylamine (202 mg, 2.00 mmol) as described above. Workup after 12 h at 25 °C by flash column chromatography on silica gel with *n*-pentane/dichloromethane (2/1) afforded the compound (3*Z*)-**12b** (148 mg, 59%, R_f = 0.4 in dichloromethane, yellow crystals from 10/1 *n*-pentane/dichloromethane at −20 °C, mp 119−120 °C).

12b. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.11 (1 H, q, ^3J = 7 Hz, =CH), 4.60, 4.27, 3.80, and 3.54 (1 H each, m each, 2 NCH_2), 4.01 and 3.73 (2 H each, m each, 2 OCH_2CH_2N), 2.40 (3 H, s, CH_3CO), 1.75 (3 H, d, ^3J = 7 Hz, 4-CH_3). ^{13}C NMR ($CDCl_3$): δ 250.7 (C_q, W=C), 202.7 and 197.8 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 195.4 (C_q, C=O), 152.9 (C_q, C3), 126.2 (CH, H_2C=*C*H), 67.7 and 67.3 (2 OCH_2CH_2N), 62.4 and 53.8 (2 NCH_2), 26.1 (CH_3CO), 15.4 (4-CH_3). IR (*n*-hexane; cm^{-1} (%)): 2062.0 (75), 1975.3 (30), 1908.9 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 505 (5) [M^+], 477 (70) [M^+ − CO], 449 (35) [M^+ − 2 CO], 421 (85) [M^+ − 3 CO], 393 (80) [M^+ − 4 CO], 365 (100) [M^+ − 5 CO]. Anal. Calcd for $C_{15}H_{15}NO_7W$ (505.1): C, 35.67; H, 2.99; N, 2.77. Found: C, 35.53; H, 2.60; N, 2.66.

(4*E*)-1-(Dimethylamino)-4-ethoxy-3-(*syn*-ethylidene)-1-(pentacarbonyltungsta)-1,4-hexadiene ((4*Z*,*syn*)-9c), 2-(Dimethylamino)(2-ethoxy-3,4-dimethyl-1-cyclobutenyl)-1-(pentacarbonyltungsta)ethenes (3*S,4*R**)-10c and (3*R**,4*R**)-10c, and 2-(Dimethylamino)-3-ethylidene-1-(pentacarbonyltungsta)-1-hexen-4-one (12c).** But-2-enoic acid dimethylamide (**2a**; 113 mg, 1.00 mmol) was reacted with phosphorus oxychloride (153 mg, 1.00 mmol), pentacarbonyl-(1-ethoxy-1-propylidene)tungsten (**1e**; 205 mg, 0.50 mmol), and triethylamine (202 mg, 2.00 mmol) as described above. Workup after 12 h at 25 °C by flash column chromatography on silica gel with *n*-pentane/dichloromethane (2/1) afforded a 5/3 mixture of compounds (3*S**,4*R**)-**10c** and (3*R**,4*R**)-**10c** (72 mg, 29%, R_f = 0.8 *n*-pentane/dichloromethane 2:1, yellow oil), compound (4*Z*,*syn*)-**9c** (56 mg, 22%, R_f = 0.5 in 2/1 *n*-pentane/dichloromethane, yellowish powder from *n*-pentane, mp 57−58 °C), and compound **12c** (19 mg, 8%, R_f = 0.4 1/2 *n*-pentane/dichloromethane, yellow crystals from 10/1 *n*-pentane/dichloromethane at −20 °C, mp 121−122 °C).

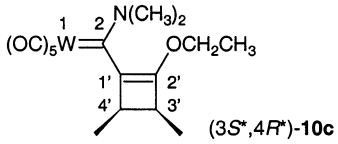
(4*Z*,*syn*)-9c.



(4*Z*, *syn*)-**9c**

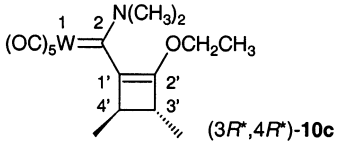
^{1}H NMR ($CDCl_3$, 25 °C): δ 5.32 (1 H, q, ^3J = 7 Hz, 1′-H), 4.46 (1 H, q, ^3J = 7 Hz, 5-H), 3.88 and 3.24 (3 H each, s each, 2 NCH_3), 3.86 (2 H, m, diastereotopic OCH_2), 1.71 (3 H, d, ^3J = 7 Hz, 6-H_3), 1.55 (3 H, d, ^3J = 7 Hz, 2′-H_3), 1.36 (3 H, t, ^3J = 7 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 256.3 (C_q, W=C), 202.5 and 198.5 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 148.8 (C_q, C4), 147.5 (C_q, C3), 114.2 (CH, C5), 110.4 (CH, C1′), 67.0 (OCH_2), 53.3 and 42.8 (NCH_3 each), 15.6 (OCH_2CH_3), 14.1 (CH_3, C2′), 11.1 (CH_3, C6). IR (*n*-hexane; cm^{-1} (%)): 2062.6 (20), 1969.1 (5), 1934.1 (98), 1926.4 (15) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 505 (10) [M^+], 477 (10) [M^+ − CO], 449 (25) [M^+ − 2 CO], 365 (35) [M^+ − 5 CO]. Anal. Calcd for $C_{16}H_{19}NO_6W$ (505.2): C, 38.04; H, 3.79; N, 2.77. Found: C, 38.01; H, 3.58; N, 2.60.

(3*S,4*R**)-10c.**



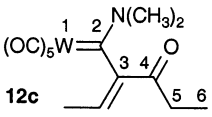
^{1}H NMR ($CDCl_3$, 25 °C): δ 3.94 (2 H, m, diastereotopic OCH_2), 3.77 and 3.41 (3 H each, s each, 2 NCH_3), 3.33 (1 H, qd, ^3J = 6.6 and 4.8 Hz, 3′-H), 3.25 (1 H, qd, ^3J = 7 and 4.8 Hz, 4′-H), 1.30 (3 H, t, OCH_2CH_3), 1.15 (3 H, d, ^3J = 7 Hz, 4′-CH_3), 1.08 (3 H, d, ^3J = 6.6 Hz, 3′-CH_3). ^{13}C NMR ($CDCl_3$): δ 241.9 (C_q, W=C), 203.5 and 199.0 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 143.7 (C_q, C2′), 128.7 (C_q, C1′), 64.8 (OCH_2), 53.5 and 44.8 (NCH_3 each), 38.0 (CH, C4′), 37.3 (CH, C3′), 15.6 (OCH_2CH_3), 15.4 (4′-CH_3), 13.6 (3′-CH_3). IR, MS, and CHN analytical data of a 5/3 mixture of compounds (3*S**,4*R**)-**10c** and (3*R**,4*R**)-**10c** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2059.9 (15), 1965.8 (1), 1927.6 (98) (ν(C≡O)). MS (70 eV; ^{184}W, *m/e* (%)): 505 (35) [M^+], 477 (40) [M^+ − CO], 449 (30) [M^+ − 2 CO], 393 (40) [M^+ − 4 CO]. Anal. Calcd for $C_{16}H_{19}NO_6W$ (505.2): C, 38.04; H, 3.79; N, 2.77. Found: C, 37.97; H, 3.90; N, 2.81.

(3*R,4*R**)-10c.**



^{1}H NMR ($CDCl_3$, 25 °C): δ 3.93 (2 H, m, diastereotopic OCH_2), 3.80 and 3.40 (3 H each, s each, 2 NCH_3), 2.74 (1 H, qd, ^3J = 6.6 and 1.2 Hz, 4′-H), 2.56 (1 H, qd, ^3J = 6.9 and 1.2 Hz, 3′-H), 1.37 (3 H, d, ^3J = 6.9 Hz, 3′-CH_3), 1.33 (3 H, t, OCH_2CH_3), 1.18 (3 H, d, ^3J = 6.6 Hz, 4′-CH_3). ^{13}C NMR ($CDCl_3$): δ 243.7 (C_q, W=C), 203.3 and 198.9 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 143.6 (C_q, C2′), 126.3 (C_q, C1′), 64.6 (OCH_2), 53.4 and 45.1 (NCH_3 each), 44.3 (CH, C3′), 42.5 (CH, C4′), 19.7 (4′-CH_3), 16.3 (3′-CH_3), 15.7 (OCH_2CH_3).

