$C{-}C_\alpha$ Insertion: Insertion of an Alkyne into the C–C Single Bond between the Carbene-Carbon Atom and the α-Carbon Atom of a Fischer Carbene Complex by an Unprecedented Metalla(di-π-methane) Skeletal Rearrangement **

Seda Ünaldi,[a] Rudolf Aumann,*[a] and Roland Fröhlich+[a]

Abstract: The first examples of insertion of a C≡C bond of an alkyne into a $C_{carbene}{-}C_\alpha$ single bond of a carbene complex ($C{-}C_\alpha$ insertion) are reported. (*prim*-Alkyl)carbene complexes $[(OC)_5M{=}C(OEt)CH_2R]$ (**1a–f**; M = Cr, W; R = *n*Pr, C_7H_7, Ph) undergo $C{-}C_\alpha$ insertion of electron-deficient alkynes $[PhC{\equiv}CC(XEt)NMe_2]BF_4$ (**5a**,**b**; X = O, S) to give zwitterionic carbiminium carbonylmetalates **3a–g**, which are thermally transformed into $(CO)_4M$ chelate carbene complexes **4a–g** by elimination of CO. The overall reaction is highly regio- and stereoselective. It involves an unprecedented metalla(di-π-methane) rearrangement as the key step.

Keywords: carbene ligands · chromium · insertion · rearrangement · tungsten

Introduction

The metal carbene complexes discovered by E. O. Fischer in the early 1960s and named "Fischer carbene complexes" after their discoverer have proved to be indispensable tools for organic synthesis. Especially since the discovery of the Dötz reaction, a formal cycloaddition of α,β-unsaturated carbene complexes to alkynes with concomitant insertion of carbon monoxide, the chemistry of Fischer carbene complexes has gained much interest among organic chemists.[2] A diversity of different co-cyclizations based on quite different reaction mechanisms has been established for Fischer carbene complexes to date. Those which have so far found the widest application in organic synthesis are initiated by insertion of an unsaturated substrate, such as an alkyne, an isocyanide or carbon monoxide. The insertion of an alkyne is commonly directed towards the M=C bond (M=C insertion).[3] Insertion into a $C_\alpha{-}H$ or $N_\alpha{-}H$ bond ($C_\alpha{-}H$ and $N_\alpha{-}H$ insertion, respectively) are also known, but have been less widely investigated.[4] To the best of our knowledge, insertion of alkynes into a C–C single bond between the carbene carbon atom and the α-carbon atom to which it is attached ($C{-}C_\alpha$ insertion) has not previously been described. We now report on the first examples of $C{-}C_\alpha$ insertions of alkynes into Fischer carbene complexes.[5]

Results and Discussion

N,*N*-Dimethyl(*X*-ethyl)phenylpropioamidium tetrafluoroborates **5**, generated in situ from propiolic amides **2** and triethyloxonium tetrafluoroborate, undergo smooth addition to (*prim*-alkyl)carbene complexes **1a–f** in the presence of triethylamine to give mesoionic carbiminium carbonylmetalates **3** (Scheme 1).[6] Compounds **3** are transformed into chelate complexes **4** on heating. Formation of **3** and **4** is highly regio- and stereoselective. The stereoisomers shown in Scheme 1 are obtained as the only products.[7]

The mechanism of the $C{-}C_\alpha$ insertion of an alkyne is outlined in Scheme 2. *N*,*N*-Dimethyl(*X*-ethyl)phenylpropioamidium tetrafluoroborates **5a**,**b** (X = O, S) are assumed to form 1,4-adducts **6** with the conjugate bases **1′a–f** of carbene complexes **1a–f**. The addition seems to be highly regioselective. 1,2-Adducts were not obtained with (*prim*-alkyl)carbene complexes **1a–f** (R ≠ H), but were generated with methylcarbene complexes **1g**,**h** (R = H, see Scheme 4), in line with Pearson's HSBA concept.[8] Of the four diastereomeric allenyl adducts **6** which could in principle be obtained, two, compounds **6A** and **6B**, are shown in Scheme 2. Diastereomers **6A** are expected to be generated faster than diastereomers **6B** on the basis of steric interactions. An *exo-trig* ring closure of compounds **6** is assumed to initially afford cyclobutene

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[a] Prof. Dr. R. Aumann, S. Ünaldi, Dr. R. Fröhlich+
Organisch-Chemisches Institut der Universitat Münster
Correnstrasse 40, 48149 Münster (Germany)
Fax: (+49) 251-833-6502
E-mail: aumannr@uni-muenster.de

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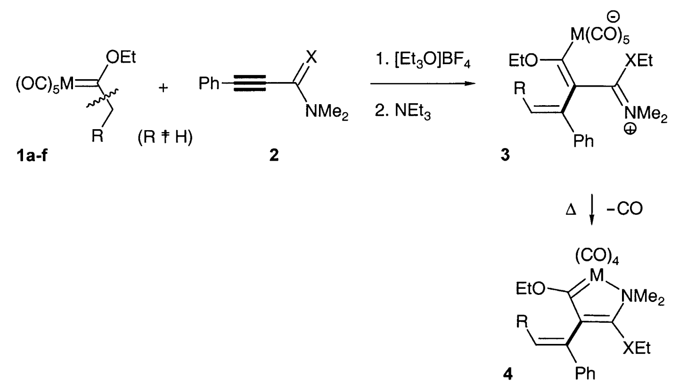
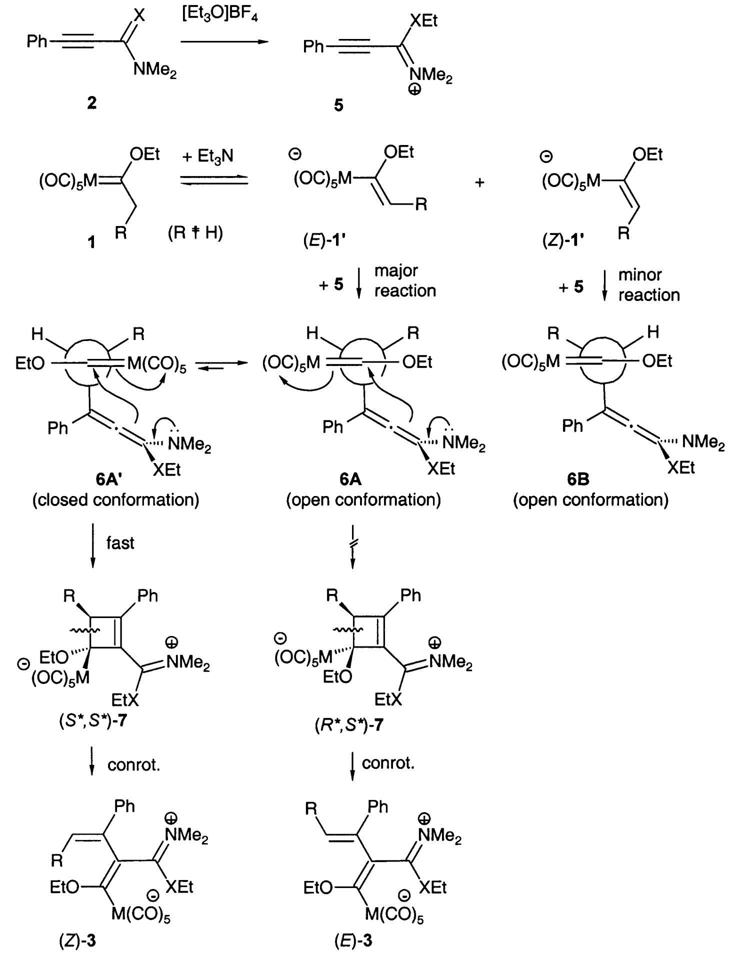


1	M	R	2	X	3,4	M	R	X	[3]%[a]	[4]%
a	W	*n*Pr	a	O	a	W	*n*Pr	O	67	48[b]
b	Cr	*n*Pr	b	S	b	Cr	*n*Pr	O	36	57[c]
c	W	C_7H_7			c	W	*n*Pr	S	60	54[b]
d	Cr	C_7H_7			d	W	C_7H_7	S	55	62[c]
e	W	Ph			e	W	C_7H_7	O	39	66[c]
f	Cr	Ph			f	W	Ph	O	66	61[c]
					g	Cr	Ph	O	40	75[c]

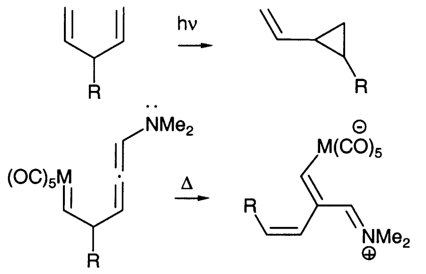
Scheme 1. $C-C_\alpha$ insertion of alkynes into (*prim*-alkyl)carbene complexes **1** gives carbiminium carbonylmetalates **3** and chelate carbene complexes **4**. [a] Chemical yields of isolated compounds **3**. [b] Chemical yields of isolated compounds **4** generated from compounds **3** at 50 °C for 6 h. [c] Chemical yields of isolated compounds **4** generated from compounds **3** at 22 °C for 24 h.



Scheme 2. Formation of carbiminium carbonylmetalates **3** by $C-C_\alpha$ insertion and skeletal rearrangement of allenyl intermediates **6**.

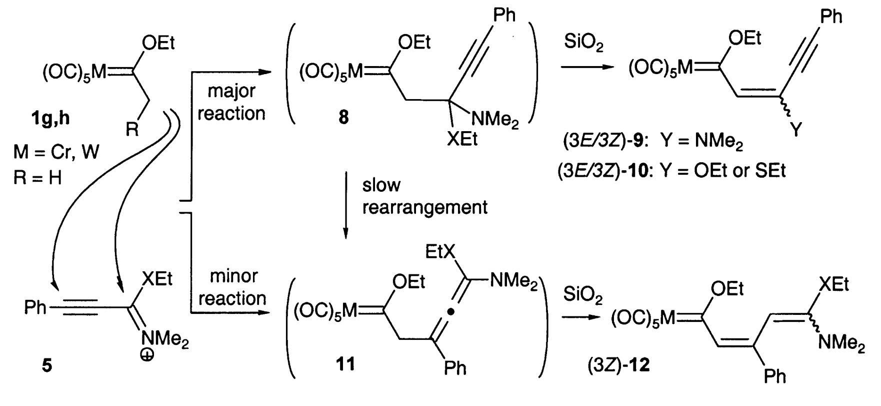
derivatives **7**, from which compounds **3** are subsequently obtained by conrotatory ring opening. The stereoselectivity of the overall reaction is remarkable: *Z* isomers of compounds **3** are formed as the only products. The high stereoselectivity of the reaction is tentatively explained on the assumption that *4-exo-trig* ring closure should be faster in "closed conformation" **6A′** than in "open conformation" **6A** because of the presumably much lower dipole moment resulting from charge separation in the transition state corresponding to the former.

Unprecedented metalla(di-π-methane) skeletal rearrangement: The key step of the $C-C_\alpha$ insertion outlined in Scheme 2 involves an unprecedented metalla(di-π-methane) skeletal rearrangement. It has been amply established that 1,4-pentadienes and related compounds in which two π systems are separated by an sp^3-carbon atom undergo a photochemically induced di-π-methane rearrangement to vinylcyclopropanes (Scheme 3, top).[9] The metalla(di-π-methane) skeletal rearrangement of 1-metalla-1,4,5-hexatrienes **6** (Scheme 3, bottom) is of a different nature: it is induced thermally and involves fission of a C–C single bond between the carbene carbon atom and its α-carbon atom. The overall reaction is highly stereoselective.



Scheme 3. Di-π-methane photo-rearrangement of 1,4-pentadienes (top) and novel thermal metalla(di-π-methane) skeletal rearrangement of 1-metalla-1,4,5-hexatrienes (bottom).

