Organometallics **1997,** *16,* 5893−5899

Dichotomy of Enamines at the C≡C Bond of a (1-Alkynyl)carbene Tungsten Complex. (1-Azoniabutadien-4-yl)carbonylmetalates $(^{-}OC)_5WC(OEt){=}CR^1C({=}N^+R_2)Me$, Stable Torsion Isomers of (2-Aminoethenyl)carbene Complexes $(OC)_5W{=}C(OEt)CR^1{=}C(NR_2)Me$[1]

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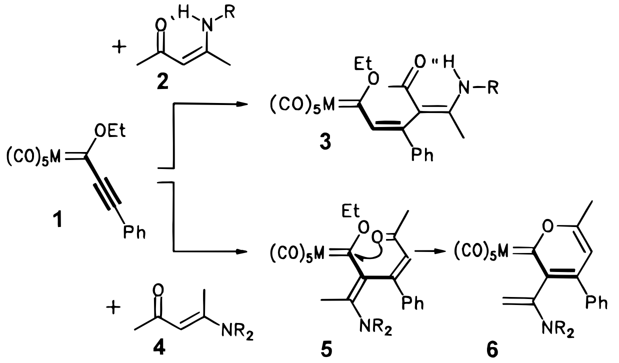
Received September 3, 1997⊗

Addition of tertiary open-chain enamines $R^1HC{=}C(NR_2)Me$ **7a**−**e** [NR_2 = pyrrolidine, N(*i*-Bu)$_2$; R^1 = Ph, CO_2Me, CO_2Et, CO_2Bz, CO_2-*t*-Bu] to the 1-alkynylcarbene complex $(CO)_5W{=}C(OEt)C{\equiv}CPh$ (**1a**) affords novel (1-azoniabutadien-4-yl)carbonylmetalates $(^{-}OC)_5WC(OEt){=}C[C({=}N^+R_2)Me]C(Ph){=}CHR^1$ (2*E*)-*torquo*-**8a**−**f** by dichotomy of the C=C(N) bond of **8** at the C≡C bond of **1**. Compounds (2*E*)-*torquo*-**8** are stable in solid state but undergo (2*E*/2*Z*) isomerization in solution to give compounds (2*Z*)-*torquo*-**8**. X-ray structure analyses are reported of compounds (2*E*)-*torquo*-**8e**, (2*E*)-*torquo*-**8f**, and (2*Z*)-*torquo*-**8a**.

1-Alkynylcarbene complexes, e.g. $(CO)_5M{=}C(OEt)C{\equiv}CPh$ **1a**,**b** (M = Cr, W), are potentially useful reagents for the synthesis of organic compounds.[2] It was shown only recently that secondary enaminones, e.g. compounds **2**,[3a,b] as well as tertiary enamines $CH{=}C(NR_2)$[3c,d] undergo 4-addition to the C≡C bond of 1-alkynylcarbene complexes **1a**,**b** under exceedingly mild conditions to afford conjugated 6-amino-1-metalla-1,3,5-hexatrienes M=CC=CC=C(N), e.g. compounds **3** (Scheme 1). Compounds of the latter type were isolated crystalline and could be easily cyclized to cyclopentadienes,[3c,d,4,5] 2,3-Homopyrroles,[3b] or pyran-2-ylidene complexes.[3a,6] While pursuing studies on reactions of enamines, and enaminones, respectively, with 1-alkynylcarbene complexes **1**, a second reaction mode significantly different from the forementioned one was found, which yields "cross-conjugated" metallatrienes M=CC[=*C(N)*]C=*C*, e.g. compounds **5** (Scheme 1), by dichotomy of the C=C(N) bond at the C≡C bond of compound **1**[7] instead of conjugated metallatrienes by a Michael-type addition. While compounds **5** have not been isolated, since they readily cyclize in situ to pyranylidene complexes **6** (Scheme 1), we now succeeded in isolating and fully characterizing cross-conjugated metallatrienes **8**, which are structurally closely related to compounds **5**. Reactions of enamines with 1-alkynylcarbene complexes leading to formation of stable cross-conjugated metallatrienes of type **5** instead of conjugated 1-metalla-1,3,5-trienes **3** have not been reported up to date,[8] even though there is ample precedence for reactions of enamines with alkynes, e.g. propargylic esters, in which cyclobutene derivatives are generated, which subsequently undergo ring opening to butadiene derivatives.[9,10] To gain more information about crucial features leading to transformation of 1-alkynylcarbene complexes and enamines into either conjugated or cross-conjugated metallatrienes (Scheme 1), and to also make cross-conjugated metallatrienes available for synthetic application, we report on reactions of enamines **7a**−**f** with 1-alkynylcarbene tungsten complex **1a**.

Scheme 1. Different Reaction Modes of Secondary and Tertiary Enaminones with 1-Alkynylcarbene Complexes 1 (M = W, Cr)



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† X-ray structure analyses.

⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1997.

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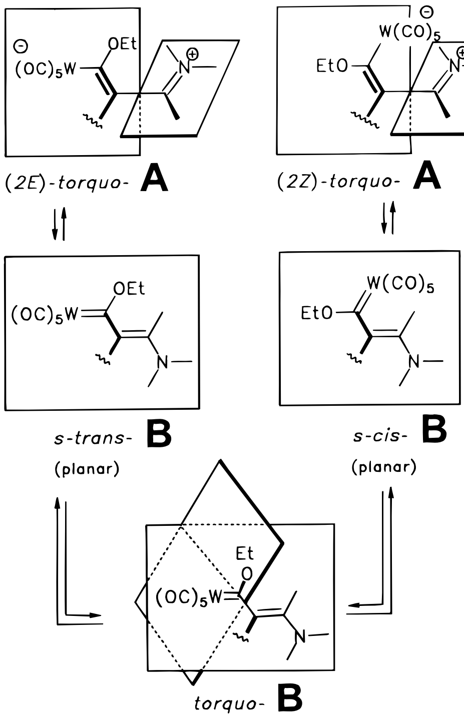
S0276-7333(97)00778-4 CCC: $14.00

Scheme 2. Interconversion of (1-Azoniabutadienyl)carbonylmetalates A via 4−Amino-1-metalla-1,3-dienes B



(1-Azoniabutadienyl)carbonylmetalates A and 4-Amino-1-metalla-1,3-dienes B

A high number of stable stereoisomers must be encountered on dealing with structures related to compounds **5** (Scheme 1). Different stereoisomers of **5** are generated not only by rotation about C,C double bonds but also by rotation about the central C,C single bonds. Hindered rotation of the C,C "single bonds" may be caused by steric congestion of substituents as well as by a partial double bond character induced by electron delocalization. Furthermore, two basic structures **A** and **B** must be distinguished of compounds **5** with respect to the geometrical arrangement of the W,C,C,C,N backbone and the electron distribution within this system (Scheme 2). Compounds of type **B** contain a 4-amino-1-metalla-1,3-diene $(OC)_5M{=}CC{=}C$-(N) unit in *s-cis*-**B** or *s-trans*-**B** conformation, which is stabilized by supposedly captodative interaction between the lone pair of the nitrogen atom and the electron-withdrawing $W(CO)_5$ moiety in essentially planar arrangement.[7,11,12] Distortion from planarity in compounds **B** may be achieved, for example, by steric congestion of substituents, which then leads to generation of structures of type *torquo*-**B**.[1,13] Compounds of type **A** exhibit structural features significantly different from those of compounds **B**. Compounds **A** are zwitterionic (1-azoniabutadienyl)carbonylmetalates $(^{-}OC)_5$-$MC{=}CC({=}N^{+})$, which are usually strongly distorted about the $C{-}C({=}N^{+})$ bond (!) due to steric interaction between substituents, for example (Scheme 2). Two different stereoisomers, (2*E*)-*torquo*-**A** and (2*Z*)-*torquo*-**A**, must be distinguished. Examples of both type compounds have been characterized by X-ray analyses (Figures 1−3). A (2*E*/2*Z*) interconversion of stereoisomers *torquo*-**A** appears to be a multistep process through

