Organic Syntheses via Transition Metal Complexes. 78.[1] Hydrazinolysis of Alkynylcarbene Complexes of Chromium and Tungsten. Formation of Hydrazinocarbene, Imidate, Pyrazolidinylidene, and Nitrile Complexes

Rudolf Aumann,* Beate Jasper, and Roland Fröhlich

Organisch-Chemisches Institut der Universität Münster, Orléans-Ring 23, D-48149 Münster, Germany

Received December 21, 1994[⊗]

Hydrazinolysis of alkynylcarbene complexes $(CO)_5M{=}C(OEt)C{\equiv}Ph$ (**1**, M = W; **1′**, M = Cr) with mono- and 1,2-dimethylhydrazine MeHNNHR (**2a,b**) (R = Me, H) affords three different-type compounds: hydrazinocarbene complexes $(CO)_5M{=}C(NMe\text{-}NHR)C{\equiv}CPh$ [(*E*/*Z*)-**3a,b**], imidate complexes $(CO)_5M[MeN{=}C(OEt)\text{-}C{\equiv}CPh]$ [(*E*/*Z*)-**4a**], and pyrazolidinylidene complexes **5a,b**. Hydrazinolysis of **1**/**1′** with 1,1-dimethylhydrazine or (unsubstituted) hydrazine H_2NNR_2 (**2c,d**) (R = Me, H) yields hydrazinocarbene complexes $(CO)_5M{=}C(NH\text{-}NR_2)C{\equiv}CPh$ [(*E*/*Z*)-**3c**], imidate complexes $(CO)_5M[HN{=}C(OEt)C{\equiv}CPh]$ [(*E*/*Z*)-**4a**], and benzonitrile complexes $(CO)_5M(N{\equiv}CPh)$ (**8**). Hydrazinolysis of **1** with H_2NNHR (**2e,f**) (R = COMe, Ph) gives pyrazoles **12e,f** as the only products. The product composition of the reactions of **2a–d** with **1** is markedly influenced by the reaction temperature. Reaction of **1** with *N*- and *O*-methylhydroxylamines (**13**, **14**) affords imidate complexes **4** only. The hydrazinocarbene complexes (*E*)-**3a** and (*Z*)-**3c** were characterized by X-ray diffraction. Both compounds crystallize in space group $P\bar{1}$ (No. 2): (*E*)-**3a**, $C_{16}H_{12}N_2O_5W$, cell parameters a = 8.501(2) Å, b = 9.645(2) Å, c = 11.860(2) Å, α = 103.56(2)°, β = 95.59(2)°, γ = 111.76(2)°, Z = 2, R_1 = 0.043, and wR^2 = 0.083; (*Z*)-**3c**, $C_{16}H_{12}N_2O_5W$, cell parameters a = 9.380(3) Å, b = 9.685(4) Å, c = 10.804(3) Å, α = 84.77(5)°, β = 80.74(3)°, γ = 66.47(3)°, Z = 2, R_1 = 0.036, and wR^2 = 0.086.

The hydrazinolysis of alkoxycarbene complexes $(CO)_5M{=}C(OR)R^1$ (M = Cr, Mo, W) has been studied to a much less an extent than the aminolysis of such compounds. Usually the hydrazinolysis takes a nonuniform course and yields several and also seemingly different-type products. Some features of the hydrazinolysis of carbene complexes have been unraveled so far.[2,3] To date, four main reaction paths have been distinguished, which consist in the formation of hydrazinocarbene complexes (by 1-substitution at the carbene carbon atom), imidate complexes (by insertion of a =NR group into the M=C bond),[2] pyrazinylidene complexes (by retaining of the N–N bridge), and nitrile complexes (by fragmentation of the ligand). We wish to report on our studies of reactions of hydrazines **2a–f** as well as of hydroxylamines **13** and **14** with alkynylcarbene complexes $(CO)_5M{=}C(OEt)\text{-}C{\equiv}CPh$ (**1**, M = W; **1′**, M = Cr). A great diversity of parallel reactions has been anticipated as a consequence of the ambident character of both the reagent and the substrate: compounds **1** are prone to both electrophilic 1-addition and 3-addition reactions and compounds **2**, **13**, and **14** on the other hand possesses two different nucleophilic centers. By probing the influence of substituents as well as the reaction temperature on the product distribution, we could obtain some insight into the mechanism of the hydrazinolysis of carbene complexes.