Rearrangement of 1-metalla-1,4,5-hexatrienes 11 into 1-metalla-1,3,5-hexatrienes 12: The ratio in which 1,4- and 1,2-adducts respectively of carbene complexes **1** to electron-deficient alkynes **5** are formed is expected to be strongly influenced by an α substituent R. Whilst conjugate bases of (*prim*-alkyl)carbene complexes **1a–f** ($R \neq H$) gave 1,4-addition products only (see above), conjugate bases of methylcarbene complexes **1g,h** ($R = H$) gave both 1,2- and 1,4-adducts (Scheme 4). 1,2-Adducts **8** are assumed to be generated as major products from methylcarbene complexes, but they were readily transformed into more stable conjugated 1-metalla-1,3-hexadienes **9** and **10** by elimination of $HNMe_2$ and HOEt or HSEt, respectively, on attempted isolation by chromatography. 1,4-Adducts **11** are



8-15	M	X	[9+10]%	9:10[a]	(3*E*/3*Z*)-9	(3*E*/3*Z*)-10	(3*Z*)-12	13	14	15
a	W	O	46[b]	1:5	1/0	4/1	–	–	23[b]	10[b]
b	Cr	O	60[b]	1:2	1/0	4/1	–	–	20[b]	–
c	W	S	67[b]	1:0	1/0	–	9[b]	–[b]	–	–
c	W	S	4[c]	1:0	1/0	–	44[c]	–[c]	–	–
c	W	S					–[d]	52[d]	–	–

Scheme 4. Addition of methylcarbene complexes **1g,h** (R = H) to electron-deficient alkynes **5**, and rearrangement of 1-metalla-hex-1-en-5-ynes **8** into 1-metalla-1,4,5-hexatrienes **11**. [a] Molar ratio of **9** and **10**. [b] Chemical yield of product isolated by chromatography of the reaction mixture after 1 h at 20 °C in CH_2Cl_2 (see also Scheme 5). [c] Chemical yield of product isolated by chromatography of reaction mixture after 24 h at 20 °C in CH_2Cl_2. [d] Chemical yield of **13c** isolated from the thermolysis of **12c** at 60 °C for 7 h in cyclohexane (see Scheme 5).

assumed to be derived from methylcarbene complexes **1g,h** in a minor reaction. These primary adducts were not stable under the reaction conditions and were transformed into more stable conjugated 1-metalla-1,3,5-hexatrienes **12**, presumably by base-induced migration of an α-hydrogen atom. Remember that nonconjugated 1-metalla-1,4,5-trienes **6** with $R \neq H$ did not undergo this type of isomerisation to conjugated systems (Scheme 2). The different reactivity of compounds **6** and **11** is tentatively explained by the assumption that the (secondary) α-hydrogen atom H* of an adduct **11** would be more acidic than the geminal α-hydrogen atom, since the conformation of the carbanion derived from the C–H* moiety (but not from the geminal C–H group) could be arranged for optimal π conjugation with the neighboring $M(CO)_5$ unit (Figure 1). If the atom H* is replaced by a group R, as in adduct **6**, base-induced hydrogen migration seems to be slower and therefore is outrun by a metalla(di-π-methane) rearrangement (Figure 1).

Concerning the question whether metalated cyclobutenyl derivatives **7** (Scheme 2) might be generated directly from a conjugate base **1′** and an electron-deficient alkyne **5** by [2+2] cycloaddition, it appears to us that this process should be more facile with methylcarbene complexes **1g,h** (R = H) than with (*prim*-alkyl)carbene complexes **1a–f** ($R \neq H$) for steric reasons. Furthermore, it would be difficult to explain formation of conjugated 1-metalla-1,3,5-hexatrienes **12** from [2+2] cycloadducts generated directly from methylcarbene complexes **1g,h** (Scheme 4).

Skeletal rearrangement of 1-metallahex-1-en-5-ynes 8 into 1-metalla-1,4,5-hexatrienes 11: Whilst compounds **9** and **10** are stable thermally in C_6D_6 solution at 60 °C for at least 8 h,[10] compounds **12** undergo further transformation under these conditions. Interestingly, the yield of **12** increased markedly at the cost of **9** and **10** when the reaction time was extended to 24 h (see legend to Scheme 4). Since direct transformation of compounds **9** or **10** into compounds **12** has been excluded experimentally, it is assumed that it is the precursor compound **8** which undergoes a skeletal rearrangement to the intermediate **11**. We therefore conclude that an early workup of the reaction would result in transformation of compounds **8** into compounds **9** and **10** on contact with silica gel, whilst an extension of the reaction time would lead to transformation of compounds **8** into compounds **11** and accordingly to formation of larger amounts of compounds **12**.

The thiolate **12c** (X = S) could be isolated by chromatography without major decomposition and was transformed into the cyclopentadiene **13c** by π cyclization at 60 °C for 7 h in 52 % yield.[6d, 11] The alkoxy derivatives **12a,b** (X = O), on the other hand, were quite sensitive to hydrolysis on silica gel, and afforded 1-metalla-1,3-hexadienes **14** and 1-metalla-1,4-hexadienes **15** on attempted isolation by chromatography (Scheme 5 and Scheme 4).

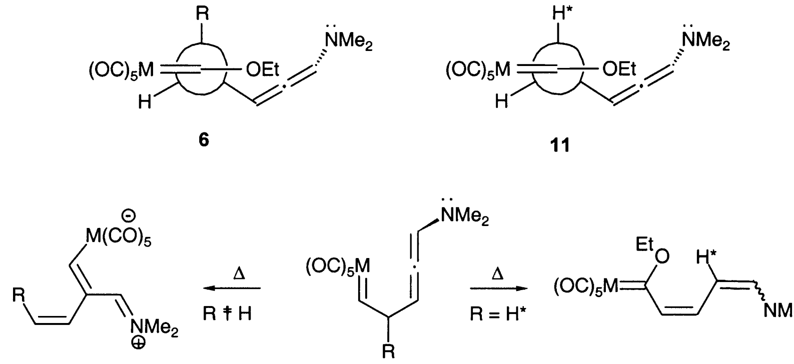
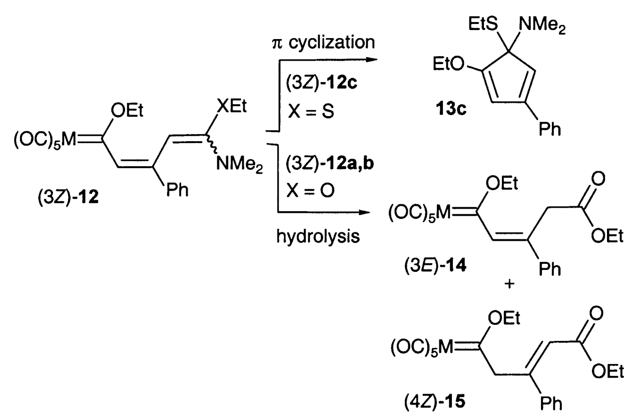


Figure 1. Newman projection of 1,4-adducts **6** and **11**, and influence of substituents R on rearrangement of 1-metalla-1,4,5-hexatrienes.

Structure elucidation: The molecular structures of the zwitterionic iminium carbonylmeta-



Scheme 5. π-Cyclization and hydrolysis of 1-metalla-1,3,5-hexatrienes **12** (M=Cr, W).

lates **3a–g** and the chelate carbene complexes **4a–g** are based on ^{1}H and ^{13}C NMR data. Compounds **3** and **4** are readily distinguished on the basis of characteristic shift differences of certain NMR signals, for example, =CH (**3a**: $\delta_H = 5.66$ ppm, $\delta_C = 132.8$ ppm; **4a**: $\delta_H = 6.18$ ppm, $\delta_C = 132.1$ ppm), (MC)OCH_2 (**3a**: $\delta_H = 4.01$ ppm, $\delta_C = 71.2$ ppm; **4a**: $\delta_H = 4.65$ ppm, $\delta_C = 78.4$ ppm), C=N$^+$Me$_2$ and C–NMe$_2$ groups, respectively (**3a**: $\delta_C = 182.3$ ppm, **4a**: $\delta_C = 176.1$ ppm). Note that the signal of the "carbene carbon atom" of the *meso*-ionic carbiminium carbonylates (e.g., **3a**: $\delta_C = 242.3$ ppm) is shifted significantly upfield compared to the (cyclic) tetracarbonyltungsten carbene complexes (e.g., **4a**: $\delta_C = 306.2$ ppm), as a consequence of different bonding modes of the MC units in these compounds.[6] A further way to easily distinguish the (CO)$_5$W compounds **3** from (CO)$_4$W compounds **4** is the pattern of the ν(C≡O) bands in the IR spectrum (e.g., **3a**: $\tilde{\nu} = 2051.7$ (30), 1959.2 (10), 1890.3 (100); **4a**: $\tilde{\nu} = 2004.5$ (60), 1877.3 (100), 1830.9 (80) cm^{-1}), which are similar to those of other zwitterionic carbiminium pentacarbonyltungstates (e.g., [(OC)$_5$WC(OEt)=C{CMe(=N$^+$Bu$_2$)Me}CPh=CH(CO$_2$Me)]$^-$: $\tilde{\nu} = 2049.4$, 1955.3, 1891.5 cm^{-1})[6f] and chelated tetracarbonyltungsten carbene complexes (e.g., $\tilde{\nu} = 2008$ (51), 1902 (100), 1853 cm^{-1} (57)), respectively.[6a] The configurational assignment of structures **3** and **4** is also based on NOE experiments (see Experimental Section). For example, irradiation of the =CH signal in compound **3a** results in a positive intensity enhancement of the signals for the *o*-Ph and CH_2CH$_2$CH$_3$ protons. An intensity enhancement of the CH_2CH$_2$CH$_3$ signal is also observed on irradiation of MC(OCH_2CH$_3$).

Charge compensation of zwitterionic carbiminium carbonylmetalates **3** is hindered by the nonplanar arrangement of the conformationally unstable ligand backbone.[6] Fast rotation of the C–[C(XEt)=N$^+$Me$_2$] single bond leads to dynamic NMR spectra. A "frozen" spectrum of compound **3a** is observed at 223 K, 600 MHz, in which the proton signals of the diastereotopic (W–C)OCH_2 group ($\delta = 3.96$, 3.93 ppm), the diastereotopic C(OCH_2)=N$^+$Me$_2$ group ($\delta = 4.65$, 4.45 ppm) and the methyl signals of the =N$^+$(CH_3)$_2$ unit ($\delta = 3.45$, 3.12 ppm) are separated. Coalescence of the C(OCH_2)=N$^+$Me$_2$ signals is observed at 273 K, which corresponds to $\Delta G^{\neq} \approx 13$ kcal mol^{-1} for the rotational barrier of the C–[C(OCH$_2$)=N$^+$Me$_2$] bond. This small rotational barrier is in line with a zwitterionic carbiminium carbonylmetallate **3a**, but inconsistent with a cross-conjugated metallatriene structure in which charge compensation has occurred. A similar $\Delta G^{\neq}$ value was obtained for the exchange of the magnetic environments of the diastereotopic methylene protons of the (WC)OCH_2 unit of compound **3a**, but a slightly higher rotational barrier of $\Delta G^{\neq} \approx 14$ kcal mol^{-1} was found for the exchange of the magnetic environments of the methyl groups in the C=N$^+$(CH_3)$_2$ unit.