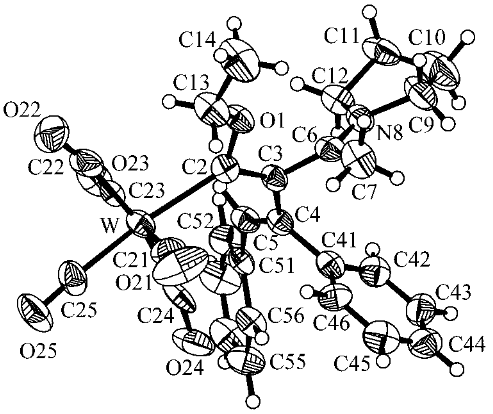


Figure 1. Molecular structure of (1-azoniabutadienyl)-carbonylmetalate (2*E*)-*torquo*-**8e.**

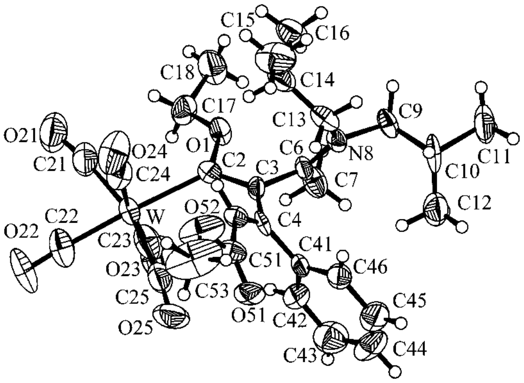


Figure 2. Molecular structure of (1-azoniabutadienyl)-carbonylmetalate (2*E*)-*torquo*-**8f.**

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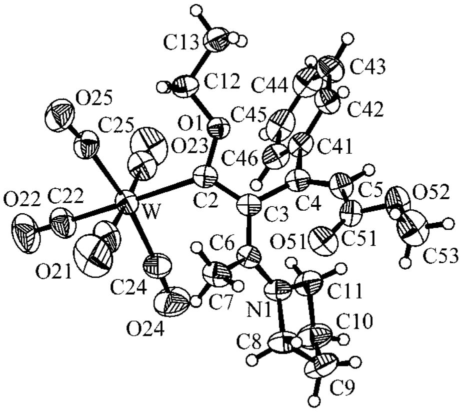


Figure 3. Molecular structure of the (1-azoniabutadienyl)carbonylmetalate (2*Z*)-*torquo*-**8a**.

intermediate formation of several discrete species of type **B** (Scheme 2).

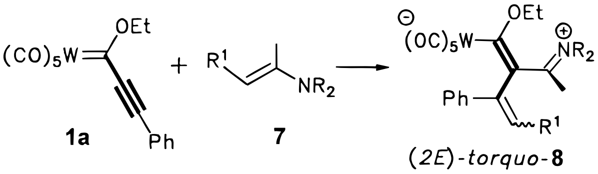
(1-Azoniabutadienyl)carbonylmetalates (2*E*)-*torquo*-8

Addition of tertiary enamines (*E*)-**7a**−**f** to the 1-alkynylcarbene tungsten complex **1a** in unpolar solvents, like pentane, leads to formation of a yellow precipitate of (analytically almost clean) (1-azoniabutadienyl)carbonylmetalates (2*E*)-*torquo*-**8a**−**f** in 81−96% yield within 1 h at 20 °C (Scheme 3).

The molecular structures of (1-azoniabutadienyl)carbonylmetalates (2*E*)-*torquo*-**8** are based on ^{13}C NMR measurements as well as on X-ray structure analyses of (2*E*)-*torquo*-**8e** and (2*E*)-*torquo*-**8f** (Table 2). The W−C2−C3−C6 unit exhibits a pattern of alternating bond distances [(2*E*)-*torquo*-**8e**: W−C2 227.5(7) pm, C2−C3 137.8(9) pm, C3−C6 147.2(10) pm; (2*E*)-*torquo*-**8f**: W−C2 230.4(13) pm, C2−C3 138(2) pm, C3−C6 147(2) pm] and is arranged in an (*E*) configuration with respect to the C2−C3 bond [W−C2−C3−C6 of (2*E*)-*torquo*-**8e**, 159.5(5)°; (2*E*)-*torquo*-**8f**, 158.3(5)°]. The distance W−C2 is significantly longer [(2*E*)-*torquo*-**8e**, 227.5(7) pm; (2*E*)-*torquo*-**8f**, 230.4(13) pm] than the W=C bond of, e.g. $(CO)_5W{=}C(OMe)Ph$ (205 pm),[14] in line with the single-bond character proposed of the W−C2 bond in compounds (2*E*)-*torquo*-**8**. On the other hand, the distance C6−N8 of the C=N$^+$ unit is significantly shorter [(2*E*)-*torquo*-**8e**, 128.4(8) pm; (2*E*)-*torquo*-**8f**, 131.7(13) pm] than the distance =CN in, e.g. $(CO)_5Cr{=}C(OEt)CH{=}C[N(COPh)Ph]Ph$ [142.0(4) pm],[13] but very similar to the distance C=N$^+$ 127.7(4) pm found of the cationic iminium carbene complex $\{(CO)_5Cr{=}C(OEt)CH_2[(-)(C{=}N^+Me)(CH_2)_3(-)]\}^+BF_4^-$.[12c] Furthermore, the C2−C3−C6−N8 unit is strongly twisted [(2*E*)-*torquo*-**8e**, 129.4(0.7)°; (2*E*)-*torquo*-**8f**, 119.4], which indicates little (or no) π interaction within the C3−C6 bond. Strong distortion from planarity is observed also for the C2=C3−C4=C5 unit [**8e**, 62.4(10)°; **8f**, −48.3(16)°].

In line with the zwitterionic structures, which we propose for compounds (2*E*)-*torquo*-**8** is the significant upfield shift of the ^{13}C NMR signal of the W−C2 unit [e.g. (2*E*)-*torquo*-**8a**, δ 245.0 (see Scheme 3)] compared to, for example, $(CO)_5W{=}C(OEt)CH{=}C[N(COPh)Ph]Ph$ (δ 304.2)[13] or the cationic iminium tungsten complex $[(CO)_5W{=}C(OEt)CH_2C(Ph){=}N^+Me_2]^+BF_4^-$ (δ 316.3),[12c] as well as the deshielding of the carbon signals *C*=N$^+$ {e.g. (2*E*)-*torquo*-**8a**, δ 181.0 (see Scheme 3); $[(CO)_5W{=}C(OEt)CH_2C(Ph){=}N^+Me_2]^+BF_4^-$; δ 176.1} compared to, for example, $(CO)_5W{=}C(OEt)CH{=}C[N(COPh)Ph]Ph$ (δ 142.0).