12c.



^{1}H NMR ($CDCl_3$, 25 °C): δ 6.10 (1 H, q, ^3J = 7 Hz, 1′-H), 3.91 and 3.22 (3 H each, s each, 2 NCH_3), 2.79 (2 H, m, diastereotopic CH_2CO), 1.75 (3 H, d, ^3J = 7 Hz, 2′-H_3), 1.17 (3 H, t, ^3J = 7 Hz, 6-H_3). ^{13}C NMR ($CDCl_3$): δ 253.6 (C_q, W=C), 202.9 and 198.1 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 198.0 (C_q, C=O), 153.3 (C_q, C3), 124.5 (CH, C1′), 53.3 and 43.5 (NCH_3 each), 31.5 (CH_2, C5), 8.1 (CH_3, C6), 15.1 (CH_3, C2′). IR (*n*-hexane; cm^{-1} (%)): 2063.9 (20), 1970.5 (2), 1931.6 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m/e* (%)): 477 (5) [M^+], 449 (20) [M^+ − CO], 421 (10) [M^+ − 2 CO], 393 (25) [M^+ − 3 CO], 365 (30) [M^+ - 4 CO], 337 (25) [M^+ − 5 CO]. Anal. Calcd for $C_{14}H_{15}NO_6W$ (477.1): C, 35.24; H, 3.17; N, 2.94. Found: C, 35.16; H, 3.00; N, 2.90.

(4*E*)-4-Ethoxy-3-(*syn*-ethylidene)-2-morpholino-1-(pentacarbonyltungsta)-1,4-hexadiene ((4*Z*,*syn*)-9d), 2-(2-Ethoxy-3,4-dimethyl-1-cyclobutenyl)-2-morpholino-1-(pentacarbonyltungsta)ethenes (3*S,4*R**)-10d and (3*R**,4*R**)-10d, and 3-Ethylidene-2-morpholino-1-(pentacarbonyltungsta)-1-hexen-4-one (12d).** 1-(Morpholin-4-yl)but-2-en-1-one (**2b**; 155 mg, 1.00 mmol) was reacted with phosphorus oxychloride (153 mg, 1.00 mmol), pentacarbonyl(1-ethoxy-1-propenylidene)tungsten (**1e**; 205 mg, 0.50 mmol), and triethylamine (202 mg, 2.00 mmol) as described above. Workup after 12 h at 25 °C by flash column chromatography on silica gel with *n*-pentane/dichloromethane (2/1) afforded a 5/1 mixture of compounds (3*S**,4*R**)-**10d** and (3*R**,4*R**)-**10d** (42 mg, 15%, R_f = 0.6 in 1/1 *n*-pentane/dichloromethane, yellow oil), compound (4*Z*,*syn*)-**9d** (47 mg, 17%, R_f = 0.6 in 1/1 *n*-pentane/dichloromethane), and compound **12d** (52 mg, 20%, R_f = 0.3 in 1/2 *n*-pentane/dichloromethane).

(4*Z*,*syn*)-9d. ^{1}H NMR ($CDCl_3$, 25 °C): δ 5.40 (1 H, q, ^3J = 7 Hz, 1′-H), 4.52 (1 H, q, ^3J = 7 Hz, 5-H), 4.54, 4.25, 3.82, and 3.70 (1 H each, m each, 2 NCH_2), 3.96, 3.80, and 3.78 (2 H each, m each, diastereotopic OCH_2CH_3 and 2 OCH_2CH_2N), 1.75 (3 H, d, ^3J = 7 Hz, 6-H_3), 1.63 (3 H, d, ^3J = 7 Hz, 2′-H_3), 1.40 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 255.0 (C_q, W=C), 202.6 and 198.4 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 149.4 (C_q, C4), 146.4 (C_q, C3), 114.9 (CH, C5), 111.1 (CH, C1′), 67.8 and 67.2 (OCH_2CH_2N each), 67.1 (OCH_2CH_3), 62.5 and 53.0 (NCH_2 each), 15.7 (OCH_2CH_3), 14.7 and 11.3 (CH_3 each, C2′ and C6). IR (*n*-hexane; cm^{-1} (%)): 2062.6 (15), 1968.4 (2), 1934.7 (90) (ν(C≡O)). MS (70 eV; ^{184}W, *m/e* (%)): 547 (25) [M^+], 519 (10) [M^+ − CO], 491 (35) [M^+ − 2 CO], 463 (10) [M^+ − 3 CO], 407 (30) [M^+ − 5 CO]. Anal. Calcd for $C_{18}H_{21}NO_7W$ (547.2): C, 39.51; H, 3.87; N, 2.56. Found: C, 39.86; H, 3.72; N, 2.47.

(3*S,4*R**)-10d.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 4.43, 4.23, 3.86, and 3.76 (1 H each, m each, 2 NCH_2), 3.97, 3.95, and 3.84 (2 H each, m each, diastereotopic OCH_2CH_3 and 2 OCH_2CH_2N), 3.38 (1 H, qd, ^3J = 5 Hz and 6.8, 3′-H), 3.27 (1 H, qd, ^3J = 5 and 7 Hz, 4′-H), 1.28 (3 H, t, OCH_2CH_3), 1.12 (3 H, d, ^3J = 7 Hz, 4′-CH_3), 1.04 (3 H, d, ^3J = 6.8 Hz, 3′-CH_3). ^{13}C NMR ($CDCl_3$): δ 240.4 (C_q, W=C), 203.1 and 198.6 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 142.6 (C_q, C2′), 127.8 (C_q, C1′), 67.9 and 67.8 (2 OCH_2CH_2N), 64.8 (OCH_2CH_3), 62.7 and 54.4 (2 NCH_2), 42.6 (CH, C4′), 37.6 (CH, C3′), 15.5 (OCH_2CH_3), 15.4 and 13.7 (3′-CH_3 and 4′-CH_3). IR, MS, and CHN analytical data of a 5/1 mixture of compounds (3*S**,4*R**)-**10d** and (3*R**,4*R**)-**10d** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2060.2 (15), 1934.5 (2), 1929.0 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m/e* (%)): 547 (50) [M^+], 519 (40) [M^+ − CO], 491 (35) [M^+ − 2 CO], 463 (30) [M^+ − 3 CO], 407 (100) [M^+ − 5 CO]. Anal. Calcd for $C_{18}H_{21}NO_7W$ (547.2): C, 39.51; H, 3.87; N, 2.56. Found: C, 39.94; H, 3.88; N, 2.98.

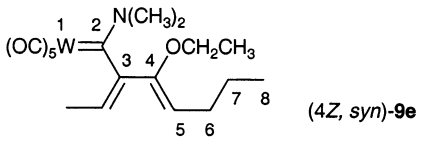
(3*R,4*R**)-10d.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 4.32, 4.09, 3.90, and 3.74 (1 H each, m each, 2 NCH_2), 4.00−3.70 (6 H, m, diastereotopic OCH_2CH_3 and 2 OCH_2CH_2N), 2.90 (1 H, qd, ^3J = 7 and 1.2 Hz, 3′-H), 2.77 (1 H, qd, ^3J = 6.8 and 1.2 Hz, 4′-H), 1.37 (3 H, d, ^3J = 6.8 Hz, 3′-CH_3), 1.29 (3 H, t, ^3J = 7 Hz, OCH_2CH_3), 1.15 (3 H, d, ^3J = 6.8 Hz, 4′-CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 242.5 (C_q, W=C), 203.0 and 198.7 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 142.9 (C_q, C2′), 125.2 (C_q, C1′), 67.9 and 67.8 (2 OCH_2CH_2N), 64.7 (OCH_2CH_3), 62.8 and 54.8 (2 NCH_2), 44.5 (CH, C3′), 38.1 (CH, C4′), 19.7 and 16.8 (3′-CH_3 and 4′-CH_3), 15.6 (OCH_2CH_3).