The zwitterionic carbiminium carbonyltungstate **3f** and the corresponding cyclic carbene complex **4f** were also characterized by crystal structure analyses (Figures 2 and 3). The pattern of bond lengths in the ligand backbone W–C1=C2–C7 of compound **3f** (W–C1 2.310(3), C1–C2 1.401(4), C2–C7 1.494(4) Å) is characteristically different from that of

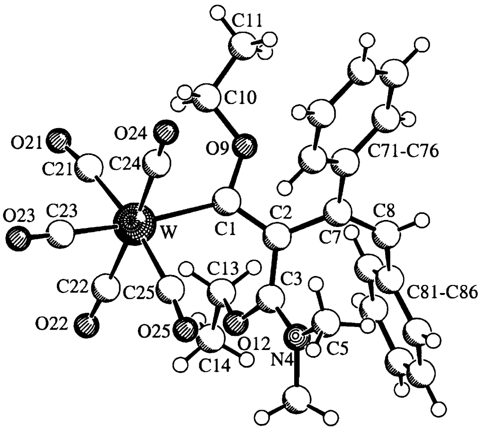


Figure 2. Molecular structure of the carbiminium carbonyltungstate **3f**. Selected bond lengths [Å] and angles [°]: W–C1 2.310(3), C1–O9 1.351(3), C1–C2 1.401(4), C2–C3 1.437(3), C2–C7 1.494(4), C3–N4 1.298(3), C3–O12 1.330(3); O9-C1-C2 107.1(2), O9-C1-W 123.9(2), C2-C1-W 126.5(2), C1-C2-C3 118.9(2), C1-C2-C7 122.8(2), C3-C2-C7 118.3(2), N4-C3-O12 111.7(2), N4-C3-C2 125.3(3), O12-C3-C2 123.0(2), C8-C7-C2 124.2(3); C1-C2-C3-N4 −135.8(3), C1-C2-C7-C8 −145.9(3).

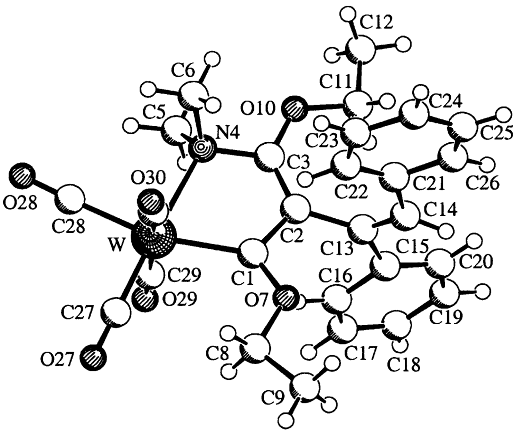


Figure 3. Molecular structure of the chelate carbene complex **4f**. Selected bond lengths [Å] and angles [°]: W–C1 2.142(4), W–N4 2.331(3), C1–O7 1.323(4), C1–C2 1.446(5), C2–C3 1.355(5), C2–C13 1.552(8), C3–O10 1.322(4), C3–N4 1.441(4), C13–C14 1.318(13); C1-W-N4 73.85(12), O7-C1-C2 108.3(3), O7-C1-W 132.6(3), C2-C1-W 119.1(3), C3-C2-C1 116.0(3), C3-C2-C13 122.9(4), C1-C2-C13 119.0(4), O10-C3-C2 131.0(3), C3-N4-W 111.2(2), C14-C13-C2 114.3(7); W-C1-C2-C3 4.8(6), C1-C2-C3-N4 2.6(7), C2-C3-N4-W −7.8(5), C15-C13-C14-C21 177.5(5).

W=C1−C2=C3 in the cyclic carbene complex **4f** (W=C1 2.142(4), C1−C2 1.446(5), C2−C3 1.355(5) Å). Most notably, the W−C distance of compound **3f** (2.310(3) Å) is significantly longer than the W=C distance of carbene complex **4f** (2.142(4) Å). A similar trend was previously established for related carbene complexes [e.g., $[(CO)_5W{=}C(OEt)CH{=}C(Ph)N{=}C(OEt)CH{=}CHMe]$, 2.215(5)][12] and zwitterionic compounds such as $[(^-OC)(OC)_4W{-}C(OEt){=}C[C({=}N^+R_2)Me]C(Ph){=}CHPh]$ (2.275(7) Å).[13] The C3−N4 distance of compound **3f** (1.298(3) Å) is significantly shorter than the corresponding C−N distance in the carbene complex **4f** (1.441(4) Å) but is similar to the $C{=}N^+$ distance of the carbiminium carbene complex $[(^-OC)(OC)_4WC{-}(OEt){=}C\{C({=}N^+R_2)Me\}C(Ph){=}CHPh]$ (1.284(8) Å}.[13] Furthermore, the C1-C2-C3-N4 unit of compound **3f** is strongly twisted by −135.8(3)°, which indicates little or no π interaction in the C2−C3 bond. A strong distortion from planarity by −145.9(3)° is also observed for the C1-C2-C7-C8 unit.

The chelate carbene complex **4f** has an essentially planar metallacyclic ring according to the torsion angles W-C1-C2-C3 (4.8(6)°), C1-C2-C3-N4 (2.6(7)°), and C2-C3-N4-W (−7.8(5)°). The exocyclic vinyl group is almost perpendicular to the neighboring ring, with an angle of 96.4° between the planes defined by W-C1-C2-C3-N4 and C15-C13-C14-C21.

Conclusion

To date it has been generally assumed that addition of an alkyne to a transition metal carbene complex would result in insertion of the C≡C bond into the M=C bond. This assumption is no longer valid, since we have demonstrated that a C≡C bond of an alkyne can also insert into a $C_{carbene}{-}C_\alpha$ single bond of a carbene complex [$(C{-}C_\alpha)$-insertion]. Addition of electron-deficient alkynes $[PhC{\equiv}CC(XEt)NMe_2]BF_4$ (**5a**,**b**; X = O, S) to (*prim*-alkyl)carbene complexes $[(OC)_5M{=}C(OEt)CH_2R]$ (**1a**–**f**; M = Cr, W; R = *n*Pr, C_7H_7, Ph) was shown to proceed by $C{-}C_\alpha$ insertion to give zwitterionic carbiminium carbonylmetalates **3** and chelate carbene complexes **4** derived therefrom. The mechanism of the $C{-}C_\alpha$ insertion was elucidated and was found to involve a metalla(di-π-methane) rearrangement as the key step. The scope of $C{-}C_\alpha$ insertion reactions is strongly influenced by the α substituent R. So far the reaction is limited to (*prim*-alkyl)carbene complexes **1a**–**f** (R ≠ H). Addition of electron-deficient alkynes **5a**,**b** to methylcarbene complexes $[(OC)_5M{=}C(OEt)CH_3]$ (**1g**,**h**; M = Cr, W), on the other hand, was shown to follow a different reaction path leading to 1-metallahexa-1,3-dien-5-ynes **9**/**10** and 1-metalla-1,3,5-hexatrienes **12**. The latter reaction seems to involve a skeletal rearrangement of 1-metallahex-1-en-5-ynes **8** into 1-metalla-1,4,5-hexatrienes **11**.

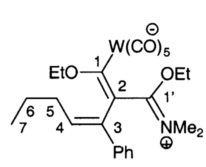
The $C{-}C_\alpha$ insertion of alkynes requires special electronic properties which are provided by Fischer carbene complexes, but not by organic compounds like esters, which are considered isolobal to Fischer carbene complexes. This reaction, which is currently under further investigation, may be applied for chain extension and possibly also for the enlargement of cyclic compounds.

Experimental Section

All operations were carried out in an atmosphere of argon. All solvents were dried and distilled prior to use. All ^1H and ^{13}C NMR spectra were routinely recorded on Bruker ARX300 and AM360 instruments. IR spectra were recorded on a Bruker Vektor 22 instrument. $^1J(H,C)$, $^2J(H,C)$, $^3J(H,C)$ decoupling and NOE experiments were performed on a Bruker AMX 400 instrument. Elemental analyses were determined on a Perkin-Elmer 240 elemental analyzer. Analytical TLC plates, Merck DC-Alufolien Kieselgel 60_{F240}, were viewed under UV light (254 nm) and stained with iodine. R_f values refer to TLC tests. Chromatographic purifications were performed on Merck Kieselgel 60. Compounds **1c**,**d**,[14] **1e**,**f**,[15] **1g**,**h**[16] and **2**[17] were prepared according to literature methods.

(1Z,3Z)-1-Ethoxy-2-[dimethyl(ethoxymethylenyl)ammonium]-3-phenyl-1,3-heptadien-1-yl-pentacarbonyltungstate (3a) and [η¹-*W*,*N*]-(4Z)-2-ethoxy-3-[dimethylamino(ethoxymethylene)]-4-phenyl-1-tetracarbonyl-tungsta-1,4-octadiene (4a): *N*,*N*-Dimethyl(*O*-ethyl)phenylpropioamidium tetrafluoroborate (**5a**), generated by reaction of *N*,*N*-dimethylpropynoic acid amide (**2a**, 85 mg, 0.50 mmol) with triethyloxonium tetrafluoroborate (95 mg, 0.50 mmol) in dry dichloromethane (3 mL) at 20 °C for 20 h, was added to a solution of pentacarbonyl(1-ethoxypentylidene)tungsten (**1a**, 218 mg, 0.50 mmol) and triethylamine (50 mg, 0.50 mmol) in dry dichloromethane (1 mL). Flash chromatography on silica gel (column 2 × 40 cm) after 1 h at 20 °C afforded a brown fraction of a 6:1 mixture (according to ^1H NMR spectrum, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2) of compound **3a** (211 mg, 67 %, yellow oil) and **4a** (31 mg, 11 %, brown oil). Compound **3a** (100 mg) in cyclohexane (3 mL) at 50 °C for 6 h under argon is partially transformed into the chelate complex **4a** (48 mg, 48 %).

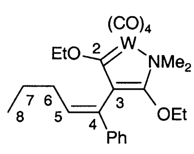
Data for 3a: ^1H NMR (300 MHz, $CDCl_3$, 30 °C, time-averaged spectrum): $\delta = 7.07-7.41$ (m, 5H; *m*-, *o*- and *p*-H Ph), 5.66 (t, $^3J = 6.6$ Hz, 1H; 4-H, NOE (+) with *o*-H Ph, $CH_2CH_2CH_3$), 4.51 (q, 2H; 1′-OCH_2, NOE (+) with *o*-H Ph), 4.01 (q, 2H; NOE (+) with $CH_2CH_2CH_3$, 1-OCH_2), 3.12 (br, 6H, $N(CH_3)_2$), 1.96 (q, 2H; 5-H_2), 1.47 (m, 2H; 6-H_2), 1.35 (t, 3H; 1′-OCH_2CH_3), 1.20 (t, 3H; 1-OCH_2CH_3), 1.10 ppm (t, 3H; 7-H_3); ^1H NMR (300 MHz, $CDCl_3$, −50 °C, "frozen" spectrum): $\delta = 7.32-7.54$ (m, 5H; *m*-, *o*- and *p*-H Ph), 5.69 (t, $^3J = 6.6$ Hz, 1H; 4-H), 4.65 and 4.45 (q, 2H; diastereotopic protons of 1′-OCH_2), 3.96 and 3.93 (q, 2H; diastereotopic protons of 1-OCH_2), 3.45 and 3.12 (s, 6H; diastereotopic CH_3 groups of $N(CH_3)_2$), 1.88 (q, 2H; 5-H_2), 1.58 (m, 2H; 6-H_2), 1.42 (t, 3H; 1′-OCH_2CH_3), 1.02 (t, 3H; 1-OCH_2CH_3), 1.11 ppm (t, 3H; 7-H_3); ^{13}C NMR ($CDCl_3$, 30 °C): δ = (C_q; C1),[18] 202.8 and 201.2 (each C_q, *trans*- and *cis*-CO of $W(CO)_5$), 182.3 (C_q; $C{=}N^+$), 143.1 (C_q; *i*-CPh), 137.2 (C_q; C3), 132.8 (CH; C4); 128.6, 128.4, 128.0, 127.9 and 127.6 (each CH; Ph), 118.1 (C_q; C2), 71.2 (1-OCH_2), 70.0 (1′-OCH_2), 40.5 (broad signal due to dynamic line broadening, $N(CH_3)_2$), 33.3 (CH_2; C5), 22.1 (CH_2; C6), 15.6 (1-OCH_2CH_3), 14.7 (1′-OCH_2CH_3), 14.0 ppm (CH_3; C7); ^{13}C NMR ($CDCl_3$, −50 °C): δ = 242.3 (C_q; C1); 203.4 and 200.4 (each C_q, *trans*- and *cis*-CO of $W(CO)_5$], 178.7 (C_q; $C{=}N^+$), 143.2 (C_q; *i*-CPh), 137.5 (C_q; C3), 132.7 (CH; C4); 129.5, 128.7, 128.2, 127.9 and 127.5 (each CH; Ph), 117.0 (C_q; C2), 71.6 (1-OCH_2), 70.4 (1′-OCH_2), 44.4 and 38.6 (diastereotopic CH_3 groups of $N(CH_3)_2$), 33.2 (CH_2; C5), 22.4 (CH_2; C6), 14.6 (CH_3; C7), 15.5 (1′-OCH_2CH_3), 15.1 ppm (1-OCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2051.7$ (30), 1959.2 (10), 1890.3 (100) ($\nu(C{\equiv}O)$), 1559.1 (10); MS (70 eV): *m*/*z* for ^{184}W (%): 639 (10) $[M]^+$, 611 (20) $[M - CO]^+$, 555 (100) $[M - 2CO]^+$, 497 (30) $[M - 5CO - 2H]^+$; elemental analysis (%) calcd for $C_{25}H_{29}O_7NW$ (639.3): C 46.90, H 4.57, N 2.19; found: C 46.03, H 4.53, N 2.37.