Scheme 3. Generation of Iminium Carbonylmetalates (2*E*)-*torquo*-8 from 1-Alkynylcarbene Complexes and Tertiary Enamines (*E*)-7


1a + **7** → (2*E*)-*torquo*-**8**

7,(2*E*)-torquo-**8**	NR$_2$	R^1	[a]	δ(W=C)[b]	δ(C=N$^+$)[b]	δ(5-H)[b]
a	N(CH$_2$)$_4$	CO$_2$Me	96	245.0	181.0	5.84
b	N(CH$_2$)$_4$	CO$_2$Et	95	243.0	181.2	5.88
c	N(CH$_2$)$_4$	CO$_2$CH$_2$Ph	87	242.9	181.1	5.84
d	N(CH$_2$)$_4$	CO$_2$*t*-Bu	93	242.9	181.1	5.88
e	N(CH$_2$)$_4$	Ph	81	237.8	181.1	7.04[c]
f	N(*i*-Bu)$_2$	CO$_2$Me	81	244.0	187.0	6.29[c]

[a] Chemical yields of (2*E*)-*torquo*-**8** in percent. [b] Typical NMR chemical shifts in $CDCl_3$, exept (2*E*)-*torquo*-**8b** in C_6D_6. [c] A (5*E*) configuration of the PhC=CR^1 bond has been determined by X-ray structure analyses (Figures 1 and 2). Compounds (2*E*)-torquo-**8a**−**d** exhibit a (5*Z*) configuration.

Thermal (*E*/*Z*) Isomerization of (1-Azoniabutadienyl)carbonylmetalates (2*E*)-*torquo*-8

(1-Azoniabutadienyl)carbonylmetalates (2*E*)-*torquo*-**8** generated from compounds **1a** and **7** are configurationally stable in solid state, but undergo an (*E*/*Z*) isomerization to compounds (2*Z*)-*torquo*-**8** in solution within 6−8 h at 20 °C (Scheme 4). For this reason, stereochemically pure compounds (2*E*)-*torquo*-**8** are obtained only if generated in unpolar solvents, like pentane, in which they are sparsely soluble and therefore are precipitated fast from the reaction mixture. It is obvious that compounds (2*E*)-*torquo*-**8** are obtained in a kinetically controlled reaction, and the better charge compensation, which is achieved in the (2*Z*) stereoisomers, plays an important role as a driving force of the (2*E*/2*Z*) isomerization of these compounds (Scheme 4). The (2*E*/2*Z*) rearrangement can be followed by ^{1}H NMR spectra (in $CDCl_3$), in which the signal 5-H of compounds (2*E*)-*torquo*-**8** [e.g. (2*E*)-*torquo*-**8a**: δ 5.84] becomes broader and smaller, while the intensity of signal 5-H of the rearrangement product (2*Z*)-*torquo*-**8** [e.g. (2*Z*)-*torquo*-**8a**: δ 6.20] increases concomitantly. It is quite unfortunate that due to dynamic line broading of the signals 5-H, which supposedly is caused by hindered rotation, e.g., of the *C*−*C*(=N$^+$) and/or the =C−C(Ph)= bond, an estimation of rotation barriers by ^{1}H-NMR experiments is not feasible. A structural correlation of NMR chemical shifts of (1-azoniabutadienyl)carbonylmetalate complexes *torquo*-**8** could be achieved only after several solid state structures of compounds **8** had been carried out, three of which are included in this paper.

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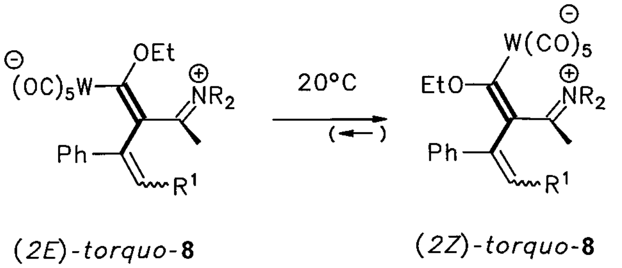
Table 1. Typical Bond Distances (pm) and ^{13}C NMR Shifts (δ Values) of (1-Azoniabutadienyl)carbonylmetalates (2*E*)-*torquo*-8e and (2*Z*)-*torquo*-8a

	W−C2	C2=C3	C3−C(=N$^+$)	C=N$^+$	δ C2	δ C=N$^+$
(2*E*)-*torquo*-**8e**	227.5(7)	137.8(9)	147.2(10)	128.4(8)	237.8	181.1
(2*Z*)-*torquo*-**8a**	230.1(7)	140.2(10)	143.5(9)	130.9(10)	259.0	175.0

Scheme 4. Thermal (*E*/*Z*) Isomerization of Iminium Carbonylmetalates (2*E*)-*torquo*-8



(2*Z*)-*torquo*-**8**	NR$_2$	R^1	^{a}	δ(W=C)^b	δ(C=N$^+$)^b	δ(5-H)^b
a	N(CH$_2$)$_4$	CO$_2$Me	> 90	259.0	175.0	6.20
b	N(CH$_2$)$_4$	CO$_2$Et	> 90	-^{c}	-^{c}	6.19
c	N(CH$_2$)$_4$	CO$_2$CH$_2$Ph	> 90	-^{c}	-^{c}	6.26
d	N(CH$_2$)$_4$	CO$_2$*t*-Bu	> 90	-^{c}	-^{c}	6.01
e	N(CH$_2$)$_4$	Ph	0	-	-	-
f	N(*i*-Bu)$_2$	CO$_2$Me	0	-	-	-

[a] Estimated chemical yields of (2*Z*)-*torquo*-**8** in percent. [b] Typical NMR chemical shifts in CDCl$_3$, exept (2*Z*)-*torquo*-**8b** in C$_6$D$_6$. [c] Signal not assigned.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (2*E*)-*torquo*-8e

W−C(2)	2.275(7)	C(2)−C(3)−C(6)	117.8(6)
C(2)−C(3)	1.378(9)	C(53)−C(54)−C(55)	120.6(8)
C(2)−O(1)	1.399(8)	C(56)−C(55)−C(54)	118.9(8)
O(1)−C(13)	1.419(8)	C(55)−C(56)−C(51)	121.5(7)
C(51)−C(56)	1.402(10)	C(2)−C(3)−C(4)	127.2(6)
C(52)−C(53)	1.395(10)	C(6)−C(3)−C(4)	114.2(6)
C(53)−C(54)	1.343(11)	N(8)−C(6)−C(3)	121.0(7)
C(54)−C(55)	1.395(11)	N(8)−C(6)−C(7)	117.3(7)
C(55)−C(56)	1.388(9)	C(3)−C(6)−C(7)	121.4(6)
C(3)−C(6)	1.472(10)	C(6)−N(8)−C(12)	125.0(6)
C(3)−C(4)	1.489(9)	C(6)−N(8)−C(9)	125.3(7)
C(6)−N(8)	1.284(8)	C(12)−N(8)−C(9)	109.6(6)
C(6)−C(7)	1.503(10)	N(8)−C(9)−C(10)	104.5(7)
N(8)−C(12)	1.484(9)	N(8)−C(12)−C(11)	103.5(6)
N(8)−C(9)	1.490(9)	C(5)−C(4)−C(3)	121.8(7)
C(11)−C(12)	1.523(9)	C(5)−C(4)−C(41)	123.4(6)
C(4)−C(5)	1.338(9)	C(3)−C(4)−C(41)	114.6(6)
C(4)−C(41)	1.502(10)	C(46)−C(41)−C(4)	118.9(6)
C(5)−C(51)	1.466(9)	C(42)−C(41)−C(4)	122.3(6)
C(51)−C(52)	1.379(9)	C(4)−C(5)−C(51)	129.5(7)
C(3)−C(2)−O(1)	106.0(6)	C(52)−C(51)−C(56)	117.2(6)
C(3)−C(2)−W	129.1(5)	C(52)−C(51)−C(5)	119.4(7)
O(1)−C(2)−W	124.8(4)	C(56)−C(51)−C(5)	123.4(6)
C(2)−O(1)−C(13)	121.5(5)	C(51)−C(52)−C(53)	121.5(8)
O(1)−C(13)−C(14)	111.0(6)	C(54)−C(53)−C(52)	120.4(8)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for (2*E*)-*torquo*-8f