12d. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.08 (1 H, q, ^3J = 7 Hz, 1′-H), 4.60, 4.29, 3.79, and 3.57 (1 H each, m each, 2 NCH_2), 4.01 and 3.72 (2 H each, m each, 2 OCH_2CH_2N), 2.79 (2 H, q, ^3J = 7 Hz, CH_2CO), 1.74 (3 H, d, ^3J = 7 Hz, 2′-H_3), 1.13 (3 H, t, ^3J = 7 Hz, 6-H_3). ^{13}C NMR ($CDCl_3$): δ 251.0 (C_q, W=C), 202.7 and 197.9 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 198.3 (C_q, C=O), 152.4 (C_q, C3), 124.7 (CH, C1′), 68.1 and 67.8 (OCH_2-CH_2N each), 62.5 and 53.8 (NCH_2 each), 31.6 (CH_2CO), 15.3 (CH_3, C2′), 8.0 (CH_3CH_2CO). IR (*n*-hexane; cm^{-1} (%)): 2063.9 (22), 1933.9 (100) (ν(C≡O)), 1653.0 (ν(C=O)). MS (70 eV; ^{184}W, *m/e* (%)): 519 (5) [M^+], 491 (30) [M^+ − CO], 463 (15) [M^+ − 2 CO], 435 (40) [M^+ − 3 CO], 407 (30) [M^+ − 4 CO], 379 (40) [M^+ − 5 CO]. Anal. Calcd for $C_{15}H_{15}NO_7W$ (519.2): C, 37.02; H, 3.30; N, 2.70. Found: C, 37.61; H, 3.73; N, 2.45.

(4*E*)-2-(Dimethylamino)-4-ethoxy-3-(*syn*-ethylidene)-1-(pentacarbonyltungsta)-1,4-octadiene ((4*Z*,*syn*)-9e), 2-(Dimethylamino)-2-(2-ethoxy-4-methyl-3-(*n*-propyl)-1-cyclobutenyl)-1-(pentacarbonyltungsta)ethenes (3*S,4*R**)-10e and (3*R**,4*R**)-10e, and 2-(Dimethylamino)-3-ethylidene-1-(pentacarbonyltungsta)-1-octen-4-one (12e).** But-2-enoic

acid dimethylamide (**2a**; 226 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxy-1-pentenylidene)tungsten (**1f**; 438 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give a 4/1 mixture of compounds (3*S**,4*R**)-**10e** and (3*R**,4*R**)-**10e** (168 mg, 32%, R_f = 0.6 in 2/1 *n*-pentane/dichloromethane, yellow oil), compound (4*Z*,*syn*)-**9e** (106 mg, 20%, R_f = 0.4 in 2/1 *n*-pentane/dichloromethane), and compound **12e** (30 mg, 6%, R_f = 0.5 in 1/2 *n*-pentane/dichloromethane).

(4*Z*,*syn*)-9e.



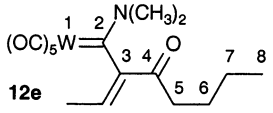
(4*Z*, *syn*)-**9e**

^{1}H NMR ($CDCl_3$, 25 °C): δ 5.32 (1 H, q, ^3J = 7 Hz, 1′-H), 4.37 (1 H, t, ^3J = 7 Hz, 5-H), 3.87 and 3.24 (3 H each, s each, 2 NCH_3), 3.83 (2 H, m, diastereotopic OCH_2CH_3), 2.16 and 1.25 (2 H each, m each, 6-H_2 and 7-H_2), 1.72 (3 H, d, ^3J = 7 Hz, 2′-H_3), 1.35 (3 H, t, OCH_2CH_3), 0.92 (3 H, t, ^3J = 7 Hz, 8-H_3). ^{13}C NMR ($CDCl_3$): δ 256.8 (C_q, W=C), 202.7 and 198.1 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 148.0 (C_q, C4), 147.6 (C_q, C3), 119.7 (CH, C5), 110.7 (CH, C1′), 67.5 (OCH_2), 53.3 and 42.7 (NCH_3 each), 27.8, 22.5, and 14.0 ($CH_2CH_2CH_3$), 15.6 (OCH_2CH_3), 14.3 (CH_3, C2′). IR (*n*-hexane; cm^{-1} (%)): 2062.2 (20), 1967.7 (2), 1933.0 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 533 (30) [M$^+$], 477 (10) [M$^+$ − 2 CO], 421 (20) [M$^+$ − 4 CO], 393 (20) [M$^+$ − 5 CO], 164 (100). Anal. Calcd for $C_{18}H_{23}NO_6W$ (533.2): C, 40.54; H, 4.35; N, 2.63. Found: C, 40.76; H, 4.21; N, 2.63.

(3*S,4*R**)-10e.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 3.86 (2 H, m, diastereotopic OCH_2), 3.76 and 3.41 (3 H each, s each, 2 NCH_3), 3.34 (1 H, qd, ^3J = 6.9 and 4.8 Hz, 4′-H), 3.08 (1 H, qd, ^3J = 5.1 and 4.8 Hz, 3′-H), 1.60−1.20 (4 H, m, 3′-$CH_2CH_2CH_3$), 1.26 (3 H, t, OCH_2CH_3), 1.08 (3 H, t, ^3J = 7 Hz, 3′-$CH_2CH_2CH_3$), 1.06 (3 H, d, ^3J = 6.9 Hz, 4′-CH_3). ^{13}C NMR ($CDCl_3$): δ 243.5 (C_q, W=C), 203.4 and 199.0 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 142.0 (C_q, C2′), 129.2 (C_q, C1′), 64.8 (OCH_2), 53.2 and 44.8 (NCH_3 each), 43.7 (CH, C3′), 37.5 (CH, C4′); 30.8, 21.4, and 14.3 (3′-$CH_2CH_2CH_3$), 15.6 (OCH_2CH_3), 15.3 (4′-CH_3). IR, MS, and CHN analytical data of a 4/1 mixture of compounds (3*S**,4*R**)-**10e** and (3*R**,4*R**)-**10e** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2060.1 (15), 1966.5 (2), 1928.0 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 533 (35) [M$^+$], 505 (30) [M$^+$ − CO], 477 (30) [M$^+$ − 2 CO], 421 (50) [M$^+$ − 4 CO], 393 (100) [M$^+$ − 5 CO]. Anal. Calcd for $C_{18}H_{23}NO_6W$ (533.2): C, 40.54; H, 4.35; N, 2.63. Found: C, 40.52; H, 4.52; N, 2.75.

(3*R,4*R**)-10e.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 3.82 (2 H, m, diastereotopic OCH_2), 3.77 and 3.39 (3 H each, s each, 2 NCH_3), 2.78 (1 H, qd, ^3J = 6.6 and 1.2 Hz, 4′-H), 2.45 (1 H, qd, ^3J = 5.1 and 1.2 Hz, 3′-H), 1.60−1.20 (4 H, m, 3′-$CH_2CH_2CH_3$), 1.29 (3 H, t, OCH_2CH_3), 1.17 (3 H, d, ^3J = 6.6 Hz, 4′-CH_3), 0.96 (3 H, t, ^3J = 7 Hz, 3′-$CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 244.5 (C_q, W=C), 202.5 and 199.0 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 143.1 (C_q, C2′), 126.7 (C_q, C1′), 64.9 (OCH_2), 53.5 and 45.1 (NCH_3 each), 49.7 (CH, C3′), 41.1 (CH, C4′), 34.7, 21.5, and 14.4 (3′-$CH_2CH_2CH_3$), 20.3 (4′-CH_3), 16.0 (OCH_2CH_3).

12e.

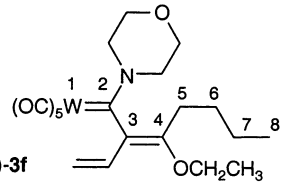


12e

^{1}H NMR ($CDCl_3$, 25 °C): δ 6.9 (1 H, q, ^3J = 7 Hz, CH), 3.88 and 3.17 (3 H each, s each, 2 NCH_3), 2.73, 1.63, and 1.36 (2 H each, m each, $CH_2CH_2CH_2CH_3$), 1.72 (3 H, d, ^3J = 7 Hz, CH_3), 0.93 (3 H, t, ^3J = 7 Hz, $(CH_2)_3CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 253.9 (C_q, W=C), 202.9 and 198.2 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 197.7 (C_q, C=O), 153.5 (C_q, C=CH), 124.9 (CH, C=CH), 53.3 and 43.4 (NCH_3 each), 37.9, 26.3, 22.4, and 13.8 ($CH_2CH_2CH_2CH_3$), 15.1 (CH_3). IR (*n*-hexane; cm^{-1} (%)): 2063.7 (20), 1971.1 (3), 1931.0 (100) (ν(C≡O)), 1675.4 (6), 1539.3 (5). MS (70 eV; ^{184}W, *m*/*e* (%)): 505 (5) [M$^+$], 477 (20) [M$^+$ − CO], 449 (10) [M$^+$ − 2 CO], 421 (30) [M$^+$ −3 CO], 393 (20) [M$^+$ −4 CO], 365 (10) [M$^+$ − 5 CO].