3a

Data for 4a: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.11-7.31$ (m, 5H; *m*-, *o*- and *p*-H Ph), 6.18 (dd, $^3J = 6.7$, 6.6 Hz, 1H; 5-H), 4.65 (q, 2H; $W{=}COCH_2$); 4.33 and 3.95 (q, 2H; diastereotopic protons of OCH_2); 3.34 and 3.33 (s, 6H; CH_3 of $N(CH_3)_2$), 1.97 (q, 2H; 6-H_2), 1.48 (m, 2H; 7-H_2), 1.33 (t, 3H; $W{=}COCH_2CH_3$), 1.18 (t, 3H; 8-H_3), 1.19 ppm (t, 3H; CH_2CH_3); ^{13}C NMR

($CDCl_3$): $\delta = 306.2$ (C_q; C2); 220.6, 215.2, 205.5 and 205.1 (each C_q, $W(CO)_4$), 176.1 (C_q; =CN), 142.3 (C_q; *i*-CPh), 137.8, (C_q; C4), 132.1 (CH; C5), 128.4, 128.0, 127.0, 126.9 and 126.6 (each CH; Ph), 123.2 (C_q; C3), 78.4 (W=COCH_2), 69.4 (OCH_2); 57.0 and 55.6 (diastereotopic CH_3 groups of $N(CH_3)_2$), 32.7 (CH_2, C6), 22.5 (CH_2; C7), 15.6 (W=$COCH_2CH_3$), 14.6 (OCH_2CH_3), 14.0 ppm (CH_3; C8); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2004.5$ (60), 1877.3 (100), 1830.9 (80) (ν(C≡O)), 1596.3 (10); MS (70 eV): *m*/*z* for ^{184}W (%): 611 (10) $[M]^+$, 555 (100) $[M-CO]^+$, 499 (30) $[M-4CO]^+$; elemental analysis (%) calcd for $C_{24}H_{29}O_6NW$ (611.1): C 47.15, H 4.78, N 2.29; found: C 47.21, H 4.75, N 2.29.



4a

(1*Z*,3*Z*)-1-Ethoxy-2-[dimethyl(ethoxymethylenyl)ammonium]-3-phenyl-1,3-heptadien-1-yl-pentacarbonylchromate (3b) and [η^1-*Cr*,*N*]-2-ethoxy-3-[dimethylamino(ethoxymethylene)]-4-phenyl-1-tetracarbonylchroma-1,4-octadiene ((4*Z*)-4b): *N*,*N*-Dimethyl(*O*-ethyl)phenylpropioamidium tetrafluoroborate (**5a**, 0.50 mmol), generated as described above, was treated with pentacarbonyl(1-ethoxypentylidene)chromium (**1b**, 153 mg, 0.50 mmol) and triethylamine (101 mg, 1.00 mmol) in dry dichloromethane (1 mL). Workup after 1 h at 20 °C by flash chromatography on silica gel (column 2 × 40 cm) with dichloromethane/*n*-pentane (1/2) afforded a brown fraction with a 1/1 mixture (NMR analysis) of **3b** (76 mg, 36%, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2, brown oil) and **4b** (75 mg, 36%, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2, red crystal from *n*-pentane, m.p. 60 °C). According to NMR analysis, 57% of **3b** (100 mg) in [D_6]benzene (1 mL) at 22 °C is converted after 24 h to the corresponding chelate complex **4b**.

Data for 3b: ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.16-7.59$ (m, 5H; Ph), 5.69 (t, $^3J = 7$ Hz, 1H; 4-H), 4.50 (q, 2H; 1′-$COCH_2$), 3.92 (q, 2H; 1-OCH_2), 3.21 (br, 6H; $N(CH_3)_2$), 1.97 (q, 2H; 5-H_2), 1.51 (m, 2H; 6-H_2), 1.32 (t, 3H; 1′-OCH_2CH_3), 1.26 (t, 3H; 1-OCH_2CH_3), 0.94 ppm (t, 3H, 7-H_3); ^{13}C NMR ($CDCl_3$): $\delta = 260.5$ (C_q; C2); 216.2 and 215.0 (C_q; *trans*- and *cis*-CO of $Cr(CO)_5$), 179.7 (C_q; C=N^+), 144.5 (C_q; *i*-CPh), 138.7 (C_q; C3), 135.1 (CH; C4); 129.8, 129.5, 128.4, 128.3 and 128.1 (each CH; Ph), 119.0 (C_q; C2), 72.7 (1-OCH_2), 70.8 (1′-OCH_2), 43.3 (br, $N(CH_3)_2$), 34.8 (CH_2; C5), 23.9 (CH_2; C6), 16.7 (1-OCH_2CH_3), 15.5 (1′-OCH_2CH_3), 15.3 ppm (CH_3; C7); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2042.7$ (20), 1948.3 (15), 1882 (100) (ν(C≡O)), 1606.3 (10); MS (70 eV): *m*/*z* for ^{52}Cr (%): 507 (2) $[M]^+$, 451 (5) $[M-2CO]^+$, 367 (100) $[M-4CO]^+$; elemental analysis (%) calcd for $C_{25}H_{29}O_7NCr$ (507.1): C 59.16, H 5.76, N 2.76; found: C 58.56, H 5.80, N 2.67.

Data for 4b: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.16-7.59$ (m, 5H; Ph), 6.18 (dd, $^3J = 7.1$, 6.9 Hz, 1H; 5-H), 4.82 (q, 2H; Cr=$COCH_2$), 4.31 and 3.90 ("m", 2H; diastereotopic protons of OCH_2), 3.01 (br s due to dynamic line broadening, 6H; $N(CH_3)_2$), 1.97 (q, 2H; 6-H_2), 1.51 (t, 2H; 7-H_2), 1.33 (t, 3H; Cr=$COCH_2CH_3$), 1.24 (t, 3H; 8-H_3), 1.10 ppm (q, 3H; OCH_2CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 329.4$ (C_q; C2); 232.2, 231.4, 221.5, 218.5 (each C_q, $Cr(CO)_4$), 177.6 (C_q; =CN), 145.1 (C_q; *i*-CPh), 141.9 (C_q; C4); 133.2 (CH; C5), 129.8, 129.5, 128.3, 127.4 and 126.8 (each CH; Ph), 124.3, (C_q; C3), 77.2 (Cr=COCH_2), 70.5 (OCH_2); 56.9 and 55.4 ($N(CH_3)_2$), 33.5 (CH_2; C6), 23.7 (CH_2; C7), 16.4 (Cr=$COCH_2CH_3$), 15.9 (OCH_2CH_3), 15.2 ppm (CH_3, C8); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2000.7$ (60), 1890.1 (80), 1881.0 (100) 1835.2 (70) (ν(C≡O)), 1607.9 (10); MS (70 eV): *m*/*z* for ^{52}Cr (%): 479 (10) $[M]^+$, 451 (5) $[M-CO]^+$, 394 (40) $[M-3CO]^+$, 367 (100) $[M-4CO]^+$; elemental analysis (%) calcd for $C_{24}H_{29}O_6NCr$ (479.1): C 60.11, H 6.10, N 2.92; found: C 60.22, H 6.07, N 2.95.

(1*Z*,3*Z*)-1-Ethoxy-2-[dimethyl(ethylsulfanyl)methylenylammonium]-3-phenyl-1,3-heptadien-1-yl-pentacarbonyltungstate (3c) and [η^1-*W*,*N*]-2-ethoxy-3-[dimethylamino(ethylsulfanyl)methylene]-4-phenyl-1-tetracarbonyltungsta-1,4-octadiene ((4*Z*)-(4c): *N*,*N*-Dimethyl(*S*-ethyl)phenylpropioamidium tetrafluoroborate (**5b**), generated by reaction of 3-phenylpropynethionic acid dimethylamide (**2b**, 95 mg, 0.50 mmol) with triethyloxonium tetrafluoroborate (95 mg, 0.50 mmol) in dry dichloromethane (3 mL) at 20 °C for 20 h, was added to a solution of pentacarbonyl(1-ethoxypentylidene)tungsten (**1a**, 218 mg, 0.50 mmol) and triethylamine (50 mg, 0.50 mmol) in dry dichloromethane (1 mL). Flash chromatography on silica gel (column 2 × 40 cm) after 1 h at 20 °C afforded a red fraction of a 6/1 mixture (according to a ^{1}H NMR spectrum, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2) of **3c** (196 mg, 60%, red oil) and **4c** (33 mg, 12%, red oil). Heating the carbiminium metallate **3c** (100 mg) at 50 °C for 6 h in cyclohexane ether under argon affords the corresponding chelate complex **4c** (52 mg, 54%, red oil).

Data for 3c: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.21-7.38$ (m, 5H; Ph), 5.85 (t, 1H, $^3J = 6.6$ Hz; 4-H), 4.32 (q, 2H; 1-OCH_2), 3.14 (s, 6H; $N(CH_3)_2$), 3.04 (q, 2H; SCH_2), 2.01 (q, 2H; 5-H_2), 1.53 (m, 2H; 6-H_2), 1.32 (t, 3H; OCH_2CH_3), 1.28 (t, 3H, SCH_2CH_3), 0.98 ppm (q, 3H; 7-H_3); ^{13}C NMR ($CDCl_3$): $\delta =$ (C_q, C1);[18] 204.0 and 200.8, (each C_q; *trans*- and *cis*-CO of $W(CO)_5$), 182.0 (C_q; C=N^+), 144.0 (C_q; *i*-CPh), 140.5 (C_q; C3), 134.3 (CH; C4); 129.1, 128.8, 127.6, and 127.3 (each CH; Ph), 126.4 (C_q; C2), 74.0 (OCH_2), 45.0 (br; $N(CH_3)_2$), 34.6 (CH_2; C5), 31.9 (SCH_2), 23.1 (CH_2; C6), 16.2 (CH_3; C7), 14.9 (OCH_2CH_3), 13.9 ppm (SCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2052.2$ (50), 1960.1 (40), 1894.4 (100) (ν(C≡O)), 1516.3 (30); MS (70 eV): *m*/*z* for ^{184}W (%): 654 (20) $[M]^+$, 626 (80) $[M-CO]^+$, 542 (90) $[M-2CO]^+$, 486 (100) $[M-5CO]^+$; elemental analysis (%) calcd for $C_{25}H_{29}O_6SNW$ (654.1): C 45.79, H 4.46, N 2.14; found: C 46.07, H 4.56, N 2.43.