W−C(2)	2.302(11)	O(1)−C(2)−C(3)	107.3(9)
C(2)−O(1)	1.382(12)	O(1)−C(2)−W	124.2(7)
C(2)−C(3)	1.374(14)	C(3)−C(2)−W	128.0(8)
O(1)−C(17)	1.411(12)	C(2)−C(3)−C(4)	126.1(9)
C(17)−C(18)	1.52(2)	C(2)−C(3)−C(6)	116.6(9)
C(3)−C(4)	1.458(14)	C(4)−C(3)−C(6)	117.3(9)
C(3)−C(6)	1.481(14)	N(8)−C(6)−C(7)	121.2(10)
C(6)−N(8)	1.317(13)	N(8)−C(6)−C(3)	119.2(10)
C(6)−C(7)	1.47(2)	C(7)−C(6)−C(3)	119.5(9)
N(8)−C(9)	1.484(13)	C(6)−N(8)−C(9)	122.9(10)
N(8)−C(13)	1.502(14)	C(6)−N(8)−C(12)	124.0(9)
C(9)−C(10)	1.55(2)	C(9)−N(8)−C(12)	113.0(9)
C(10)−C(12)	1.50(2)	C(5)−C(4)−C(3)	121.6(11)
C(10)−C(11)	1.56(2)	C(5)−C(4)−C(41)	122.2(10)
C(13)−C(14)	1.51(2)	C(3)−C(4)−C(41)	116.2(10)
C(14)−C(15)	1.54(2)	C(46)−C(41)−C(4)	123.4(13)
C(4)−C(5)	1.347(14)	C(4)−C(5)−C(51)	128.5(11)
C(4)−C(41)	1.47(2)	O(52)−C(51)−C(5)	110.4(11)
C(5)−C(51)	1.448(14)		
C(14)−C(16)	1.53(2)		

Structural details of a (1-azoniabutadienyl)carbonylmetalate of the (*Z*) configuration were obtained from an X-ray structure analysis of compound (2*Z*)-*torquo*-**8a** (Table 3). The dihedral angle W−C2−C3−C6 −38.8(8)° clearly indicates that the C=C double bond [140.2(10) pm] between C2 and C3 adopts the (*Z*) configuration. Furthermore, the C2−C3−C6−N 144.4(0.7)° as well as the carbon skeleton C2−C3−C4−C5 135.2(8)° are strongly distorted, in line with the presumptive zwitterionic structure of compound (2*Z*)-*torquo*-**8a**. Furthermore, the NMR signal of the carbene carbon atom (δ 259.0) is shifted significantly upfield compared, for example, to the carbene carbon atom of (CO)$_5$W=*C*(OEt)-CH=C[N(COPh)Ph]Ph (δ 304.2),[13] while the signal *C*=N$^+$ (δ 175.0) is shifted downfield compared to the corresponding carbon atom of the (enamino)carbene complex (CO)$_5$W=C(OEt)CH=*C*[N(COPh)Ph]Ph (δ 142.0), for which a captodative interaction is not expected due to strong distortion of the enamine unit. The pattern of bond distances of the W,C,C,C,N backbone of compound (2*Z*)-*torquo*-**8a** is similar to that of (2*E*)-*torquo*-**8e** (Table 1). Small deviations in the carbon chemical shifts of W−C2 and C=N may be attributed to a γ effect.[11]

Mechanistic Considerations

A reaction path leading to compounds (2*E*)-*torquo*-**8** is outlined in Scheme 5. It is assumed that the reaction is initiated by [2 + 2] addition of the C=C(N) bond of the tertiary enamine **7** to the C≡C bond of the 1-alkynylcarbene complex **1a** to give a cyclobutene derivative **C**, in which the (*E*) configuration of the enamine is retained, provided a concerted mechanism is effective. (1-Azoniabutadienyl)carbonylmetalates (2*E*,4*E*)- as well as (2*E*,4*Z*)-*torquo*-**8** are expected to be generated from compounds **C** by conrotatory ring opening of the cyclobutene ring (paths a and b). On the basis of the steric considerations it is expected that the 1-metalla-1,3-diene unit in compounds **C** would adopt preferentially a *s-cis* conformation, from which subsequently the stereoisomers (2*E*)-*torquo*-**8** but no stereoisomers (2*Z*)-*torquo*-**8** (Scheme 4) are obtained.

It should be noted that "cross-conjugated" metallatrienes **8** could be described as fully conjugated polyene compounds, from which a fascinating number of stable diastereoisomers can be derived through rotation of the bonds indicated by a−e. The rotation barrier energies of these bonds are influenced by steric as well as electronic factors.

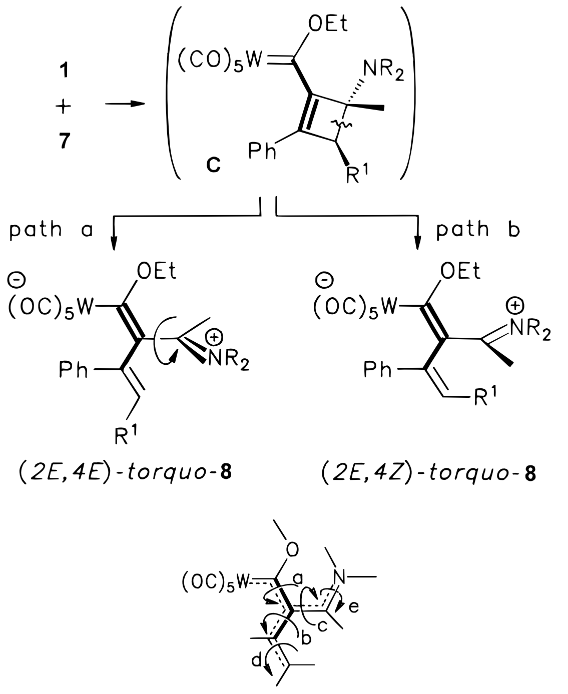
Experimental Section

All operations were performed under an atmosphere of dry argon. Solvents were dried prior to use. Melting points are