(3*E*)-4-Ethoxy-3-ethenyl-2-morpholino-1-(pentacarbonyltungsta)-1,3-octadiene ((3*E*)-3f), (4*E*)-4-Ethoxy-3-(*syn*-ethylidene)-2-morpholino-1-(pentacarbonyltungsta)-1,4-octadiene ((4*Z*,*syn*)-9f), 2-(2-Ethoxy-4-methyl-3-(*n*-propyl)-1-cyclobutenyl)-2-morpholino-1-(pentacarbonyltungsta)ethenes (3*S,4*R**)-10f and (3*R**,4*R**)-10f, and 3-Ethylidene-2-morpholino-1-(pentacarbonyltungsta)-1-octen-4-one (12f).** 1-(Morpholin-4-yl)but-2-en-1-one (**2b**; 310 mg, 2.00 mmol) was reacted with phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxy-1-pentenylidene)tungsten (**1f**; 438 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) as described above to give a 20/1 mixture of compounds (3*S**,4*R**)-**10f** and (3*R**,4*R**)-**10f** (64 mg, 11%, R_f = 0.5 in 2/1 *n*-pentane/dichloromethane, yellow oil), compound (3*E*)-**3f** (112 mg, 20%, R_f = 0.3 in 3/2 *n*-pentane/dichloromethane), and compound **12f** (100 mg, 18%, R_f = 0.5 in 1/2 *n*-pentane/dichloromethane). According to NMR spectra, compound (3*E*)-**3f** in C_6D_6 is smoothly transformed into compound (4*Z*)-**9f**.

(3*E*)-3f.



(3*E*)-**3f**

^{1}H NMR ($CDCl_3$, 25 °C): δ 6.81 (1 H, dd, ^3J = 18.0 and 11.4 Hz, 1′-H), 5.15 (1 H, d, ^3J = 11.4 Hz, *cis*-H H_2C=), 4.65 (1 H, d, ^3J = 18.0 Hz, *trans*-H H_2C=), 4.25 and 4.05 (1 H each, m each, NCH_2), 3.98−3.68 (6 H, m, NCH_2 and 2 OCH_2CH_2N), 3.61 (2 H, m, diastereotopic OCH_2CH_3), 2.37 and 1.95 (1 H each, m each, diastereotopic 5-H_2), 1.62−1.17 (4 H, m, 6-H_2 and 7-H_2), 1.33 (3 H, t, ^3J = 7 Hz, OCH_2CH_3), 0.93 (3 H, t, ^3J = 7 Hz, 8-H_3). ^{13}C NMR ($CDCl_3$): δ 255.4 (C_q, W=C), 202.7 and 198.4 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 146.0 and 134.0 (C_q each, C3 and C4), 128.0 (CH, C1′), 114.8 (CH_2, C2′), 67.8 and 67.7 (2 OCH_2CH_2N), 65.1 (OCH_2CH_3), 62.5 and 53.4 (NCH_2 each), 30.7, 28.7 and 23.0 (CH_2 each, C-5−C-7), 15.4 (OCH_2CH_3), 13.8 (CH_3, C8). IR (*n*-hexane; cm^{-1} (%)): 2062.6 (25), 1969.7 (5), 1935.5 (100), 1928.2 (20) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 575 (10) [M$^+$], 547 (5) [M$^+$ − CO], 519 (15) [M$^+$ − 2 CO], 491 (5) [M$^+$ − 3 CO], 463 (5) [M$^+$ − 4 CO], 435 (15) [M$^+$ − 5 CO], 206 (100).

(4*Z*,*syn*)-9f. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.02 (1 H, q, ^3J = 7 Hz, 1′-H), 4.62, 4.21, 4.00, and 3.9−3.4 (1:1:2:6 H, m each, morpholinyl and OCH_2), 4.07 (1 H, t, ^3J = 7 Hz, 5-H), 2.80 (2 H, m, 6-H_2), 1.92 (3 H, d, ^3J = 7 Hz, 2′-H_3), 1.45 (2 H, m, 7-H_2), 1.20 (3 H, t, OCH_2CH_3), 0.95 (3 H, t, ^3J = 7 Hz, 8-H_3). ^{13}C NMR ($CDCl_3$): δ 251.2 (C_q, W=C), 202.7 and 198.0 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 152.7 (C_q, C4), 147.6 (C_q, C3), 125.7 (CH, C5), 110.7 (CH, C1′), 67.7 (2 OCH_2CH_2N), 62.5 (OCH_2CH_3), 62.5 and 53.8 (NCH_2 each), 30.7, 26.1, and 22.9 (CH_2 each, C-5−C-7), 15.3 (OCH_2CH_3), 13.8 (CH_3, C2′). IR (*n*-hexane; cm^{-1} (%)): 2062.0 (20), 1968.0 (5), 1933.0 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 575 (10) [M$^+$], 547 (10) [M$^+$ − CO], 519 (25) [M$^+$ − 2 CO], 491 (5) [M$^+$ − 3 CO], 463 (15) [M$^+$ − 4 CO], 435 (15) [M$^+$ − 5 CO], 206 (100).

(3*S,4*R**)-10f.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 4.37, 4.29, 4.03, and 3.73 (1 H each, m each, 2 NCH_2), 4.00−3.80 (6 H, m, diastereotopic OCH_2CH_3 and 2 OCH_2CH_2N), 3.41 (1 H, qd, ^3J = 6.9 and 4.8 Hz, 4′-H), 3.12 (1 H, qd, ^3J = 6.4 and 4.8 Hz,

3′-H), 1.55−1.25 (4 H, m, $CH_2CH_2CH_3$), 1.26 (3 H, t, OCH_2CH_3), 1.06 (3 H, d, ^3J = 6.9 Hz, 4′-CH_3), 0.94 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 241.2 (C_q, W=C), 202.8 and 198.3 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 141.5 (C_q, C2′), 128.5 (C_q, C1′), 68.0 and 67.8 (2 OCH_2CH_2N), 65.0 (OCH_2CH_3), 62.6 and 54.5 (NCH_2 each), 43.8 (CH, C3′), 37.8 (CH, C4′); 30.8, 21.3, and 14.3 ($CH_2CH_2CH_3$), 15.6 (OCH_2CH_3), 15.3 (4′-CH_3). IR, MS, and CHN analytical data of a ca. 20/1 mixture of compounds (3*S**,4*R**)-**10f** and (3*R**,4*R**)-**10f** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2060.2 (20), 1967.0 (2), 1929.2 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 575 (40) [M^+], 547 (40) [M^+ − CO], 519 (45) [M^+ − 2 CO], 491 (25) [M^+ − 3 CO], 463 (45) [M^+ − 4 CO], 435 (100) [M^+ − 5 CO]. Anal. Calcd for $C_{20}H_{25}NO_7W$ (575.3): C, 41.76; H, 4.38; N, 2.43. Found: C, 42.24; H, 4.40; N, 2.26.

(3*R,4*R**)-10f.** Some typical signals which could be collected from the reaction mixture are given. ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.92 (1 H, qd, ^3J = 6.9 Hz, ^3J = 1.2 Hz, 4′-H), 2.42 (1H, qd, ^3J = 6.4 Hz, ^3J = 1.2 Hz, 3′-H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 68.3, 67.8, 55.5 (morpholino), 48.3 and 39.1 (CH, C3′ and C4′).