Data for 4c: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.07-7.30$ (m, 5H; Ph), 6.07 (dd, 1H, $^3J = 6.6$, 6.5 Hz, 5-H; NOE (+) with *o*-H Ph, 5-H and 6-H), 4.48 (q, 2H; OCH_2), 3.0 (br, 6H; $N(CH_3)_2$), 3.17 (q, 2H; SCH_2), 1.76 (q, 2H; 6-H_2), 1.26 (m, 2H; 7-H_2), 1.41 (t, 3H; OCH_2CH_3), 0.96 (t, 3H; SCH_2CH_3), 1.01 ppm (q, 3H; 8-H_3); ^{13}C NMR ($CDCl_3$): $\delta = 295.3$ (C_q; C2); 214.2, 211.2, 205.1 and 202.8 (each C_q, $W(CO)_4$), 174.9 (C_q; =CN), 136.5 (C_q; C4), 128.7 (CH; C5); 129.1, 128.9, 128.8, 128.4, and 127.1 (each CH; Ph), 123.5 (C_q; C3), 78.1 (OCH_2), 44.1 ($N(CH_3)_2$), 33.7 (CH_2; C6), 31.2 (SCH_2), 22.6 (CH_2; C7), 15.3 (OCH_2CH_3), 15.0 (SCH_2CH_3), 14.3 ppm (CH_3; C8); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2005.1$ (60), 1878.2 (100), 1838.4 (90) (ν(C≡O)), 1544.6 (40); MS (70 eV): *m*/*z* for ^{184}W (%): 626 (80) $[M]^+$, 542 (100) $[M-3CO]^+$; elemental analysis (%) calcd for $C_{24}H_{29}O_5SNW$ (626.4): C 46.01, H 4.63, N 2.23; found: C 47.07, H 4.56, N 2.43.

(1*Z*,3*Z*)-1-Ethoxy-2-[dimethyl(ethylsulfanyl)methylenylammonium]-4-(2′,4′,6′-cycloheptatrienyl)-3-phenyl-1,3-butadien-1-yl-pentacarbonyltungstate (3d) and [η^1-*W*,*N*]-2-ethoxy-3-[dimethylamino(ethylsulfanyl)methylene]-5-(2′,4′,6′-cycloheptatrienyl)-4-phenyl-1-tetracarbonyltungsta-1,4-pentadiene ((4*Z*)-4d): *N*,*N*-Dimethyl(*S*-ethyl)phenylpropioamidium tetrafluoroborate (**5b**), generated from 3 phenylpropynethionic acid dimethylamide (**2b**, 95 mg, 0.50 mmol) and triethyloxonium tetrafluoroborate (95 mg, 0.50 mmol) in dry dichloromethane (3 mL) at 20 °C for 20 h, was added to pentacarbonyl 2-(2,4,6-cycloheptatrienyl)-1-ethoxyethylidenetungsten (**1c**, 243 mg, 0.50 mmol) and triethylamine (50 mg, 0.50 mmol) in dry dichloromethane (1 mL). Flash chromatography on silica gel (column 2 × 40 cm) after 1 h at 20 °C afforded a red fraction of a 1/2 mixture (according to a ^{1}H NMR spectrum, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2) of compound **3d** (201 mg, 55%, red oil) and **4d** (44 mg, 11%, red oil). Compound **3d** (100 mg) undergoes 62% conversion to the corresponding chelate complex **4b** (59 mg) over 22 °C at 24 h.

Data for 3d: H NMR (300 MHz, $CDCl_3$): $\delta = 7.27-7.34$ (m, 5H; Ph), 6.68 (m, 2H; 4′-H), 6.18 (m, 2H; 3′-H), 6.02 (d, $^3J = 10.5$ Hz, 1H; 4-H), 5.13 (m, 2H; 2′-H), 4.02 (q, 2H; OCH_2), 3.10 (s, 6H; $N(CH_3)_2$), 2.91 (q, 2H; SCH_2), 2.01 (m, 1H; 1′-H), 1.29 (t, 3H; OCH_2CH_3), 0.98 ppm (t, 3H; SCH_2CH_3); ^{13}C NMR ($CDCl_3$): $\delta =$ (C_q; C1);[18] 202.1, and 199.9 (each C_q; *trans*- and *cis*-CO of $W(CO)_5$), 174.1 (C_q; C=N^+), 142.9 (*i*-C; Ph), 141.1 (C_q; C3), 131.3 (CH; C-4), 130.8 (CH; C4′); 128.4, 128.1, 127.2, 126.9, 125.9, and 124.4 (each CH; Ph), 122.4 (C_q; C2), 124.2 (CH; C3′), 123.4 (CH; C2′), 72.5 (OCH_2), 44.6 (CH; C1′), 43.6 ($N(CH_3)_2$), 40.8 (SCH_2), 15.2 (OCH_2CH_3), 14.6 ppm (SCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2051.3$ (40), 1959.1 (20), 1897.3 (100), (ν(C≡O)), 1517.7 (10); MS (70 eV): *m*/*z* for ^{184}W (%): 702 $[M]^+$, 674 (50) $[M-CO]^+$, 591 (10) $[M-3CO]^+$, 534 (100) $[M-5CO]^+$; elemental analysis (%) calcd for $C_{29}H_{28}O_6SNW$ (702.1): C 49.49, H 4.16, N 1.99; found: C 50.92, H 4.09, N 2.52.

Data for 4d: H NMR (300 MHz, $CDCl_3$): $\delta = 7.27-7.34$ (m, 5H; Ph), 6.65 (m, 2H; 4′-H), 6.21 (m, 2H; 3′-H), 6.48 [dd, $^3J = 10.5$ and 10.6 Hz, 1H; 5-H, (+) NOE with *o*-H Ph, 1′-H, 2′-H, 3′-H, and 4′-H), 5.11 (m, 2H; 2′-H), 4.41 (q, 2H; $COCH_2$), 3.09 (s, 6H; $N(CH_3)_2$), 3.12 (q, 2H; SCH_2), 2.03 (m, 1H; 1′-H), 1.26 (t, 3H; OCH_2CH_3), 0.91 ppm (t, 3H; SCH_2CH_3); ^{13}C NMR

($\mathrm{CDCl_3}$): $\delta = 295.1$ ($\mathrm{C_q}$; C2); 228.9, 217,4, 213.2 and 212.1 (each $\mathrm{C_q}$; $\mathrm{W(CO)_4}$), 173.7 ($\mathrm{C_q}$;=CN), 141.1 ($\mathrm{C_q}$; C4), 128.8 (CH; C5), 130.8 (CH; C4′); 128.4, 128.1, 127.2, 126.9, 125.9 and 124.4 (each CH; Ph), 124.2 (CH; C3′), 123.4 (CH; C2′), 76.6 ($\mathrm{OCH_2}$), 44.4 (CH; C1′), 43.6 ($\mathrm{N(CH_3)_2}$), 40.3 ($\mathrm{SCH_2}$), 15.2 ($\mathrm{OCH_2\mathit{CH}_3}$), 13.0 ppm ($\mathrm{SCH_2\mathit{CH}_3}$); IR (*n*-hexane) [$\mathrm{cm^{-1}}$ (%)]: $\tilde{\nu} =$ 2005.0 (50), 1880 (100), 1840 (80) (ν(C≡O)), 1545.9 (25); MS (70 eV): *m/z* for ^{184}W (%): 674 (50) $[M]^+$, 591 (10) $[M-2\,\mathrm{CO}]^+$, 534 (100) $[M-5\,\mathrm{CO}]^+$; elemental analysis (%) calcd for $\mathrm{C_{28}H_{28}O_5SNW}$ (674.1): C 49.77, H 4.33, N, 2.07; found: C 50.51, H 3.90, N 1.97.

(1Z,3Z)-1-Ethoxy-2-[dimethyl(ethoxymethylenyl)ammonium]-4-(2′,4′,6′-cycloheptatrienyl)-3-phenyl-1,3-butadien-1-yl-pentacarbonyltungstate (3e) and [η^1-*W,N*]-2-ethoxy-3-[dimethylamino(ethoxymethylene)]-5-(2′,4′,6′-cycloheptatrienyl)-4-phenyl-1-tetracarbonyltungsta-1,4-pentadiene ((*4Z*)-4e): *N,N*-Dimethyl(*O*-ethyl)phenylpropioamidium tetrafluoroborate (**5a**, 0.50 mmol), generated as described above, was treated with pentacarbonyl-2-(2,4,6-cycloheptatrienyl)-1-ethoxyethylidenetungsten (**1c**, 243 mg, 0.50 mmol) and triethylamine (51 mg, 0.50 mmol) in dry dichloromethane (1 mL). Workup after 1 h at 20 °C by flash chromatography on silica gel (column 2 × 40 cm) with dichloromethane/*n*-pentane (1/2) afforded a 1/1 mixture of **3e** (121 mg, 39%, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2, yellow crystals from *n*-pentane at −20 °C, m.p. 70 °C) and **4e** (121 mg, 39%, brown oil). Compound **3e** (100 mg) undergoes slow conversion in [$\mathrm{D_6}$]benzene to the corresponding chelate complex **4e** (63 mg, 66%) at 22 °C over 24 h.

Data for 3e: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.28-7.32$ (m, 5H; Ph), 6.66 (m, 2H; 3′-C), 6.33 (d, $^3J = 10.5$ Hz, 1H; 4-H), 6.13 (m, 2H; 2′-H), 4.51 (br, 2H; 1′-$\mathrm{OCH_2}$), 4.21 (q, 2H; 1-$\mathrm{OCH_2}$), 3.28 (s, 6H; $\mathrm{N(CH_3)_2}$), 2.11 (m, 1H; 1′-H), 1.28 (t, 3H; 1′-$\mathrm{OCH_2\mathit{CH}_3}$), 0.98 ppm (t, 3H; $\mathrm{OCH_2\mathit{CH}_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 242.2$ ($\mathrm{C_q}$; C1); 202.3 and 200.9 (each $\mathrm{C_q}$; *trans*- and *cis*-CO of $\mathrm{W(CO)_5}$), 179.1 ($\mathrm{C_q}$; $\mathrm{C{=}N^+}$), 147.3 (CH; C-4), 143.2 ($\mathrm{C_q}$; C3), 131.7 (CH; C4′), 130.2 (CH; C3′); 128.7, 128.1, 127.3, 126.9 126.3 (each CH; Ph), 124.4 (CH; C3′), 122.3 ($\mathrm{C_q}$; C2), 72.3 (1-$\mathrm{OCH_2}$), 70.6 (1′-$\mathrm{OCH_2}$), 40.7 (CH; C1′), 41.0 ($\mathrm{N(CH_3)_2}$), 15.5 (1′-$\mathrm{OCH_2CH_3}$), 14.7 ppm (1-$\mathrm{OCH_2CH_3}$); IR (*n*-hexane) [$\mathrm{cm^{-1}}$ (%)]: $\tilde{\nu} = 2052.3$ (30), 1957.3 (15), 1898.4 (100) (ν(C≡O)), 1554.9 (10); MS (70 eV): *m/z* for ^{184}W (%): 687 (5) $[M]^+$, 659 (100) $[M-\mathrm{CO}]^+$, 603 (100) $[M-3\,\mathrm{CO}]^+$; elemental analysis (%) calcd for $\mathrm{C_{29}H_{29}O_7NW}$ (687.1): C 50.64, H 4.25, N, 2.04; found: C 50.52, H 3.99, N 1.92.