Table 4. Selected Bond Lengths (Å) and Angles (deg) for (2*Z*)-*torquo*-8a

W−C(2)	2.301(7)	O(1)−C(2)−C(3)	107.5(6)
C(2)−O(1)	1.348(8)	O(1)−C(2)−W	123.4(5)
C(2)−C(3)	1.402(10)	C(3)−C(2)−W	126.8(5)
C(3)−C(6)	1.435(9)	C(2)−C(3)−C(6)	121.5(6)
C(3)−C(4)	1.480(10)	C(2)−C(3)−C(4)	119.1(6)
C(6)−N(1)	1.309(10)	C(6)−C(3)−C(4)	119.2(6)
C(6)−C(7)	1.518(10)	N(1)−C(6)−C(3)	123.2(6)
C(12)−C(13)	1.501(11)	N(1)−C(6)−C(7)	115.8(6)
O(1)−C(12)	1.429(9)	C(3)−C(6)−C(7)	120.9(6)
N(1)−C(11)	1.480(10)	C(6)−N(1)−C(11)	126.0(6)
N(1)−C(8)	1.490(9)	C(6)−N(1)−C(8)	124.4(6)
C(11)−C(10)	1.508(11)	C(11)−N(1)−C(8)	109.6(6)
C(10)−C(9)	1.513(14)	C(11)−C(10)−C(9)	102.6(8)
C(9)−C(8)	1.503(13)	C(8)−C(9)−C(10)	103.6(7)
C(4)−C(5)	1.344(11)	N(1)−C(8)−C(9)	104.2(7)
C(4)−C(41)	1.521(9)	C(5)−C(4)−C(3)	127.7(6)
C(5)−C(51)	1.462(10)	C(5)−C(4)−C(41)	114.2(6)
C(51)−O(51)	1.218(9)	C(3)−C(4)−C(41)	118.0(6)
C(51)−O(52)	1.340(9)	C(4)−C(5)−C(51)	129.0(7)
O(52)−C(53)	1.426(11)	O(51)−C(51)−O(52)	122.5(7)
		O(51)−C(51)−C(5)	128.3(7)
		O(52)−C(51)−C(5)	109.2(6)
		C(51)−O(52)−C(53)	115.6(7)
		C(2)−O(1)−C(12)	125.6(6)
		O(1)−C(12)−C(13)	106.8(6)
		N(1)−C(11)−C(10)	102.3(7)

Scheme 5. Generation of Compounds (2*E*)-*torquo*-8 from a Cyclobutene Precursor



not corrected. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were obtainend with Bruker ARX 300, Bruker AM 360, und Varian U 600 spectrometers. (Multipilicities were determined by DEPT. Chemical shifts refer to $\delta_{TMS} = 0.00$ ppm.) Other analyses: IR Digilab FTS 45; MS Finnigan MAT 312; elemental analysis; Perkin-Elmer 240 elemental analyzer; TLC, Merck DC-Alufolien Kieselgel 60 F$_{254}$. R_f values refer to TLC tests. Column chromatographic purification was achieved with Merck Kieselgel 100.

Pentacarbonyl[4-carbomethoxy-1-ethoxy-3-phenyl-2-(1-pyrrolidiniumethyl)buta-1,3-dien-1-yl]tungstate [(2*E*)-*torquo*-8a and (2*Z*)-*torquo*-8a]. To 3-pyrrolidinobut-2-enoic acid methyl ester (269 mg, 1.00 mmol) in a 20-mL centrifuge tube is added pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) in 15 mL of pentane with vigorous stirring. The light-yellow precipitate consisting of complex (2*E*)-*torquo*-**8a** [625 mg, 96%, $R_f = 0.1$ in pentane/diethyl ether (1:1), yellow microcrystalline powder, mp 99 °C, dec] is collected after the initially brown color of supernatant has changed to almost colorless (ca. 1 h at 20 °C), washed with pentane (3 × 3 mL), and dried in vacuo. NMR data were collected from a CDCl$_3$ solution prepared at −30 °C and measured immediately at 25 °C. Complete isomerization of compound (2*E*)-*torquo*-**8a** to (2*Z*)-*torquo*-**8a** [$R_f = 0.3$ in pentane/diethyl ether (1:1)] is achieved within 6−8 h at 20 °C.

(2*E*)-*torquo*-8a. ^{1}H NMR (CDCl$_3$): δ 7.25 (5 H, s, Ph), 5.84 (1 H, s, 5-H), 4.11 (2 H, q, OCH$_2$), 3.65 (4 H, m broad, 2 NCH$_2$), 3.56 (3 H, s, OCH$_3$), 2.39 (3 H, s, N=CCH$_3$), 2.00 (4 H, m, 2 NCH$_2$C*H*$_2$), 1.09 (3 H, t, OCH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 245.0 (W=C), 203.0 and 200.0 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 181.0 (C$_q$, C=N$^+$), 167.0 (C$_q$, *C*OOCH$_3$), 154.6 (C$_q$, C4), 139.4 (C$_q$, C3), 135.5 (C$_q$, *i*-C Ph), 128−127 (5 CH, Ph), 118.9 (CH, C5), 72.9 (OCH$_2$), 53.7 (NCH$_2$), 50.7 (OCH$_3$), 27.8 (N=C*C*H$_3$), 24.6 (NCH$_2$*C*H$_2$), 15.1 (OCH$_2$*C*H$_3$). IR (diffuse reflection, cm^{-1}): 2048.4, 1951.6, and 1897.2 [ν(C≡O)], 1708.4 [ν(C=O)].

(2*Z*)-*torquo*-8a. ^{1}H NMR (CDCl$_3$): δ 7.60 (2 H, "d", *o*-H Ph), 7.32 (3 H, m, *m*- and *p*-H Ph), 6.20 (1 H, s broad, 5-H), 4.11 (3 H, q broad, OCH$_2$), 3.62 (4 H, m broad, 2 NCH$_2$), 3.62 (3 H, s broad, OCH$_3$), 2.44 (3 H, s, N=CCH$_3$), 2.02 (4 H, m broad, 2 NC*H*$_2$CH$_2$), 1.10 (3 H, t broad, OCH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 259.0 (W=C, broad), 203.7 and 200.4 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 175.0 (C$_q$, broad, C=N), 166.8 (C$_q$, *C*OOCH$_3$), 156.2 (C$_q$, C4), 143.1 (C$_q$, C3), (C$_q$, *i*-C Ph), 128−127 (5 CH, Ph), 116.9 (CH, C5), 72.7 (OCH$_2$), 50.8 (OCH$_3$), 44.1 (NCH$_2$, broad), 25.4 (N*C*H$_2$CH$_2$), 25.3 (N=C*C*H$_3$), 15.5 (OCH$_2$-CH$_3$). IR (diffuse reflection, cm^{-1}): 2052.2, 1961.1, and 1899.7 [ν(C≡O)], 1712.7 [ν(C=O)]. MS (70 eV), *m*/*e* (%): 651 (1.5) [M$^+$], 511 (6) [M$^+$ − 5CO], 270 (100). Anal. Calcd for $C_{25}H_{25}NO_8W$ (651.3): C, 46.10; H, 3.87; N, 2.15. Found: C, 46.02; H, 3.97; N, 2.36.