12f. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.11 (1 H, q, ^3J = 7 Hz, 1′-H), 4.61, 4.28, 3.79, and 3.54 (1 H each, m each, 2 NCH_2), 4.00 and 3.73 (2 H each, m each, 2 OCH_2CH_2N), 2.75, 1.61, and 1.37 (2 H each, m each, $CH_2CH_2CH_2CH_3$), 1.74 (3 H, d, ^3J = 7 Hz, 2′-H_3), 0.93 (3 H, t, ^3J = 7 Hz, 8-H_3). ^{13}C NMR ($CDCl_3$): δ 251.1 (C_q, W=C), 202.7 and 197.9 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 197.8 (C_q, C=O), 152.6 (C_q, C3), 125.1 (CH, C1′), 67.8 and 67.4 (OCH_2CH_2N each), 62.5 and 53.8 (NCH_2 each), 37.9, 26.1, and 22.4 (CH_2 each, C-5−C-7), 13.8 (CH_3, C8), 15.3 (OCH_2CH_3). IR (*n*-hexane; cm^{-1} (%)): 2064.2 (30), 1933.2 (100) (ν(C≡O)), 1700.3 (75), 1684.4 (50). MS (70 eV; ^{184}W, *m*/*e* (%)): 519 (5) [M^+ − CO], 491 (5) [M^+ − 2 CO], 463 (5) [M^+ − 3 CO], 407 (5) [M^+ − 5 CO], 57 (100). Anal. Calcd for $C_{18}H_{21}NO_7W$ (547.2): C, 39.51; H, 3.87; N, 2.56. Found: C, 39.52; H, 3.76; N, 2.40.

2-(Dimethylamino)-2-(2-ethoxy-4-methyl-3-phenyl-1-cyclobutenyl)-1-(pentacarbonyltungsta)ethenes (3*S,4*R**)-10g and (3*R**,4*R**)-10g and (*Z*)-1-Ethoxy-2-phenylethene (11).** But-2-enoic acid dimethylamide (**2a**; 226 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl-(1-ethoxy-(2-phenylethanylidene))tungsten (**1g**; 472 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give compound **11** (57 mg, 39%, R_f = 0.3 in 1/1 *n*-pentane/dichloromethane, colorless oil), compound (3*S**,4*R**)-**10g** (31 mg, 6%, R_f = 0.6 in 1/1 *n*-pentane/dichloromethane, yellow oil), and compound (3*R**,4*R**)-**10g** (39 mg, 7%, R_f = 0.5 in 1/1 *n*-pentane/dichloromethane, yellow oil).

(3*S,4*R**)-10g.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.33, 7.27, and 7.13 (2:1:2 H, m each, Ph), 4.45 (1 H, d, ^3J = 4.8 Hz, 3′-H), 3.84 (2 H, q, OCH_2), 3.81 and 3.55 (3 H each, s each, 2 NCH_3), 3.66 (1 H, qd, ^3J = 6.9 Hz and 4.8, 4′-H), 1.23 (3 H, t, OCH_2CH_3), 0.67 (3 H, d, ^3J = 6.9 Hz, 4′-CH_3). ^{13}C NMR ($CDCl_3$): δ 241.6 (C_q, W=C), 203.2 and 198.9 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 138.8 (C_q, C2′), 138.5 (C_q, *i*-C Ph), 130.2 (C_q, C1′); 128.4, 128.2, and 127.0 (2:1:2, CH each, Ph), 65.4 (OCH_2), 53.6 and 45.2 (2 NCH_3), 49.2 (CH, C3′), 40.5 (CH, C4′), 16.5 (4′-CH_3), 15.6 (OCH_2CH_3). IR (*n*-hexane; cm^{-1} (%)): 2059.9 (16), 1983.9 (3), 1966.9 (2), 1927.7 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 567 (20) [M^+], 539 (35) [M^+ − CO], 511 (20) [M^+ − 2 CO], 483 (20) [M^+ − 3 CO], 455 (30) [M^+ − 4 CO], 427 (100) [M^+ − 5 CO], 243 (5) [M^+ −$W(CO)_5$). Anal. Calcd for $C_{21}H_{21}NO_6W$ (567.3): C, 44.47; H, 3.73; N, 2.47. Found: C, 44.63; H, 3.75; N, 2.40.

(3*R,4*R**)-10g.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.34−7.26 (5 H, m, Ph), 3.83 and 3.45 (3 H each, s each, 2 NCH_3), 3.81 (2 H, m, diastereotopic OCH_2), 3.66 (1 H, d, ^3J = 1.2 Hz, 3′-H), 2.89 (1 H, qd, ^3J = 6.3 and 1.2 Hz, 4′-H), 1.29 (3 H, d, ^3J = 6.3 Hz, 4′-CH_3), 1.20 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 243.6 (C_q, W=C), 203.1 and 199.0 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 143.3 (C_q, C2′), 139.4 (C_q, *i*-C Ph), 128.8, 127.1, and 127.0 (2:1:2, CH each, Ph), 127.6 (C_q, C1′), 65.1 (OCH_2), 54.9 (CH, C3′), 53.9 and 45.5 (2 NCH_3), 45.3 (CH, C4′), 19.6 (4′-CH_3), 15.4 (OCH_2CH_3). IR (*n*-hexane; cm^{-1} (%)): 2060.0 (20), 1983.7 (5), 1966.9 (2), 1926.6 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 567 (15) [M^+], 539 (30) [M^+ − CO], 511 (15) [M^+ − 2 CO], 483 (15) [M^+ − 3 CO], 455 (25) [M^+ − 4 CO], 427 (100) [M^+ − 5 CO].

11. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.60 (2 H, m, Ph), 7.30−7.10 (3 H, m, Ph), 6.19 and 5.2 (1 H each, d each, ^3J = 7 Hz), 3.96 (2 H, q, OCH_2), 1.35 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 146.5 and 105.5 (CH each, (O)*C*H=*C*H), 136.1, 128.1 ,and 125.6 (1:2:2, Ph), 69.0 and 15.4 (OCH_2CH_3). IR (neat; cm^{-1} (%)): 1652.3 (100), 1261.3 (8), 1098.8 (72), 1074.0 (24), 779.4 (20), 685.1 (25). MS (70 eV), *m*/*e* (%): 148 (90) [M^+], 91 (100).

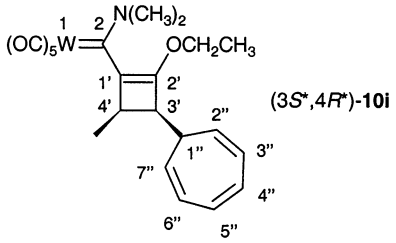
2-(2-Ethoxy-4-methyl-3-phenyl-1-cyclobutenyl)-2-morpholino-1-(pentacarbonyltungsta)ethenes (3*S,4*R**)-10h and (3*R**,4*R**)-10h.** 1-(Morpholin-4-yl)but-2-en-1-one (**2b**; 310 mg, 2.00 mmol) was reacted with phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxy-(2-phenylethanylidene-))tungsten (**1g**; 472 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) as described above to give compound **11** (53 mg, 36%, R_f = 0.3 in 1/1 *n*-pentane/dichloromethane, colorless oil), compound (3*S**,4*R**)-**10h** (32 mg, 5%, R_f = 0.5 in 3/2 *n*-pentane/dichloromethane, yellow oil), and compound (3*R**,4*R**)-**10h** (42 mg, 7%, R_f = 0.4 in 3/2 *n*-pentane/dichloromethane, yellow oil).

(3*S,4*R**)-10h.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.30 (3 H, m, Ph), 7.09 (2 H, "d", Ph), 4.53, 4.29, 4.24, and 4.03 (1 H each, m each, 2 NCH_2), 4.48 (1 H, d, ^3J = 4.8 Hz, 3′-H), 3.96−3.83 (6 H, m, diastereotopic OCH_2CH_3 and 2 OCH_2CH_2N), 3.71 (1 H, m, ^3J = 6.4 and 4.8 Hz, 4′-H), 1.20 (3 H, t, OCH_2CH_3), 0.67 (3 H, d, ^3J = 6.4 Hz, 4′-CH_3). ^{13}C NMR ($CDCl_3$): δ 239.8 (C_q, W=C), 202.9 and 198.6 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 138.5 and 138.1 (C_q each, C2′ and *i*-C−Ph), 129.1, 128.5, and 128.2 (1:2:2, CH each, Ph), 127.1 (C_q, C1′), 68.0 and 67.8 (2 OCH_2CH_2N), 65.4 (OCH_2CH_3), 62.8 and 54.9 (2 NCH_2), 49.2 (CH, C3′), 40.7 (CH, C4′), 16.5 (4′-CH_3), 15.4 (OCH_2CH_3). IR (*n*-hexane; cm^{-1} (%)): 2060.1 (20), 1929.2 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 609 (5) [M^+], 581 (15) [M^+ − CO], 553 (5) [M^+ − 2 CO], 525 (10) [M^+ − 3 CO], 497 (10) [M^+ − 4 CO], 469 (35) [M^+ − 5 CO].