Data for 4e: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.28-7.32$ (m, 5H; Ph), 6.68 (m, 2H; 4′-C), 6.17 (m, 2H; 3′-H), 5.94 (d, $^3J = 10.5$ Hz, 1H; 4-H), 5.11 (q, 2H; $\mathrm{W{=}CO\mathit{CH}_2}$), 4.02 and 4.21 (q, 2H; diastereotopic $\mathrm{OCH_2}$), 3.10 (br, 6H; $\mathrm{N(CH_3)_2}$), 2.05 (m, 1H; 1′-H), 1.27 (t, 3H; $\mathrm{W{=}COCH_2\mathit{CH}_3}$), 0.98 ppm (t, 3H; $\mathrm{OCH_2\mathit{CH}_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 303.3$ ($\mathrm{C_q}$; C2); 220.3, 214.6, 205.3 and 204.3 (each $\mathrm{C_q}$, $\mathrm{W(CO)_4}$), 177.1 ($\mathrm{C_q}$;=CN), 146.9 ($\mathrm{C_q}$; C4), 142.8 (CH; C5), 131.0 (CH; C4′), 130.2 (CH; C3); 128.1, 128.7, 127.3, 126.7 and 124.7 (each CH; Ph), 124.0 (CH; C3′), 123.4 (CH; C2′), 78.3 ($\mathrm{W{=}CO\mathit{C}H_2}$), 72.3 ($\mathrm{OCH_2}$), 38.2 (CH; C1′), 55.1 ($\mathrm{N(CH_3)_2}$), 15.3 ($\mathrm{W{=}COCH_2\mathit{C}H_3}$), 14.7 ppm ($\mathrm{OCH_2\mathit{C}H_3}$); IR (*n*-hexane) [$\mathrm{cm^{-1}}$ (%)]: $\tilde{\nu} = 2006.4$ (560), 1908.1 (100), 1840 (5) (ν(C≡O)), 1554.9; MS (70 eV): *m/z* for ^{184}W (%): 659 $[M]^+$, 518 (100) $[M-5\,\mathrm{CO}-\mathrm{H}]^+$; elemental analysis (%) calcd for $\mathrm{C_{28}H_{29}O_6NW}$ (659.1): C 50.97, H 4.43, N 2.12; found: C 51.02, H 4.43, N 2.10.

(1Z,3Z)-1-Ethoxy-2-[dimethyl(ethoxymethylenyl)ammonium]-3,4-diphenyl-1,3-butadien-1-yl-pentacarbonyltungstate (3f) and [η^1-*W,N*]-2-ethoxy-3-[dimethylamino(ethoxymethylene)]-4,5-diphenyl-1-tetracarbonyltungsta-1,4-pentadiene ((*4Z*)-4f): *N,N*-Dimethyl(*O*-ethyl)phenylpropioamidium tetrafluoroborate (**5a**, 0.50 mmol), generated as described above, was treated with pentacarbonyl(1-ethoxy-2-phenylethylidene)tungsten (**1e**, 171 mg, 0.50 mmol) and triethylamine (51 mg, 0.50 mmol) in dry dichloromethane (1 mL). Workup after 1 h at 20 °C by flash chromatography on silica gel (column 2 × 40 cm) with dichloromethane/*n*-pentane (1/2) afforded a brown fraction with a 7/1 mixture of **3f** (127 mg, 66%, $R_f =$ 0.8 in dichloromethane/*n*-pentane 1/2, yellow crystals, m.p. 104 °C) and **4f** (64 mg, 10%, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2, brown oil). Compound **3f** (100 mg) is slowly converted to the corresponding chelate complex **4f** (57 mg) at 22 °C over 24 h.

Data for 3f: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.09-7.40$ (m, 5H; Ph), 6.58 (s, 1H; 4-H), 4.32 (q, 2H; 1′-$\mathrm{OCH_2}$), 4.01 (q, 2H; 1-$\mathrm{OCH_2}$), 2.76 (br, 6H; $\mathrm{N(CH_3)_2}$), 1.29 (t, 3H; 1′-$\mathrm{OCH_2\mathit{CH}_3}$), 0.87 ppm (t, 3H; 1-$\mathrm{OCH_2\mathit{CH}_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 250.1$ ($\mathrm{C_q}$; C1); 202.8 and 201.3 (each $\mathrm{C_q}$; *trans*- and *cis*-CO of $\mathrm{W(CO)_5}$), 178.1 ($\mathrm{C_q}$; $\mathrm{C{=}N^+}$), 144.4 (*i*-C; Ph), 139.3 ($\mathrm{C_q}$; C3), 133.3 (CH; C4); 129.9, 129.3, 129.2, 129.0, 128.6, 128.5, 128.2, 127.6, 127.4, 126.9 and 126.2 (each CH; Ph), 117.1, ($\mathrm{C_q}$; C2), 71.3 (1-$\mathrm{OCH_2}$), 70.0 (1′-$\mathrm{OCH_2}$), 41.9 (br, $\mathrm{N(CH_3)_2}$), 15.6 (1-$\mathrm{OCH_2\mathit{C}H_3}$), 14.5 ppm (1′-$\mathrm{OCH_2CH_3}$); IR (*n*-hexane) [$\mathrm{cm^{-1}}$ (%)]: $\tilde{\nu} = 2052.5$ (50), 1959.1 (25), 1897.1 (100) (ν(C≡O)), 1575.6 (15); MS (70 eV): *m/z* for ^{184}W (%): 673 (10) $[M]^+$, 645 (40) $[M-\mathrm{CO}]^+$, 589 (100) $[M-3\,\mathrm{CO}]^+$; elemental analysis (%) calcd for $\mathrm{C_{28}H_{27}O_7NW}$ (673.1): C 49.92, H 4.04, N 2.08; found: C 50.05, H 4.07, N 2.10.

X-ray crystal structure analysis of 3f: $\mathrm{C_{28}H_{27}O_7NW}$, $M_r = 673.36$, yellow crystal, 0.30 × 0.25 × 0.20 mm, $a = 9.929(1)$, $b = 11.906(1)$, $c = 12.699(1)$ Å, $\alpha = 93.89(1)$, $\beta = 111.02(1)$, $\gamma = 96.51(1)°$, $V = 1382.7(2)$ Å^3, $\rho_{\mathrm{calcd}} =$ 1.617 g cm^{-3}, $\mu = 42.22$ cm^{-1}, empirical absorption correction ($0.364 \leq T \leq 0.486$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 0.71073$ Å, $T = 293$ K, ω and φ scans, 17788 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.68$ Å^{-1}, 6884 independent ($R_{\mathrm{int}} = 0.026$) and 6127 observed reflections [$I \geq 2\sigma(I)$], 338 refined parameters, $R = 0.025$, $wR_2 = 0.052$, max./min. residual electron density 0.57/−0.86 e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.[19]

Data for 4f: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.18-7.45$ (m, 5H; Ph), 7.09 (s, 1H; 5-H), 4.58 (q, 2H; $\mathrm{W{=}CO\mathit{CH}_2}$), 4.24 and 3.97 (q, 2H; diastereotopic H of $\mathrm{OCH_2}$); 2.93 and 3.20 (s; $\mathrm{N(CH_3)_2}$), 1.21 (t, 3H; $\mathrm{W{=}CH_2\mathit{CH}_3}$), 1.08 ppm (t, 3H; $\mathrm{OCH_2\mathit{CH}_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 305.0$ ($\mathrm{C_q}$, C2); 219.3, 213.8, 203.8 and 203.7 (each $\mathrm{C_q}$; $\mathrm{W(CO)_4}$), 174.4 ($\mathrm{C_q}$; =CN), 137.6 ($\mathrm{C_q}$; C4), 133.5 (CH; C5); 129.6, 128.5, 127.9, 127.7, 127.5, 127.2, 127.0, 126.9, 126.8, 126.7 and 125.9 (each CH; Ph), 124.8 ($\mathrm{C_q}$; C3), 76.5 ($\mathrm{W{=}CO\mathit{C}H_2}$), 68.8 ($\mathrm{OCH_2}$); 55.8 and 56.4 (diastereotopic $\mathrm{CH_3}$ groups of $\mathrm{N(CH_3)_2}$), 14.3 ($\mathrm{W{=}COCH_2\mathit{C}H_3}$), 13.7 ppm ($\mathrm{OCH_2\mathit{C}H_3}$); IR (*n*-hexane) [$\mathrm{cm^{-1}}$ (%)]: $\tilde{\nu} =$ 2005.1 (50), 1890.1 (90), 1877.9 (100), 1822.2 (60) (ν(C≡O)); MS (70 eV): *m/z* for ^{184}W (%): 645 (40) $[M]^+$, 589 (100) $[M-2\,\mathrm{CO}]^+$, 533 (40) $[M-4\,\mathrm{CO}]^+$; elemental analysis (%) calcd for $\mathrm{C_{27}H_{27}O_6NW}$ (645.1): C 50.22, H 4.22, N 2.17; found: C 50.42, H 4.21, N 2.26.

X-ray crystal structure analysis of compound 4f: formula $\mathrm{C_{27}H_{27}NO_6W}$, $M_r = 645.35$, red crystal, 0.30 × 0.25 × 0.10 mm, $a = 9.230(1)$, $b = 32.151(1)$, $c = 9.688(1)$ Å, $\beta = 112.76(1)°$, $V = 2651.1(4)$ Å^3, $\rho_{\mathrm{calcd}} = 1.617$ g cm^{-3}, $\mu =$ 43.97 cm^{-1}, empirical absorption correction ($0.352 \leq T \leq 0.668$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 22630 reflections collected ($\pm h$, $\pm k$, $\pm l$), $\sin\theta/\lambda = 0.67$ Å^{-1}, 6404 independent ($R_{\mathrm{int}} = 0.038$) and 5101 observed reflections ($I \geq 2\sigma(I)$), 339 refined parameters, $R = 0.027$, $wR_2 = 0.059$, max./min. residual electron density 0.64/−1.02 e Å^{-3}, positional disorder of the atoms C13 and C14 refined with split positions in a ratio of 0.57(1) to 0.43, hydrogen atoms calculated and refined as riding atoms.

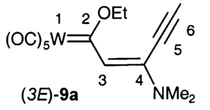
(1Z,3Z)-1-Ethoxy-2-[dimethyl(ethoxymethylenyl)ammonium]-3,4-diphenyl-1,3-butadien-1-yl-pentacarbonylchromate (3g) and [η^1-*Cr,N*]-(3*E*,4*Z*)-2-ethoxy-3-[dimethylamino(ethoxymethylene)]-4,5-diphenyl-1-tetracarbonylchroma-1,4-pentadiene (4g): *N,N*-Dimethyl-(*O*-ethyl)phenylpropioamidium tetrafluoroborate (**5a**, 0.50 mmol), generated as described above, was treated with pentacarbonyl(1-ethoxy-2-phenylethylidene)chromium (**1f**, 171 mg, 0.50 mmol) and triethylamine (51 mg, 0.5 mmol) in dry dichloromethane (1 mL). Workup after 1 h at 20 °C by flash chromatography on silica gel (column 2 × 40 cm) with dichloromethane/*n*-pentane (1/2) afforded a brown fraction of a 1/1 mixture of **3g** (90 mg, 40%, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2, yellow oil) and **4g** (90 mg, 40%, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2, red crystals from *n*-pentane at −20 °C, m.p. 75 °C). Compound **3g** (100 mg) in [$\mathrm{D_6}$]benzene is partially converted to the corresponding chelate complex **4g** (71 mg, 75%) at 22 °C over 24 h.

Data for 3g: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.51-7.15$ (m, 5H; Ph), 6.47 (br, 1H; 4H), 4.31 (q, 2H; 1′-$\mathrm{OCH_2}$), 3.95 (q, 2H; 1-$\mathrm{OCH_2}$), 2.78 (s, 6H; $\mathrm{N(CH_3)_2}$), 1.26 (t, 3H; 1′-$\mathrm{OCH_2\mathit{CH}_3}$), 1.05 ppm (t, 3H; 1-$\mathrm{OCH_2\mathit{CH}_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta =$ ($\mathrm{C_q}$; C1);[18] 216.0 and 215.1 (each $\mathrm{C_q}$; *trans*- and *cis*-CO of $\mathrm{Cr(CO)_5}$), 174.1 ($\mathrm{C_q}$; $\mathrm{C{=}N^+}$), 139.2 ($\mathrm{C_q}$; C3); 133.2 (CH; C4); 127.7, 127.6, 127.5, 127.1, 172.2, 126.8, 126.7, 126.4, 125.9 and 124.4 (each CH; Ph), 119.2 ($\mathrm{C_q}$; C2), 71.8 (1-$\mathrm{OCH_2}$), 70.1 (1′-$\mathrm{OCH_2}$), 41.1 ($\mathrm{N(CH_3)_2}$), 14.0 (1-$\mathrm{OCH_2\mathit{C}H_3}$), 13.8 ppm (1′-$\mathrm{OCH_2CH_3}$); IR (*n*-hexane) [$\mathrm{cm^{-1}}$ (%)]: $\tilde{\nu} =$ 2042.6 (70), 1881.4 (100), 1834.8 (80) (ν(C≡O)), 1601.7 (10); MS (70 eV): *m/z* for ^{52}Cr (%): 541 (10) $[M]^+$, 513 (5) $[M-\mathrm{CO}]^+$, 485 (10) $[M-2\,\mathrm{CO}]^+$, 429 (10) $[M-4\,\mathrm{CO}]^+$, 401 (100) $[M-5\,\mathrm{CO}]^+$; elemental analysis (%) calcd for $\mathrm{C_{28}H_{27}O_7NCr}$ (541.1): C 62.09, H 5.03, N 2.59; found: C 62.30, H 5.10, N 2.65.