X-ray crystal structure analysis of (2*Z*)-*torquo*-8a: formula $C_{25}H_{25}NO_8W$, $M = 651.31$, 1.50 × 0.20 × 0.15 mm, $a = 17.244(1)$ Å, $b = 6.858(1)$ Å, $c = 22.030(2)$ Å, $\beta = 102.30(1)°$, $V = 2545.5(5)$ Å^3, $\rho_{calc} = 1.700$ g cm^{-3}, $\mu = 45.86$ cm^{-1}, empirical absorption correction via ϕ scan data ($0.922 \le C \le 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 293$ K, ω scans, 5321 reflections collected ($\pm h, +k, -l$), [(sin θ)/λ] = 0.62 Å^{-1}, 5175 independent and 4341 observed reflections [$I \ge 2\sigma(I)$], 319 refined parameters, $R = 0.048$, $wR^2 = 0.129$, max. residual electron density 3.37 (−2.74) e Å^{-3} close to W, hydrogens calculated and refined as riding atoms (remark: cutting of the big crystals led to broad ω scans). All data sets were collected on a Enraf-Nonius CAD4-diffractometer: data reduction, MolEN; structure solution, SHELXS-86; structure refinement, SHELXL-93; graphics, DIAMOND.

Pentacarbonyl[4-carbethoxy-1-ethoxy-3-phenyl-2-(1-pyrrolidiniumethyl)buta-1,3-dien-1-yl]tungstate [(2*E*)-*torquo*-8b and (2*Z*)-*torquo*-8b]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 3-pyrrolidinobut-2-enoic acid ethyl ester (183 mg, 1.00 mmol) are reacted as described above to give yellow (2*E*)-*torquo*-**8b** [631 mg, 95%, $R_f = 0.1$ in pentane/diethyl ether (1:1)]. (2*E*)-*torquo*-**8b** in CDCl$_3$ affords (2*Z*)-*torquo*-**8b** within 8 h at 20 °C in essential quantitative yield [yellow crystals, $R_f = 0.3$ in pentane/diethyl ether (1:1)].

(2*E*)-*torquo*-8b. ^{1}H NMR (CDCl$_3$): δ 7.24 (5 H, s, Ph), 5.84 (1 H, s, 5-H), 4.13 (2 H, q, COOCH$_2$), 4.08 (2 H, q, 2-OCH$_2$), 3.60 (4 H, m, 2 NCH$_2$), 2.39 (3 H, s, N=CCH$_3$), 2.01 (4 H, m, 2 NCH$_2$C*H*$_2$), 1.17 (3 H, t, COOCH$_2$C*H*$_3$), 1.08 (3 H, t, OCH$_2$C*H*$_3$). ^{13}C NMR (C$_6$D$_6$): δ 243 (W=C), 203.6 and 201.6 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 181.2 (C$_q$, C=N$^+$), 166.6 (C$_q$, COOEt), 154.1 (C$_q$, C4), 140.7 (C$_q$, C3), 136.1 (C$_q$, *i*-C Ph), 128−127 (5 CH, Ph), 121.0 (CH, C5), 73.3 (OCH$_2$), 60.0 (COO*C*H$_2$), 53.8 (2 NCH$_2$), 27.8 (N=C*C*H$_3$), 24.6 (2 NCH$_2$*C*H$_2$), 15.6 (2-OCH$_2$CH$_3$), 14.3 (COOCH$_2$*C*H$_3$). IR (diffuse reflection, cm^{-1}): 2050.2, 1956.1, and 1900.1 [ν(C≡O)], 1709.8 [ν(C=O)].

(2*Z*)-*torquo*-8b. ^{1}H NMR (CDCl$_3$): δ 7.58 (2 H, "d", *o*-H Ph), 7.35 (3 H, m, *m*- and *p*-H Ph), 6.19 (1 H, s, 5-H), 4.10 (4 H, m, COOCH$_2$ and 2-OCH$_2$), 3.64 (4 H, m broad, 2 NCH$_2$), 2.45 (3 H, s, $\mathrm{N{=}CCH_3}$), 2.02 (4 H, m broad, 2 $\mathrm{NCH_2C}H_2$), 1.26 (3 H, t, $\mathrm{COOCH_2C}H_3$), 1.05 (3 H, t, $\mathrm{OCH_2C}H_3$). IR (diffuse reflection, cm^{-1}): 2052.4, 1958.1, and 1913.6 [ν(C≡O)], 1706.9 [ν(C=O)]. MS (70 eV), *m/e* (%): 637 (8) [M$^+$ − CO], 524 (8) [M$^+$ − 5CO], 341 (30) [ligand$^+$], 268 (100). Anal. Calcd for $\mathrm{C_{26}H_{27}NO_8W}$ (665.4): C, 46.09; H, 4.09; N, 2.11. Found: C, 45.94; H, 3.79; N, 2.47.

Pentacarbonyl[4-carbobenzoxy-1-ethoxy-3-phenyl-2-(1-pyrrolidiniumethyl)buta-1,3-dien-1-yl]tungstate [(2*E*)-*torquo*-8c and (2*Z*)-*torquo*-8c]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 3-pyrrolidinobut-2-enoic acid benzyl ester (246 mg, 1.00 mmol) is reacted as described above to give yellow (2*E*)-*torquo*-**8c** [677 mg, 93%, R_f = 0.1 in pentane/diethyl ether 1:1, mp 91 °C dec]. (2*E*)-*torquo*-**8c** in $\mathrm{CDCl_3}$ affords (2*Z*)-*torquo*-**8c** within 8 h at 20 °C in essentially quantitative yield [yellow crystals, R_f = 0.3 in pentane/diethyl ether (1:1)].

(2*E*)-*torquo*-8c. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.05 (10 H, m, 4-$\mathrm{C_6H_5}$ and $\mathrm{OCH_2C_6}H_5$), 5.84 (1 H, s, 5-H), 5.03 (2 H, s broad, $\mathrm{O}CH_2$-Ph), 4.16 (2 H, q, 2-$\mathrm{OCH_2}$), 2.75 (4 H, m broad, 2 $\mathrm{NCH_2}$), 1.83 (3 H, s, $\mathrm{N{=}CCH_3}$), 1.28 (4 H, m broad, 2 $\mathrm{NCH_2C}H_2$), 0.94 (3 H, t, $\mathrm{OCH_2CH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 242.9 (W=C), 202.9 and 200.1 [1:4, *trans*- and *cis*-CO, $\mathrm{W(CO)_5}$], 181.1 ($\mathrm{C_q}$, $\mathrm{C{=}N^+}$), 166.1 ($\mathrm{C_q}$, *C*OOEt), 154.9 ($\mathrm{C_q}$, C4), 139.3 ($\mathrm{C_q}$, C3), 135.9 and 135.3 (each $\mathrm{C_q}$, 2 *i*-C Ph), 129−127 (10 CH, 2 Ph), 119.5 (CH, C5), 72.6 (2−$\mathrm{OCH_2}$), 65.3 ($\mathrm{O}CH_2$Ph), 53.5 (2 $\mathrm{NCH_2}$), 27.4 ($\mathrm{N{=}C}CH_3$), 24.4 (2 $\mathrm{NCH_2C}H_2$), 15.1 ($\mathrm{OCH_2C}H_3$). IR (diffuse reflection, cm^{-1}): 2050.9, 1956.6, and 1897.9 [ν(C≡O)], 1712.5 [ν(C=O)].