Substitution and Fragmentation of 1 on Reaction with (Symmetrical) 1,2-Dimethylhydrazine (2a)

The basic features of the hydrazinolysis of carbene complexes can be derived from the reaction of (symmetrical) 1,2-dimethylhydrazine (**2a**) with alkynylcarbene complexes **1** (M = W; **1′**, M = Cr). This reaction affords three different-type products: hydrazinocarbene complexes (*E*/*Z*)-**3a**, imidate complexes (*E*/*Z*)-**4a**, and pyrazinylidene complexes **5a** (Scheme 1). It has been demonstrated by ^{1}H NMR measurements that compounds **3–5** are not interconverted under the reaction conditions and therefore appear to be formed in parallel reactions. Most strikingly, a strong influence of the temperature on the product distribution is observed (Table 1). Although complexes (*E*/*Z*)-**3a** are generated on reaction of **1** with **2a** at −78 °C in 27% yield, they are formed in only trace amounts at 20 °C. Since compounds (*E*/*Z*)-**3a** are quite stable at 20 °C, its appears that the 1-addition of **2a** to **1** becomes favored at −78 °C over the 3-addition (Scheme 1).[4]

Both, compounds **3a** and **4a** are generated *via* 1-addition of **2a** to the carbene complex **1**. Zwitterionic

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1995.

(1) Part 77: Aumann, R.; Jasper, B. *Organometallics* **1995**, *14*, 1461.

(2) (a) Fischer, E. O.; Aumann, R. *Angew. Chem.* **1967**, *79*, 191; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 181. (b) Fischer, E. O.; Aumann, R. *Chem. Ber.* **1968**, *101*, 963.

(3) Fischer, H.; Roth, G.; Reindl, G.; Troll, C. *J. Organomet. Chem.* **1993**, *454*, 133–149.

(4) Similar effects are observed with the aminolysis of **1**. See e.g.: Werner, H.; Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, *28*, 367–389.

0276-7333/95/2314-2447$09.00/0

Scheme 1

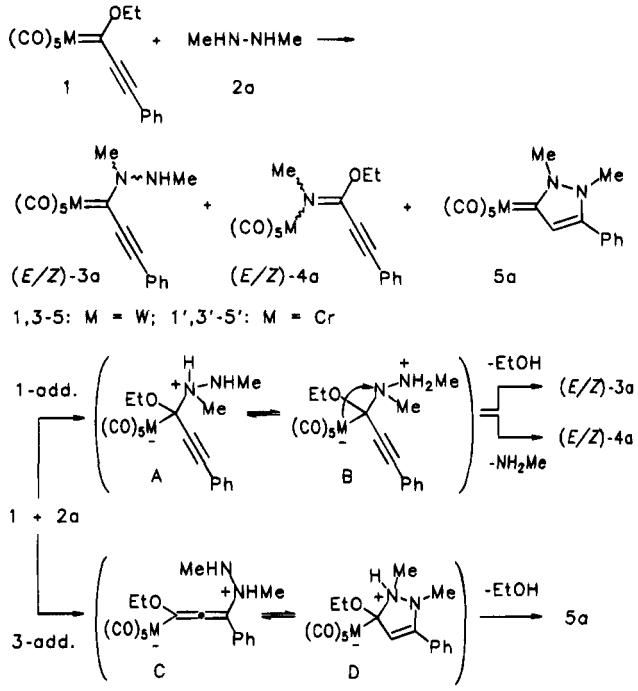


Table 1. Influence of Temperature on Product Composition in the Reaction of 2a with 1 (1')