Data for 4g: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.51-7.15$ (m, 5H; Ph), 7.04 (s, 1H; 5-H), 4.71 (q, 2H; $\mathrm{Cr{=}CO\mathit{CH}_2}$); 4.21 and 3.89 (q, 2H; diastereotopic OCH_2); 2.86 and 2.59 (s, 6H; $N(CH_3)_2$), 1.27 (t, 3H; $Cr{=}COCH_2CH_3$), 1.07 ppm (t, 3H; OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ = 327.6 (C_q; C2); 230.6, 228.9, 222.7, 219.7 (each C_q; $Cr(CO)_4$), 174.1 (C_q;=CN), 140.0 (C_q; C4), 131.9 (CH; C5); 129.5, 129.3, 128.4, 127.8, 127.6, 127.5, 127.2, 126.8 and 126.7 (each CH; Ph), 124.8 (C_q; C3), 76.3 ($Cr{=}COCH_2$), 68.1 (OCH_2), 52.5 and 53.0 ($N(CH_3)_2$), 14.0 ($Cr{=}COCH_2CH_3$), 13.5 ppm (OCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2000.1 (80), 1881.7 (80), 1878.4 (100), 1831.0 (90) (ν(C≡O)), 1601.7; MS (70 eV): *m*/*z* for ^{52}Cr (%): 513 (5) $[M]^+$, 485 (5) [*M* – CO], 429 (10) $[M - 3CO]^+$, 401 (100) $[M - 4CO]^+$; elemental analysis (%) calcd for $C_{27}H_{27}O_6NCr$ (513.1): C 63.14, H 5.30, N 2.73; found: C 63.30, H 5.70, N 2.90.

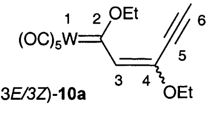
4-Dimethylamino-2-ethoxy-6-phenyl-1-pentacarbonyltungsta-1,3-hexadien-5-yne ((3*E*)-9a and (3*Z*)-9a), 2,4-diethoxy-6-phenyl-1-pentacarbonyltungsta-1,3-hexadien-5-yne ((3*E*)-10a and (3*Z*)-10a), 2-ethoxy-5-ethoxycarbonyl-4-phenyl-1-pentacarbonyltungsta-1,4-pentadiene ((*4Z*)-15a) and 2-ethoxy-5-ethoxycarbonyl-4-phenyl-1-pentacarbonyltungsta-1,3-pentadiene ((3*E*)-14a): *N*,*N*-Dimethyl(*O*-ethyl)phenylpropioamidium tetrafluoroborate (**5a**, 0.50 mmol), generated as described above, was treated with methylcarbene complex **1g** (197 mg, 0.50 mmol) and triethylamine (50 mg, 0.50 mmol) in dry dichloromethane (1 mL). Workup after 1 h at 20 °C by flash chromatography on silica gel (column 2 × 40 cm) with dichloromethane/*n*-pentane 1/2 afforded a red fraction with a 4/1 mixture of (3*E*)-**10a** and (3*Z*)-**10a** (126 mg, 38 %, R_f = 0.8 in dichloromethane/*n*-pentane 1/2; dark red crystals of (3*E*)-**10a** from *n*-pentane at –20 °C, m.p. 55 °C), a further red fraction with (3*E*)-**9a** free of its isomer (3*Z*)-**9a** (23 mg, 8 %, R_f = 0.5 in dichloromethane/*n*-pentane 1/2, red crystals from *n*-pentane, m.p. 85 °C), an orange fraction with (4*Z*)-**15a** (30 mg, 10 %, R_f = 0.5 in dichloromethane/*n*-pentane 1/2, orange oil) and a red fraction with (3*E*)-**14a** (65 mg, 23 %, R_f = 0.3 in dichloromethane/*n*-pentane 1/2, dark red crystal from *n*-pentane, m.p. 55 °C).

Data for (3*E*)-9a: ^1H NMR (300 MHz, $CDCl_3$): δ 7.52 (2H, *o*-H), 7.37 (3H; *m*- and *p*-H, Ph), 6.64 (s, 1H; 3-H), 4.66 (q, 2H; $W{=}COCH_2$), 3.23 (s, 6H; $N(CH_3)_2$), 1.39 ppm (t, 3H; $W{=}COCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ = 272.3 (C_q; C2); 203.9 and 199.3 (each C_q; *trans*- and *cis*-CO of $W(CO)_5$), 135.0 (C_q; C4); 131.5, 129.7, 128.5 (2:2:1, *m*-, *p*- and *o*-C Ph), 122.9 (CH; C3), 100.1 (C_q; C6), 84.5 (C_q; C5), 76.8 ($W{=}COCH_2$), 41.1 (CH_3; $N(CH_3)_2$), 15.3 ppm ($W{=}COCH_2CH_3$); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2060.8 (50), 1908.2 (100) (ν(C≡O)); MS (70 eV): *m*/*z* for ^{184}W (%): 551 (10) $[M]^+$, 495 (40) $[M - 2CO]^+$, 439 (30) $[M - 4CO]^+$, 411 (100) $[M - 5CO]^+$; elemental analysis (%) calcd for $C_{20}H_{17}O_6NW$ (551.0): C 43.55, H 3.11, N 2.54; found: C 43.59, H 2.91, N 2.47.



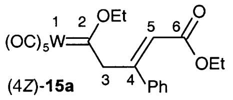
(3*E*)-**9a**

Data for (3*E*)-10a [(3*Z*)-10a]: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56 [7.56] (2H; *o*-H, Ph), 7.31 [7.31] (3H; *p*- and *m*-H, Ph), 7.29 [6.83] (s, 1H; 3-H, NOE (+) with OCH_2), 4.86 [4.75] (q, 2H; $W{=}COCH_2$), 4.19 [4.37] (q, 2H; OCH_2), 1.61 [1.59] (t, 3H; $W{=}COCH_2CH_3$), 1.44 [1.42] ppm (t, 3H; OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ = 294.2 [294.2] (C_q; C2); 203.7 and 198.5 [203.7 and 198.5] (each C_q; *trans*- and *cis*-CO of $W(CO)_5$), 139.8 [142.3] (C_q; C4); 131.7, 130.2, 129.3, 128.6, [132.1, 130.0, 130.6, 128.5] (each CH; Ph), 121.0 [120.0] (CH; C3), 98.3 [98.3] (C_q, C6), 84.6 [84.6] (C_q; C5), 78.6 [78.1] ($W{=}COCH_2$), 65.7 [68.1] (OCH_2), 14.7 [14.8] ($W{=}COCH_2CH_3$), 14.6 [14.6] ppm (OCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2194.4 (50) ($\tilde{\nu}$(C≡C)); 2060.8 (50), 1908.2 (100) (ν(C≡O)), 1525.7 (40); MS (70 eV): *m*/*z* for ^{184}W (%): 552 (10) $[M]^+$, 524 (30) $[M - CO]^+$, 468 (50) $[M - 3CO]^+$, 411 (100) $[M - 5CO]^+$; elemental analysis (%) calcd for $C_{20}H_{16}O_7W$ (552.0): C 43.48, H 2.29; found: C 43.37, H 2.65.



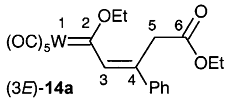
(3*E*/3*Z*)-**10a**

Data for (4*Z*)-15a: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39 (*p*- and *m*-H, 3H; Ph), 7.50 (*o*-H, 2H; Ph), 6.20 (s, 1H; 5-H), 5.14 (s, 2 H; 3-H), 4.81 (q, 2H; $W{=}COCH_2$), 4.18 (q, 2H; OCH_2), 1.32 (t, 3H; $W{=}COCH_2CH_3$), 1.21 ppm (t, 3H; OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ = 323.8 (C_q; C2); 202.7 and 197.1 (each C_q, *trans*- and *cis*-CO of $W(CO)_5$), 165.9 (C_q; C=O), 152.9 (C_q; C4), 140.4 (C_q; *i*-C Ph); 128.6, 128.5, 128.0, 127.6, 127.2 (each CH; Ph), 119.2 (CH; C5), 80.6 ($W{=}COCH_2$), 66.7 (OCH_2CH_3), 60.0 (CH; C3), 14.1 ($W{=}COCH_2CH_3$), 13.9 ppm (OCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2065.8 (50), 1918.5 (100) (ν(C≡O)), 1734.3 (20), 1710.0 (10) (ν(C=O)); MS (70 eV): *m*/*z* for ^{184}W (%): 570 (10) $[M]^+$, 486 (100) $[M - 3CO]^+$, 429 (50) $[M - CO]^+$.



(4*Z*)-**15a**

Data for (3*E*)-14a: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50 (*o*-H, 2H; Ph), 7.39 (*p*- and *m*-H, 3H; Ph), 7.72 (s, 1H; 3-H, NOE (+) with *o*-H Ph), 4.94 (q, 2H; $W{=}COCH_2$), 4.12 (q, 2H; OCH_2), 3.62 (s, 2H; 3-H), 1.66 (t, 3H; $W{=}COCH_2CH_3$), 1.19 ppm (t, 3H; 6-OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ = 310.2 (C_q; C2); 203.6, and 197.1 (each C_q; *trans*- and *cis*-CO of $W(CO)_5$), 169.4 (C_q; C=O), 146.2 (CH; C3), 141.5 (C_q; C4), 133.8 (C_q; *i*-C, Ph); 129.1, 128.8, 127.2 (2:2:1, each CH; Ph), 79.8 ($W{=}COCH_2$), 60.9 (OCH_2CH_3), 39.0 (CH; C5), 14.8 ($W{=}COCH_2CH_3$), 13.9 ppm (6-OCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2066.0 (100), 1917.3 (100) (ν(C≡O)), 1736.8 (10); MS (70 eV): *m*/*z* for ^{184}W (%): 570 (10) $[M]^+$, 486 (100) $[M - 3CO]^+$; elemental analysis calcd for $C_{20}H_{18}O_8W$ (570.0): C 42.10, H, 3.18; found: C 42.84, H 3.30.



(3*E*)-**14a**

4-Dimethylamino-2-ethoxy-6-phenyl-1-pentacarbonylchroma-1,3-hexadien-5-yne ((3*E*)-9b and (3*Z*)-9b), 2,4-diethoxy-6-phenyl-1-pentacarbonylchroma-1,3-hexadien-5-yne ((3*E*)-10b and (3*Z*)-10b), (3*E*)-2-ethoxy-5-ethoxycarbonyl-4-phenyl-1-pentacarbonylchroma-1,3-pentadiene ((3*E*)-14b): *N*,*N*-Dimethyl(*O*-ethyl)phenylpropioamidium tetrafluoroborate (**5a**, 0.50 mmol), generated as described above, was treated with ethoxy(methyl)carbene chromium complex **1h** (132 mg, 0.50 mmol) and triethylamine (50 mg, 0.50 mmol) in dry dichloromethane (1 mL). Workup after 1 h at 20 °C by flash chromatography on silica gel (column 2 × 40 cm) with dichloromethane/*n*-pentane (1/2) afforded a red fraction with a 4/1 mixture of (3*E*/3*Z*)-**10b** (79 mg, 38 %, R_f = 0.8 in dichloromethane/n-pentane 1/2, dark red crystals of (3*E*)-**10b** from *n*-pentane at –20 °C, m.p. 50 °C], a red fraction with (3*E*)-**9b** free of isomers (46 mg, 22 %, R_f = 0.5 in dichloromethane/*n*-pentane 1/2, red crystal from n-pentane at –20 °C, m.p. 80 °C), and a further red fraction with (*3E*)-**14b** (40 mg, 20 %, R_f = 0.3 in dichloromethane/*n*-pentane 1/2, red oil).