(2*Z*)-*torquo*-8c. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.64 and 7.39 (2 H each, "d" each, *o*-H, $\mathrm{C_6H_5}$ and $\mathrm{CH_2C_6}H_5$), 7.10 (6 H, m, *m*-and *p*-H 4-$\mathrm{C_6H_5}$ and $\mathrm{CH_2C_6}H_5$), 6.26 (1 H, s broad, 5-H), 4.92 (2 H, s broad, $\mathrm{O}CH_2$Ph), 4.14 (2 H, q broad, 2-$\mathrm{OCH_2}$), 3.00−4.00 (4 H, m broad, 2 $\mathrm{NCH_2}$), 2.01 (3 H, s broad, $\mathrm{N{=}CCH_3}$), 1.28 (4 H, m broad, $\mathrm{NCH_2C}H_2$), 0.98 (3 H, t broad, $\mathrm{OCH_2CH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ (W=C) 203.6 and 201.2 [*trans*- and *cis*-CO, $\mathrm{W(CO)_5}$], ($\mathrm{C_q}$, C=N), 166.0 ($\mathrm{C_q}$, *C*$\mathrm{OOCH_2Ph}$), 156.9 ($\mathrm{C_q}$, C4), 143.2 ($\mathrm{C_q}$, C3) 137.2 ($\mathrm{C_q}$, *i*-C $\mathrm{CH_2C_6H_5}$), ($\mathrm{C_q}$, *i*-C Ph), 129−127 (10 CH, 4-$\mathrm{C_6H_5}$ and $\mathrm{CH_2}C_6\mathrm{H_5}$), 117.0 (CH, C5), 73.9 (2-$\mathrm{OCH_2}$), 65.8 ($\mathrm{OCH_2Ph}$), 51.8 (2 $\mathrm{NCH_2}$), 25.4 ($\mathrm{N{=}C}CH_3$), 25.2 (2 $\mathrm{NCH_2C}H_2$), 15.4 ($\mathrm{OCH_2CH_3}$). IR (diffuse reflection cm^{-1}): 2051.5, 1958.1, and 1905.3 [ν(C≡O)], 1708.7 [ν(C=O)]. MS (70 eV), *m/e* (%): 404 (30) [ligand$^+$], 268 (95), 79 (100). Anal. Calcd for $\mathrm{C_{31}H_{29}NO_8W}$ (727.4): C, 51.19; H, 4.02; N, 1.93. Found: C, 51.11; H, 4.16; N, 2.41.

Pentacarbonyl[4-carbo-*tert*-butoxy-1-ethoxy-3-phenyl-2-(1-pyrrolidiniumethyl)buta-1,3-dien-1-yl]tungstate [(2*E*)-*torquo*-8d and (2*Z*)-*torquo*-8d]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 3-pyrrolidinobut-2-enoic acid *tert*-butyl ester (211 mg, 1.00 mmol) is reacted as described above to give yellow (2*E*)-*torquo*-**8d** [644 mg, 93%, R_f = 0.1 in pentane/diethyl ether (1:1), mp 100 °C dec]. (2*E*)-*torquo*-**8d** in $\mathrm{CDCl_3}$ affords (2*Z*)-*torquo*-**8d** within 8 h at 20 °C in essential quantitative yield [yellow crystals, R_f = 0.3 in pentane/diethyl ether (1:1)].

(2*E*)-*torquo*-8d. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.24 (5 H, s broad, Ph), 5.88 (1 H, s, 5-H), 4.16 (2 H, d, $\mathrm{OCH_2}$), 3.53 (4 H, m, 2 $\mathrm{NCH_2}$), 2.19 (3 H, s, $\mathrm{N{=}CCH_3}$), 2.89 (4 H, m, 2 $\mathrm{NCH_2CH_2}$), 1.22 [9 H, s, $\mathrm{C(CH_3)_3}$], 1.12 (3 H, t, $\mathrm{OCH_2CH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 242.9 (W=C), 203.6 and 200.5 [1:4, *trans*- and *cis*-CO, $\mathrm{W(CO)_5}$], 181.1 ($\mathrm{C_q}$, $\mathrm{C{=}N^+}$), 166.4 ($\mathrm{C_q}$, *C*OO-*t*-Bu), 152.8 ($\mathrm{C_q}$, C4), 140.3 ($\mathrm{C_q}$, C3), 135.8 ($\mathrm{C_q}$, *i*-C Ph); 129.4, 128.1 and 126.7 (CH each, Ph), 123.8 (CH, C5), 80.6 (*C*$\mathrm{Me_3}$), 72.9 ($\mathrm{OCH_2}$), 53.9 (2 $\mathrm{NCH_2}$), 28.2 [$\mathrm{C(}CH_3\mathrm{)_3}$] 27.7 ($\mathrm{N{=}C}CH_3$), 25.3 (2 $\mathrm{NCH_2C}H_2$), 15.7 ($\mathrm{OCH_2CH_3}$). IR (diffuse reflection, cm^{-1}): 2051.0, 1958.6, and 1899.6 [ν(C≡O)], 1705.1 [ν(C=O)].

(2*Z*)-*torquo*-8d. ^{1}H NMR ($\mathrm{CDCl_3}$, 360 MHz): δ 7.54 (2 H, "d", *o*-H Ph), 7.32 (3 H, m, *m*- and *p*-H Ph), 6.01 (1 H, s broad, 5-H), 4.06 (3 H, q broad, $\mathrm{OCH_2}$), 3.62 (4 H, m broad, 2 $\mathrm{NCH_2}$), 2.46 (3 H, s, $\mathrm{N{=}CCH_3}$), 2.02 (4 H, m broad, 2 $\mathrm{NCH_2C}H_2$), 1.42 [9 H, s, $\mathrm{C(CH_3)_3}$], 0.98 (3 H, t broad, $\mathrm{OCH_2CH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ (W=C), 203.4 and 200.2 [1:4, *trans*- and *cis*-CO, $\mathrm{W(CO)_5}$], ($\mathrm{C_q}$, C=N), 165.5 ($\mathrm{C_q}$, COO-*t*-Bu), 156.2 ($\mathrm{C_q}$, C4), 143.3 ($\mathrm{C_q}$, C3), ($\mathrm{C_q}$, *i*-C Ph), 128−127 (5 CH, $\mathrm{C_6H_5}$), (CH, C5), 79.5 (*C*$\mathrm{Me_3}$), 73.7 ($\mathrm{OCH_2}$), ($\mathrm{NCH_2}$), ($\mathrm{NCH_2C}H_2$), 28.2 [$\mathrm{C(}CH_3\mathrm{)_3}$], 25.3 ($\mathrm{N{=}C}CH_3$), 15.1 ($\mathrm{OCH_2C}H_3$). IR (diffuse reflection, cm^{-1}): 2052.1, 1958.1, and 1902.0 [ν(C≡O)], 1703.4 [ν(C=O)]. MS (70 eV), *m/e* (%): 693 (0.7) [M$^+$], 553 (7) [M$^+$ − 5CO], 369 (20) [ligand$^+$], 314 (100), 141 (97). Anal. Calcd for $\mathrm{C_{28}H_{31}NO_8W}$ (693.4): C, 48.50; H, 5.51; N, 2.02. Found: C, 47.71; H, 4.60; N, 2.06.