(3*R,4*R**)-10h.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.34−7.25 (5 H, m, Ph), 4.80, 4.35, 4.09, and 4.01 (1 H each, m each, 2 NCH_2), 3.92−3.75 (6 H, m, diastereotopic OCH_2CH_3 and 2 OCH_2CH_2N), 3.65 (1 H, d, ^3J = 1.2 Hz, 3′-H), 2.94 (1 H, qd, ^3J = 6.6 and 1.2 Hz, 4′-H), 1.28 (3 H, d, ^3J = 6.6 Hz, 4′-CH_3), 1.18 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 242.6 (C_q, W=C), 202.7 and 198.6 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 141.9 (C_q, C2′), 139.2 (C_q, *i*-C Ph); 128.8, 127.2, and 127.0 (2:1:2, CH each, Ph), 126.4 (C_q, C1′), 68.0 and 67.8 (2 OCH_2CH_2N), 65.2 (OCH_2CH_3), 63.0 and 55.1 (2 NCH_2), 54.9 (CH, C3′), 45.4 (CH, C4′), 19.7 (4′-CH_3), 15.4 (OCH_2CH_3). IR (*n*-hexane; cm^{-1} (%)): 2060.6 (20), 1967.2 (2), 1927.4 (100) (ν(C≡O)), 1700 (7), 1653.0 (8). MS (70 eV; ^{184}W, *m*/*e* (%)): 609 (15) [M^+], 581 (30) [M^+ − CO], 553 (15) [M^+ − 2 CO], 525 (20) [M^+ − 3 CO], 497 (30) [M^+ − 4 CO], 469 (100) [M^+ − 5 CO].

2-(Dimethylamino)-2-(3-(2,4,6-cycloheptatrienyl)-2-ethoxy-4-methyl-1-cyclobutenyl)-1-(pentacarbonyltungsta)ethenes (3*S,4*R**)-10i and (3*R**,4*R**)-10i and 5-(2,4,6-Cycloheptatrienyl)-2-(dimethylamino)-3-ethylidene-1-(pentacarbonyltungsta)-1-penten-4-one (12i).** But-2-enoic acid dimethylamide (**2a**; 226 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(2-(2,4,6-cycloheptatrienyl)-1-ethoxy-1-ethylidene)tungsten (**1h**; 486 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give a 7/2 mixture of compounds (3*S**,4*R**)-**10i** and (3*R**,4*R**)-**10i** (256 mg, 44%, R_f = 0.7 in 2/1 *n*-pentane/dichloromethane, yellow oil) and compound **12i** (13 mg, 2%, R_f = 0.4 in 1/1 *n*-pentane/dichloromethane).

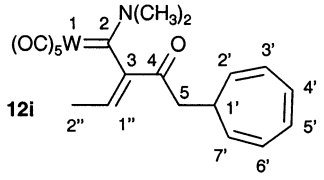
(3*S,4*R**)-10i.**



^{1}H NMR ($CDCl_3$, 25 °C): δ 6.66 (2 H, m, 5″-H and 4″-H), 6.21 (2 H, m, 3″-H and 6″-H), 5.37 and 5.15 (1 H each, m each, 2″-H and 7″-H), 3.80 (2 H, m, diastereotopic O*C*H_2CH$_3$), 3.77 and 3.42 (3 H each, s each, 2 N*C*H$_3$), 3.48 (2 H, m, 3′-H and 4′-H), 1.67 (1 H, m, 1″-H), 1.29 (3 H, t, OCH$_2$C*H*$_3$), 1.02 (3 H, d, ^3J = 6.6 Hz, 4′-CH$_3$). ^{13}C NMR ($CDCl_3$): δ 246.7 (C_q, W=*C*), 203.2 and 198.6 (C_q each, 1:4, *trans*- and *cis*-CO W(*C*O)$_5$), 139.6 (C_q, C2′), 131.0 and 130.9 (CH each, C-4″ and C-5″), 129.4 (C_q, C1′), 124.5 and 124.5 (CH each, C-3″ and C-6″), 124.1 and 124.0 (CH each, C-2″and C-7″), 65.3 (O*C*H$_2$), 53.1 and 46.8 (N*C*H$_3$ each), 45.1 (CH, C3′), 39.1 (CH, C4′), 37.3 (CH, C1″), 15.6 and 15.5 (OCH$_2$*C*H$_3$ and 4′-*C*H$_3$). IR, MS, and CHN analytical data of a 7/2 mixture of compounds (3*S**,4*R**)-**10i** and (3*R**,4*R**)-**10i** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2060.6 (20), 1966.5 (5), 1929.3 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 581 (15) [M$^+$], 553 (25) [M$^+$ − CO], 469 (25) [M$^+$ − 4 CO], 441 (35) [M$^+$ − 5 CO], 91 (100). Anal. Calcd for $C_{22}H_{23}NO_6W$ (581.3): C, 45.46; H, 3.99; N, 2.41. Found: C, 45.34; H, 4.21; N, 2.38.

(3*R,4*R**)-10i.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.64 (2 H, m, 5″-H and 4″-H), 6.21 (2 H, m, 3″-H and 6″-H), 5.32 and 5.23 (1 H each, m, 2″-H and 7″-H), 3.80 (2 H, m, diastereotopic O*C*H$_2$), 3.79 and 3.42 (3 H each, s each, 2 N*C*H$_3$), 2.88 (1 H, qd, ^3J = 6.6 and 1.6 Hz, 4′-H), 2.86 (1 H, dd, ^3J = 8.4 and 1.6 Hz, 3′-H), 1.57 (1 H, m, 1″-H), 1.29 (3 H, t, OCH$_2$C*H*$_3$), 1.22 (3 H, d, ^3J = 6.6 Hz, 4′-CH$_3$). ^{13}C NMR ($CDCl_3$): δ 246.7 (C_q, W=*C*), 203.1 and 198.8 (C_q each, 1:4, *trans*- and *cis*-CO W(*C*O)$_5$), 142.3 (C_q, C2′), 129.4 and 129.4 (CH, C-4″and C-5″), 127.4 (C_q, C1′), 125.3 and 125.3 (CH, C-3″and C-6″), 125.0 and 124.7 (CH, C-2″and C-7″), 53.5 and 45.3 (N*C*H$_3$ each), 51.4 (CH, C3′), 40.6 (CH, C4′), 38.8 (CH, C1″), 15.6 (OCH$_2$*C*H$_3$), 15.5 (4′-*C*H$_3$).

12i.



^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C): δ 6.65 (2 H, m, 5′-H and 4′-H), 6.19 (2 H, m, 3′-H and 6′-H), 6.13 (1 H, q, ^3J = 7 Hz, 1″-H), 5.28 and 5.21 (2 H each, dd each, ^3J = 6.0 and 9.6 Hz, 2′-H and 7′-H), 3.87 and 3.15 (3 H each, s each, 2 N*C*H$_3$), 3.22 and 2.97 (1 H each, ddd each, ^2J = 17.4 Hz, ^3J = 7 and 6.8 Hz, COCH$_2$), 2.39 (1 H, m, 1″-H), 1.73 (3 H, d, ^3J = 7 Hz, CH$_3$). ^{13}C NMR ($CDCl_3$): δ 253.4 (C_q, W=*C*), 202.9 and 198.1 (C_q each, 1:4, *trans*- and *cis*-CO W(*C*O)$_5$), 153.5 (C_q, C3), 131.2 and 130.7 (CH, C4′ and C5′), 126.0 (CH, C1″), 125.1 and 125.1 (CH, C3′and C6′), 125.1 and 124.9 (CH, C2′and C-7′), 53.3 and 43.5 (N*C*H$_3$ each), 40.5 (CO*C*H$_2$), 34.7 (CH, C1′), 15.3 (CH$_3$). IR (*n*-hexane; cm^{-1} (%)): 2064.0 (20), 1983.8 (20), 1966.5 (5), 1931.2 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 525 (10) [M$^+$ − CO], 469 (5) [M$^+$ − 3 CO], 441 (5) [M$^+$ − 4 CO], 413 (10) [M$^+$ − 5 CO], 91 (100).