Data for (3*E*)-10b [(3*Z*)-10b]: ^1H NMR (300 MHz $CDCl_3$). δ = 7.54–7.41 [7.54–7.41] (5H; Ph), 7.35 [6.79] (s, 1H; 3-H), 5.05 [4.89] (q, 2H; $Cr{=}COCH_2$), 4.21 [4.43] (q, 2H; OCH_2), 1.59 [1.60] (t, 3H; $Cr{=}COCH_2CH_3$), 1.43 [1.43] ppm (t, 3H; OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ = 321.8 [321.8] (C_q; C2); 224.2 and 218.7 [225.2 and 218.7] (each C_q; *trans*- and *cis*-CO of $Cr(CO)_5$), 136.4 [138.0] (C_q; C4); 132.2, 130.3, 128.7, 125.2 [131.9, 130.1, 126.9, 125.0] (each CH; Ph), 122.0 ,[122.0] (CH; C3), 99.0 [98.4] (C_q; C6), 85.9 [85.9] (C_q; C5), 77.7 [76.9] ($Cr{=}COCH_2$), 69.5 [67.3] (OCH_2; C7), 16.5 [16.1] ($Cr{=}COCH_2CH_3$), 15.9 [15.6] ppm (OCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2194.8 (10) (ν(C≡C)), 2053.2 (70), 1917.0 (100) (ν(C≡O)), 1532.6 (50); MS (70 eV): *m*/*z* for ^{52}Cr (%): 420 (10) $[M]^+$, 392 (2) $[M - CO]^+$, 336 (10) $[M - 3CO]^+$, 280 (100) $[M - 5CO]^+$; elemental analysis (%) calcd for $C_{20}H_{16}O_7Cr$ (420.0): C 57.14, H 3.84; found: C 57.40, H 3.90.

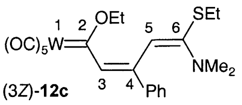
Data for (3*E*)-9b: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52 (2H; *o*-H; Ph), 7.45 (3H, *p*- and *m*-H; Ph), 6.63 (s, 1H; 3-H), 4.82 (q, 2H; $Cr{=}COCH_2$), 3.28 (s, 6H; $N(CH_3)_2$), 1.43 ppm (t, 3H, $Cr{=}COCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ = 295.7 (C_q; C2); 225.6, and 220.0 (each C_q; *trans*- and *cis*-CO of $Cr(CO)_5$), 133.1 (C_q; C4); 132.8, 131.0, 129.8; (2:2:1, each CH; Ph), 120.9 (CH; C3), 100.5 (C_q; C6), 85.7 (C_q; C5), 75.3 ($Cr{=}COCH_2$), 42.3 ($N(CH_3)_2$), 16.8 ppm ($Cr{=}COCH_2CH_3$); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2053.0 (30), 1920.4 (100) (ν(C≡O)); MS (70 eV): *m*/*z* for ^{52}Cr (%): 419 (10) $[M]^+$, 307 (10) $[M - 4CO]^+$, 279 (100) $[M - 5CO]^+$; elemental analysis (%) calcd for $C_{20}H_{17}O_6NCr$ (419.4): C 57.27, H 4.09, N 3.34; found: C 57.50, H 4.10, N 3.40.

Data for (3*E*)-14b: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.49$ (2H, *o*-H; Ph), 7.39–7.26 (3H, *p*- and *m*-H; Ph), 7.72 (s, 1H; 3-H), 5.15 (q, 2H; $Cr{=}COCH_2$), 4.11 (q, 2H; OCH_2), 3.62 (s, 2H; 3-H), 1.68 (t, 3H; $Cr{=}COCH_2CH_3$), 1.21 ppm (t, 3H; OCH_2CH_3); ^{13}C NMR ($CDCl_3$): $\delta =$ 338.0 (C_q, C2); 223.8 and 216.2 (each C_q; *trans*- and *cis*-CO of $Cr(CO)_5$), 169.7 (C_q; C=O), 142.4 (CH; C3), 141.1 (C_q; C4), 130.0 (C_q; *i*-C, Ph); 128.9, 128.6, 128.4, 127.6 and 127.1 (each CH; Ph), 78.0 ($Cr{=}COCH_2$), 60.9 (OCH_2CH_3), 38.6 (CH; C5), 15.0 ($Cr{=}COCH_2CH_3$), 14.1 ppm (OCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2057.9$ (90), 1922.0 (100) ($\nu(C{\equiv}O)$), 1737.0 (70); MS (70 eV): *m*/*z* for ^{52}Cr (%): 438 (10) $[M]^+$, 382 (5) $[M-2\,CO]^+$, 354 (10) $[M-3\,CO]^+$, 326 (50) $[M-4\,CO]^+$, 298 (100) $[M-5\,CO]^+$; elemental analysis (%) calcd for $C_{20}H_{18}O_8Cr$ (438.0): C 54.79, H 4.14; found: C 55.04, H 4.18.

4-Dimethylamino-2-ethoxy-6-phenyl-1-pentacarbonyltungsta-1,3-hexadien-5-yne ((3*E*)-9c and (3*Z*)-9c), 6-dimethylamino-2-ethoxy-6-ethylsulfanyl-4-phenyl-1-pentacarbonyltungsta-1,3,5-hexatriene ((3*Z*)-12c), and 5-dimethylamino-1-ethoxy-5-ethylsulfanyl-3-phenyl-1,3-cyclopentadiene (13c): *N*,*N*-Dimethyl(*S*-ethyl)phenylpropioamidium tetrafluoroborate (**5b**, 0.50 mmol), generated as described above, was treated with ethoxy(methyl)carbene tungsten complex **1g** (197 mg, 0.50 mmol) and triethylamine (50 mg, 0.50 mmol) in dry dichloromethane (1 mL). Workup after 1 h at 20 °C by flash chromatography on silica gel (column 2 × 40 cm) with dichloromethane/*n*-pentane (1/2) afforded a red fraction with (3*E*)-**9c** (185 mg, 67%, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2, red crystal from *n*-pentane, m.p. 85 °C), a red fraction with (3*Z*)-**12c** (29 mg, 9%, $R_f = 0.8$ in dichloromethane/*n*-pentane 1/2, red oil). When the reaction was extended to 24 h at 20 °C, the amount of (3*Z*)-**12c** was greatly increased (152 mg, 44%) at the cost of (3*E*)-**9c** (10 mg, 4%). Thermolysis of the metallahexatriene (3*Z*)-**12c** (100 mg) at 60 °C for 7 h in cyclohexane afforded the cyclopentadiene **13c** (36 mg, 52%, $R_f = 0.4$ in dichloromethane/*n*-pentane 1/2, pale orange oil).

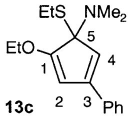
Data for (3*E*)-9c: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (2H, *o*-H), 7.37 (3H, *m*- and *p*-H, Ph), 6.64 (s, 1H; 3-H), 4.66 (q, 2H; $W{=}COCH_2$), 3.23 (s, 6H; $N(CH_3)_2$), 1.39 ppm (t, 3H; $W{=}COCH_2CH_3$); ^{13}C NMR ($CDCl_3$): $\delta = 272.3$ (C_q; C2); 203.9 and 199.3 (each C_q; *trans*- and *cis*-CO of $W(CO)_5$), 135.0 (C_q; C4); 131.5, 129.7, 128.5, (2:2:1, each CH; Ph), 122.9 (CH; C3), 100.1 (C_q; C6), 84.5 (C_q; C5), 76.8 ($W{=}COCH_2$), 41.1 (CH_3; $N(CH_3)_2$), 15.3 ppm ($W{=}COCH_2CH_3$); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2060.8$ (50), 1908.2 (100) ($\nu(C{\equiv}O)$); MS (70 eV): *m*/*z* for ^{184}W (%): 551 (10) $[M]^+$, 495 (40) $[M-2\,CO]^+$, 439 (30) $[M-4\,CO]^+$, 411 (100) $[M-5\,CO]^+$; elemental analysis (%) calcd for $C_{20}H_{17}O_6NW$ (551.0): C 43.55, H 3.11, N 2.54; found: C 43.59, H 2.91, N, 2.47.

Data for (3*Z*)-12c: ^{1}H NMR (C_6D_6): $\delta = 7.61-7.42$ (m, 5H; H-Ph), 6.50 (s, 1H; 3-H, NOE (+) with $N(CH_3)_2$), 6.01 (s, 1H, 5-H, NOE (+) with *o*-H Ph), 4.52 (q, 2H; $W{=}COCH_2$, NOE (−) with *o*-H Ph), 2.23 (s, 6H; $N(CH_3)_2$, NOE (+) with 3-H and 5-H), 2.11 (q, 2H; SCH_2CH_3), 1.14 (t, 3H; $W{=}COCH_2CH_3$), 1.01 ppm (t, 3H; SCH_2CH_3); ^{13}C NMR ($CDCl_3$): $\delta =$ 268.3 (C_q; C2); 204.3 and 200.6 (C_q; *trans*- and *cis*-CO of $W(CO)_5$), 154.1 (C_q; C6), 140.5 (C_q; *i*-CPh), 138.5 (C_q; C4), 128.3 (CH; C5); 129.0, 128.1, 127.5 and 127.4 (each CH; Ph), 120.9 (C_q; C3), 76.8 ($W{=}COCH_2$), 40.0 ($N(CH_3)_2$), 26.5 (SCH_2), 15.5 (SCH_3), 15.4 ppm (OCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} = 2055.6$ (30), 1898.2 (100) ($\nu(C{\equiv}O)$); MS (70 eV): *m*/*z* for ^{184}W (%): 612 $[M]^+$, 557 (10) $[M-2\,CO]^+$, 500 (100) $[M-4\,CO]^+$; elemental analysis (%) calcd for $C_{22}H_{23}O_6SNW$ (612.0): C 43.06, H 3.78, N 2.28; found: C 43.20, H 3.70, N 2.20.



(3*Z*)-**12c**

Data for 13c: ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.87$ (2H; *o*-H; Ph); 7.33 and 7.28 (3H; *p*-, and *m*-H; Ph), 6.55 (d, 1H, $^4J = 3.0$ Hz; 2-H), 6.27 (d, $^4J =$ 3.0 Hz, 1H; 4-H), 3.57 (q, 2H; OCH_2), 2.61 (s, 6H; $N(CH_3)_2$), 2.13 (q, 2H; SCH_2), 0.98 (t, 3H; OCH_2CH_3), 0.93 ppm (t, 3H; SCH_2CH_3); ^{13}C NMR (C_6D_6): $\delta = 147.1$ (C_q; C1), 155.0 (C_q; C3), 130.0 (*i*-C; Ph), 128.5, (CH; C4), 128.9, 128.5, 127.9, 127.7 and 126.4 (each CH; Ph), 108.4 (CH; C2), 98.0 (C_q; C5), 63.2 (CH_2; OCH_2), 40.3 (CH_3; $N(CH_3)_2$), 27.9 (CH_2; SCH_2), 15.6 (CH_3; OCH_2CH_3), 15.5 ppm (CH_3; SCH_2CH_3); IR (*n*-hexane) [cm^{-1} (%)]: $\tilde{\nu} =$ 1600.7 (25), 1506.6 (100), 1465.2 (50), 1377.3 (50); MS (70 eV): *m*/*z*: 289 (10) $[M]^+$, 257 (100) $[M-OCH_3]^+$; elemental analysis (%) calcd for $C_{17}H_{23}OSN$ (289.1): C 70.55, H 8.02, N 4.84; found: C 71.01, H 8.10, N 4.90.



13c

CCDC-201087 and CCDC-201088 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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