Pentacarbonyl[1-ethoxy-3,4-phenyl-2-(1-pyrrolidiniumethyl)buta-1,3-dien-1-yl]tungstate [(2*E*)-*torquo*-8e]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 3-phenyl-2-pyrrolidinopropene (187 mg, 1.00 mmol) is reacted as described above to give yellow (2*E*)-*torquo*-**8e** [660 mg, 81%, mp 104 °C dec, R_f = 0.1 in pentane/diethyl ether (1:1)]. ^{1}H NMR ($\mathrm{CDCl_3}$, 360 MHz): δ 7.46 and 7.40 (2 H each, "d", *o*-H Ph), 7.32 (6 H, m, *m*- and *p*-H, 2 Ph), 7.04 (1 H, s, 5-H), 4.45 (2 H, q, $\mathrm{OCH_2}$), 3.78 (4 H, m, 2 $\mathrm{NCH_2}$), 2.40 (3 H, s, $\mathrm{N{=}CCH_3}$), 2.12 (4 H, m, 2 $\mathrm{NCH_2C}H_2$), 1.48 (3 H, t, $\mathrm{OCH_2C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 237.8 (W=C), 204.1 and 201.1 [1:4, *trans*- and *cis*-CO, $\mathrm{W(CO)_5}$], 181.1 ($\mathrm{C_q}$, $\mathrm{C{=}N^+}$), 141.0 and 140.9 (each $\mathrm{C_q}$, C4 and C3), 137.9 and 137.4 ($\mathrm{C_q}$ each, 2 *i*-C Ph), 134.7 (CH, C5), 130−126 (10 CH, 2 Ph), 72.6 ($\mathrm{OCH_2}$), 53.9 (2 $\mathrm{NCH_2}$), 27.3 (2 $\mathrm{NCH_2C}H_2$), 25.2 ($\mathrm{N{=}CCH_3}$), 16.1 ($\mathrm{OCH_2CH_3}$). IR (diffuse reflection, cm^{-1}): 2048.2, 1952.0, and 1895.4 [ν(C≡O)]; 1592.7, 1444.2, and 1305.7 [ν(C=C)]. MS (70 eV), *m/e* (%): 669 (1.8) [M$^+$], 529 (8) [M$^+$ − 5CO], 345 (18) [ligand$^+$], 316 (100). Anal. Calcd for $\mathrm{C_{29}H_{27}NO_6W}$ (669.4): C, 52.04; H, 4.07; N, 2.09. Found: C, 51.52; H, 4.07; N, 2.19.

X-ray crystal structure analysis of (2*E*)-*torquo*-8e: formula $\mathrm{C_{29}H_{27}NO_6W}$, M = 669.37, 0.30 × 0.25 × 0.20 mm, a = 9.124(1) Å, b = 18.027(2) Å, c = 16.946(2) Å, β = 98.46(1)°, V = 2756.9(5) Å^3, ρ_{calc} = 1.613 g cm^{-3}, μ = 42.32 cm^{-1}, empirical absorption correction via ϕ scan data (0.858 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223 K, ω scans, 5777 reflections collected ($\pm h,-k,+l$), [(sin θ)/λ] = 0.62 Å^{-1}, 5589 independent and 3051 observed reflections [$I \geq 2\sigma(I)$], 336 refined parameters, R = 0.042, wR^2 = 0.079, max. residual electron density 0.84 (−1.05) e Å^{-3}, hydrogens calculated and refined as riding atoms. All data sets were collected on a Enraf-Nonius CAD4-diffractometer: data reduction, MolEN; structure solution, SHELXS-86; structure refinement, SHELXL-93; graphics, DIAMOND.

Pentacarbonyl[4-carbomethoxy-1-ethoxy-3-phenyl-2-[1-(diisobutyl)azoniaethyl]buta-1,3-dien-1-yl]tungstate [(2*E*)-*torquo*-8f]. Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 3-(diisobutylamino)but-2-enoic acid methyl ester (187 mg, 1.00 mmol) is reacted as described above to give yellow (2*E*)-*torquo*-**8f** [660 mg, 81%, mp 104 °C, R_f = 0.1 in pentane/diethyl ether (1:1)]. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.40−7.25 (5 H, m, Ph), 6.29 (1 H, s, 5-H), 4.41 (2 H, m broad, $\mathrm{OCH_2}$), 3.58 (3 H, s, $\mathrm{OCH_3}$), 3.25 (4 H, m broad, 2$\mathrm{NCH_2}$), 2.39 (3 H, s, $\mathrm{N{=}CCH_3}$), 1.65 (2 H, m broad, $\mathrm{NCH_2C}H_2$), 1.29 (3 H, t, $\mathrm{OCH_2CH_3}$), 0.68 [6 H, m broad, $\mathrm{NCH_2CH(}CH_3\mathrm{)_2}$]. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 244.0 (W=C), 202.8 and 200.2 [1:4, *trans*- and *cis*-CO, $\mathrm{W(CO)_5}$], 187.0 ($\mathrm{C_q}$, $\mathrm{C{=}N^+}$), 166.8 ($\mathrm{C_q}$, *C*OOMe), 155.2 ($\mathrm{C_q}$, C4), 138.8 ($\mathrm{C_q}$, C3), 135.4 ($\mathrm{C_q}$, *i*-C Ph), 129.7, 129.2, and 127.9 (CH each, Ph), 120.9 (CH, C5), 73.2 ($\mathrm{OCH_2}$), 62,1 (2 $\mathrm{NCH_2}$), 51.0 ($\mathrm{OCH_3}$), 28.6 ($\mathrm{N{=}C}CH_3$), 27.0 (2 $\mathrm{NCH_2C}H_2$), 20.1 [$\mathrm{NCH_2CH(}CH_3\mathrm{)_2}$], 15.4 ($\mathrm{OCH_2CH_3}$). IR (diffuse reflection cm^{-1}): 2049.4, 1955.3, and 1891.5 [ν(C≡O)], 1715.6 [ν(C=O)]. MS (70 eV), *m/e* (%): 569 (5) [M$^+$ − 5CO], 57 (100). Anal. Calcd for $\mathrm{C_{29}H_{35}NO_8W}$ (709.2): C, 49.07; H, 4.97; N, 1.97. Found: C, 49.06; H, 4.94; N, 2.20.

X-ray crystal structure analysis of (2*E*)-*torquo*-8f: formula $\mathrm{C_{29}H_{35}NO_8W \cdot 0.25CH_2Cl_2}$, M = 730.66, 0.40 × 0.30 × 0.10 mm, a = 12.374(2) Å, b = 21.716(2) Å, c = 13.986(2) Å, β = 100.19(1)°, V = 3698.9(9) Å^3, ρ_{calc} = 1.312 g cm^{-3}, μ = 31.98 cm^{-1}, empirical absorption correction via ϕ scan data (0.894 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 7835 reflections collected ($+h,+k,\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 7486 independent and 3160 observed reflections [$I \geq 2\sigma(I)$], 369 refined parameters, $R = 0.057$, $wR^2 = 0.130$, max. residual electron density 1.01 (−0.88) e Å^{-3}, hydrogens calculated and refined as riding atoms, disordered CH_2Cl_2 refined with restraints and only isotropic. All data sets were collected on a Enraf-Nonius CAD4-diffractometer; data reduction, MolEN; structure solution, SHELXS-86; structure refinement, SHELXL-93; graphics, DIAMOND.

Acknowledgment. Acknowledgement. This investigation was supported by a grant to K. R. of the Graduiertenkolleg "Hochreaktive Mehrfachbindungen" of the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of positional and displacement parameters, bond distances and angles, and hydrogen coordinates for (2*Z*)-*torquo*-**8a**, (2*E*)-*torquo*-**8e**, and (2*E*)-*torquo*-**8f** (22 pages). Ordering information is given on any current masthead page.

OM9707782