2-(3-(2,4,6-Cycloheptatrienyl)-2-ethoxy-4-methyl-1-cyclobutenyl)-2-morpholino-1-(pentacarbonyltungsta)-ethenes (3*S,4*R**)-10j and (3*R**,4*R**)-10j and 5-(2,4,6-Cycloheptatrienyl)-3-ethylidene-2-morpholino-1-(pentacarbonyltungsta)-1-penten-4-one (12j).** 1-(Morpholin-4-yl)-but-2-en-1-one (**2b**; 310 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(2-(2,4,6-cycloheptatrienyl)-1-ethoxy-1-ethylidene)tungsten (**1h**; 486 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give a 12/1 mixture of compounds (3*S**,4*R**)-**10j** and (3*R**,4*R**)-**10j** (286 mg, 46%, R_f = 0.6 in 2/1 *n*-pentane/dichloromethane, yellow oil) and compound **12j** (14 mg, 2%, R_f = 0.4 in 1/1 *n*-pentane/dichloromethane).

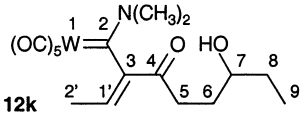
(3*S,4*R**)-10j.** ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.67 (2 H, m, 5″-H and 4″-H), 6.21 (2 H, m, 3″-H and 6″-H), 5.28 and 5.16 (1 H each, m each, 2″-H and 7″-H), 4.45, 4.24, 4.12, and 3.94 (1 H each, m each, 2 NCH$_2$), 3.93−3.64 (6 H, m, diastereotopic O*C*H_2CH$_3$ and 2 O*C*H_2CH$_2$N), 3.54 (2 H each, m, 3′-H and 4′-H), 1.66 (1 H, m, 1″-H), 1.28 (1 H, t, OCH$_2$C*H*$_3$), 1.01 (3 H, d, ^3J = 6.6 Hz, 4′-CH$_3$). ^{13}C NMR ($CDCl_3$): δ 244.3 (C_q, W=*C*), 202.9 and 198.5 (1:4, *trans*- and *cis*-CO W(*C*O)$_5$), 139.4 (C_q, C2′), 131.0 and 130.9 (CH, C4″ and C5″), 128.6 (C_q, C1′), 124.7 and 124.6 (CH, C3″ and C6″), 123.7 and 123.6 (CH, C2″and C7″), 67.8 and 67.6 (2 O*C*H$_2$CH$_2$N), 65.5 (O*C*H$_2$CH$_3$), 62.4 and 54.8 (2 N*C*H$_2$), 46.7 (CH, C3′), 39.0 (CH, C1″), 37.4 (CH, C4′), 15.5 and 15.4 (4′-CH$_3$ and OCH$_2$*C*H$_3$). IR and MS analytical data of a 12/1 mixture of compounds (3*S**,4*R**)-**10j** and (3*R**,4*R**)-**10j** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2060.8 (21), 1983.8 (11), 1967.4 (3), 1930.9 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m*/*e* (%)): 623 (10) [M$^+$], 595 (15) [M$^+$ − CO], 539 (5) [M$^+$ − 3 CO], 511 (20) [M$^+$ − 4 CO], 483 (25) [M$^+$ − 5 CO], 91 (100).

(3*R,4*R**)-10j.** Some typical signals which have been collected from the reaction mixture are given. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.64 (2 H, m, 5″-H and 4″-H), 5.36 and 5.17 (1 H each, m each, 2″-H and 7″-H), 2.99 (1 H, dq, ^3J = 1.2 and 6.8 Hz, 4′-H), 2.77 (1 H, dd, ^3J = 1.2 and 7 Hz, 3′-H), 2.05 (1 H, m, 1″-H), 1.22 (1 H, t, ^3J = 7 Hz, OCH$_2$*C*H$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 198.5, 137.8 (C_q, C2′), 131.1 and 130.9 (CH each, C-5″ and C-4″), 129.0 (C_q, C1′), 125.5 and 125.2 (CH each, C-3″ and C-6″), 124.5 and 124.3 (CH each, C-2″and C-7″), 67.9 and 67.7 (OCH$_2$*C*H$_2$N each), 65.7 (O*C*H$_2$CH$_3$), 62.8 and 55.0 (N*C*H$_2$ each), 51.4 (CH, C3′), 40.6 (CH, C1″), 38.8 (CH, C4′), 15.2 (4′-CH$_3$ or OCH$_2$*C*H$_3$).

12j. ^{1}H NMR ($CDCl_3$, 600 M, 25 °C): δ 6.65 (2 H, m, 5″-H and 4″-H), 6.18 (2 H, m, 3″-H and 6″-H), 6.15 (1 H, q, ^3J = 7 Hz, C=C*H*), 5.26 and 5.20 (1 H each, m each, 2″-H and 7″-H), 4.60, 4.23, 3.79, and 3.52 (1 H each, m each, 2 NCH$_2$), 3.71−3.66 (4 H, m, 2 O*C*H_2CH$_2$N), 3.25 and 3.00 (1 H each, dd each, ^2J = −17.3 Hz, ^3J = 6.9 and 7 Hz, diastereotopic C*H*$_2$CO), 2.37 (1 H, m, CH, 1″-H), 1.75 (3 H, t, ^3J = 7 Hz, CH$_3$). ^{13}C NMR ($CDCl_3$): δ 250.8 (C_q, W=*C*), 202.6 and 197.9 (C_q each, 1:4, *trans*- and *cis*-CO W(*C*O)$_5$), 196.14 (C_q, C=O), 152.6 (C_q, *C*=CH), 131.3 and 130.7 (CH each, C4″ and C5″), 126.2 (CH, C=*C*H), 125.2 and 125.2 (CH each, C3″ and C6″), 125.1 and 124.7 (CH each, C2″ and C7″), 67.7 and 67.3 (O*C*H$_2$CH$_2$N each), 62.5 and 53.9 (NCH$_2$*C*H$_2$O each), 40.7 (CH$_2$, *C*H$_2$CO), 34.6 (CH, C1″), 15.6 (CH$_3$). IR (*n*-hexane; cm^{-1} (%)): 2064.0 (22), 1972.2 (2), 1932.7 (100) (ν(C≡O)), 1700 (13) (ν(C=O)). 1653.0 (15). MS (70 eV; ^{184}W, *m*/*e* (%)): 567 (10) [M$^+$ − CO], 511 (5) [M$^+$ − 4 CO], 483 (5) [M$^+$ − 5 CO], 91 (100).

2-(Dimethylamino)-3-ethylidene-7-hydroxy-1-(pentacarbonyltungsta)-1-nonen-4-one (12k). But-2-enoic acid dimethylamide (**2a**; 113 mg, 1.00 mmol), phosphorus oxychloride (153 mg, 1.00 mmol), and pentacarbonyl(3-ethyl-2-oxacyclopentanylidene)tungsten (**1i**; 211 mg, 0.50 mmol) were treated with triethylamine (202 mg, 2.00 mmol) as described above for 12 h to give a 4/3 mixture of diastereomeric compounds **12k** (108 mg, 40%, R_f = 0.5 in dichloromethane/diethyl ether 4:1, yellow oil).

12k.

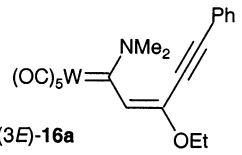


12k

This compound was a 4/3 mixture of diastereomers; chemical shifts of minor isomer are given in braces. ^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C): δ 6.17 {6.17} (1 H, q, ^3J = 7 Hz, 1′-H), 3.88 and 3.18 {3.88 and 3.19} (3 H each, s each, 2 NCH_3), 3.56 {3.56} (1 H, m, 7-H), 3.02 and 2.83 {2.95 and 2.87} (1 H each, m each, diastereotopic 5-H_2), 1.84 and 1.73 {1.94 and 1.65} (1 H each, m each, diastereotopic 6-H_2), 1.73 {1.73} (3 H, d, ^3J = 7 Hz, 2′-H_3), 1.50 {1.50} (2 H, m, 8-H_2), 0.95 {0.95} (3 H, t, ^3J = 7 Hz, 9-H_3). ^{13}C NMR ($CDCl_3$): δ 253.2 {253.1} (C_q, W=C), 202.9 and 198.1 {202.9 and 198.1} (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 198.0 {197.9} (C_q, C1′), 153.2 {153.2} (C_q, C3), 125.7 {125.7} (CH, C1′), 72.9 {72.5} (CH, C7), 53.3 and 43.5 {53.3 and 43.5} (NCH_3 each), 34.7 {34.7} (CH_2, C5), 30.7 {30.6} (CH_2, C6), 30.4 {30.3} (CH_2, C8), 15.2 {15.2} (CH_3, C2′), 9.9 {9.8} (CH_3, C9). IR (*n*-hexane; cm^{-1} (%)): 2063.5 (18), 1970.5 (2), 1931.2 (100) (ν(C≡O)). IR (neat; cm^{-1} (%)): 3413.9 (16) (ν(O−H)), 2060.1 (13), 1967.5 (7), 1916.8 (37), 1891.1 (40), 1675.9 (60) (ν(C=O)), 1341.1 (32), 1221.1 (30), 1213.6 (29), 1092.7 (24). MS-EI (70 eV; ^{184}W, *m/e* (%)): 517 (25) [$M^+ - H_2O$], 489 (10) [$M^+ - CO - H_2O$)], 461 (25) [$M^+ - 2\ CO - H_2O$], 405 (15) [$M^+ - 4\ CO - H_2O$], 377 (70) [$M^+ - 5\ CO - H_2O$)], 197 (100). ESI-MS (*m/e* (%)): 572 (100), 570 (100), 568 (70) [M^+ + Cl], 536 (25), 534 (30), 532 (20) [M^+]; isotope pattern in good agreement with expectation. Anal. Calcd for $C_{17}H_{21}NO_7W$ (535.2): C, 38.15; H, 3.95; N, 2.62. Found: C, 38.20; H, 4.07; N, 2.58.

2-((Dimethylamino)-4-ethoxy-6-phenyl)-1-(pentacarbonyltungsta)-1,3-hexadien-5-ynes (3*E*)-16a and (3*Z*)-16a. Acetic acid dimethylamide (**15a**; 174 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(3-phenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**; 486 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give an 8/1 mixture of compounds (3*E*)-**16a** and (3*Z*)-**16a** (212 mg, 39%, R_f = 0.4 in 2/1 *n*-pentane/dichloromethane, yellow crystals from 10/1 *n*-pentane/dichloromethane at −20 °C, mp 81−82 °C).

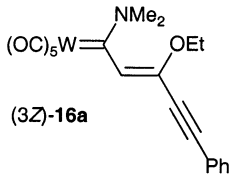
(3*E*)-16a.



(3*E*)-16a

^{1}H NMR ($CDCl_3$, 25 °C): δ 7.40 and 7.35 (2:3, m each, Ph), 6.37 (1 H, s, 3-H), 3.99 (2 H, q, OCH_2), 3.82 and 3.48 (3 H each, s each, 2 NCH_3), 1.38 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): 247.0 (C_q, W=C), 203.7 and 198.3 (C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 131.5, 129.3, and 128.5 (2:1:2, CH each, Ph), 129.3 (CH, C3), 125.1 (C_q, HC=C, C4), 121.5 (C_q, *i*-C Ph), 98.7 and 81.6 (C_q each, *C*≡*C*), 64.9 (OCH_2), 53.3 and 44.2 (NCH_3 each), 14.8 (OCH_2CH_3). IR, MS, and CHN analytical data obtained from the 8/1 mixture of compounds (3*E*)-**16a** and (3*Z*)-**16a** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2061.4 (15), 1983.9 (10), 1927.3 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m/e* (%)): 551 (20) [M^+], 523 (10) [$M^+ - CO$], 495 (20) [$M^+ - 2\ CO$], 467 (100) [$M^+ - 3\ CO$], 411 (45) [$M^+ - 5\ CO$]. Anal. Calcd for $C_{20}H_{17}NO_6W$ (551.2): C, 43.58; H, 3.11; N, 2.54. Found: C, 43.69; H, 2.90; N, 2.44.

(3*Z*)-16a.



(3*Z*)-16a

^{1}H NMR ($CDCl_3$, 25 °C): δ 7.42 and 7.34 (2:3 H, m each, Ph), 6.17 (1 H, s, 3-H), 4.13 (2 H, q, ^3J = 7 Hz, OCH_2), 3.77 and 3.37 (3 H each, s each, 2 NCH_3), 1.29 (3 H, t, ^3J = 7 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): 246.9 (C_q, W=C), 203.8 and 198.4 (C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 131.7, 129.0, and 128.4 (2:1:2, CH each, Ph), 129.4 (CH, C3), 125.1 (C_q, HC=C, C4), 121.7 (C_q, *i*-C Ph), 92.1 and 82.4 (C_q each, C≡C), 65.4 (OCH_2), 53.0 and 44.8 (NCH_3 each), 15.5 (OCH_2CH_3).

2-((Dimethylamino)-3-ethyl-4-ethoxy-6-phenyl)-1-(pentacarbonyltungsta)-1,3-hexadien-5-ynes (3*E*)-16b and (3*Z*)-16b. Butanoic acid dimethylamide (**15b**; 230 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl-(3-phenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**; 486 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give a 14/1 mixture of compounds (3*E*)-**16b** and (3*Z*)-**16b** (429 mg, 74%, R_f = 0.5 in 2/1 *n*-pentane/dichloromethane, yellow crystals from 10/1 *n*-pentane/dichloromethane at −20 °C; mp 86−87 °C).

(3*E*)-16b. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.39 and 7.31 (2:3, m each, Ph), 4.09 and 3.98 (1 H each, m each, diastereotopic OCH_2), 3.81 and 3.40 (3 H each, s each, 2 NCH_3), 2.83 and 2.47 (1 H each, m each, CCH_2CH_3), 1.32 (3 H, t, OCH_2CH_3), 1.06 (3 H, t, CCH_2CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): 253.5 (C_q, W=C), 202.9 and 198.4 (C_q, 1:4, *trans*- and *cis*-CO, $W(CO)_5$), 142.7 (C_q, C3), 131.7, 128.7, and 128.4 (2:1:2, CH each, Ph), 124.5 (C_q, C4), 122.0 (C_q, *i*-C Ph), 97.5 and 82.0 (C_q each, *C*≡*C*), 65.2 (OCH_2), 53.2 and 44.2 (NCH_3 each), 22.6 (CCH_2CH_3), 15.3 (OCH_2CH_3), 11.7 (CCH_2CH_3). IR, MS, and CHN analytical data obtained for a 14/1 mixture of compounds (3*E*)-**16b** and (3*Z*)-**16b** are as follows. IR (*n*-hexane; cm^{-1} (%)): 2061.4 (20), 1931.5 (100) (ν(C≡O)). MS (70 eV; ^{184}W, *m/e* (%)): 579 (20) [M^+], 523 (10) [$M^+ - 2\ CO$], 495 (100) [$M^+ - 3\ CO$], 467 (20) [$M^+ - 4\ CO$], 439 (20) [$M^+ - 5\ CO$]. Anal. Calcd for $C_{22}H_{21}NO_6W$ (579.3): C, 45.62; H, 3.65; N, 2.42. Found: C, 45.44; H, 3.42; N, 2.36.

(3*Z*)-16b. Only a partial assignment is given, due to overlapping signals. ^{1}H NMR ($CDCl_3$, 25 °C): δ 3.75 and 3.31 (3 H each, s each, 2 NCH_3), 2.70 (2 H, m, CCH_2CH_3), 1.26 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): 202.2 and 198.6 (C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 137.9 (C_q, C3), 131.3, 128.6, and 128.4 (2:1:2, CH each, Ph), 122.6 and 122.2 (C_q each, C4 and *i*-C Ph), 95.3 and 81.3 (C_q each, *C*≡*C*), 64.5 (OCH_2), 52.8 and 44.6 (NCH_3 each).

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Supporting Information Available: Tables giving details of the X-ray crystal structure analyses and figures giving additional views of the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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