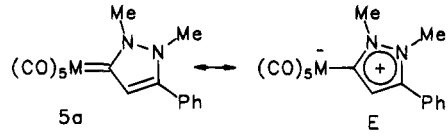
	M	(*E*)-**3**/(*Z*)-**3**/(*E*)-**4**/(*Z*)-**4**/**5**[a]	*b*	*c*
a	W	17/11/22/12/23	85	−78
a	W	0/0/3/5/80	88	20
a'	Cr	0/0/0/0/81	81	20

[a] Product ratio. [b] Total yield in %. [c] Reaction temperature in °C.

species **A** and **B** are assumed to be key intermediates in this addition. The elimination of EtOH from **A** is expected to yield hydrazinocarbene complexes (*E*/*Z*)-**3a**, while the elimination of $MeNH_2$ from **B** should result in the formation of imidate complexes (*E*/*Z*)-**4a** (Scheme 1).[2,5,6] $MeNH_2$ is trapped by the alkynylcarbene complex **1** in a Michael-type addition with formation of 1-amino and (2-aminoethenyl)carbene complexes in competing (high-yield) reaction paths.[4,12] In line with expectation, the latter products are obtained in amounts equivalent to those of the imidate complexes **4** (see Table 3 and Scheme 5). For the present case, this side reaction may be suppressed, if a (local) excess of hydrazine **2a** *vs* carbene complex **1** is guaranteed by proper reaction conditions.

Compounds **3a** and **4a** are each obtained as mixtures of stereoisomers (Scheme 1). The formation of an *anti* stereoisomer (*E*)-**4a** is slightly favored kinetically at −78 °C over the formation of the *syn* product (*Z*)-**4a**. The latter proves to be more stable thermally than the former. It has been demonstrated by NMR measurements that the chromium complex (*E*)-**4a'** smoothly rearranges to (*Z*)-**4a'** within 2 h at 40 °C in C_6D_6. Interestingly, the pyrazinylidene complex **5a** does not

Scheme 2



result from cyclization of the hydrazine complex (*E*)-**3a**. This is easily explained by consideration of sterical restrictions implied to the transition state geometry for such a reaction. Therefore, not unexpectedly, a solution of (*E*)-**3a** in C_6D_6 according to ^1H NMR measurements remains unchanged for several hours at 40 °C. Apparently, the pyrazinylidene complex **5a** is formed by 3-addition of **2a** to **1** *via* zwitterionic intermediates[7] **C** and **D**.

Spectroscopy of 3a, 4a, and 5a

The signals of the carbene carbon atoms in the ^{13}C NMR spectra of the hydrazinocarbene complexes (*E*/*Z*)-**3a** are shifted upfield [(*E*)-**3a**, δ(W=*C*) 212.3; (*Z*)-**3a**, 212.1] relative to those of aminocarbene complexes {e.g. δ[$(CO)_5W$=*C*(NHMe)-C≡CPh] 233.0}.[8] This is attributed to a strong resonance contribution of the dipolar iminium structure $(CO)_5WC(=NMe^+NHMe)C{\equiv}CPh$. In line with this assumption, a bathochromic shift of the [ν(C≡O)] E-band in the IR spectrum [(*E*)-**3a**, 1930.2 cm^{-1}, *vs* $(CO)_5W$=C(NHMe)C≡CPh, 1943.3] is also observed.

The configuration assignment of the stereoisomers (*E*/*Z*)-**3a** is based on the *de*shielding of the hydrogen as well as of the carbon atom of the 1-NCH_3 group by the *syn* $(CO)_5M$ group of compound (*E*)-**3a** [δ(1-N*CH*$_3$) 3.20, δ-(1-N*C*H$_3$) 46.6 as compared to (*Z*)-**3a** δ(1-N*CH*$_3$) 2.70, δ(1-N*C*H$_3$) 40.7]. The configuration of (*E*/*Z*)-**4a** was determined by NOE experiments which indicated a positive interaction between the N*CH*$_3$ and the O*CH*$_2$ signals in (*E*)-**4a** but not in (*Z*)-**4a**. This is in line with the highfield shift of the signals of the N*CH*$_3$ (by 0.25 ppm) and the O*CH*$_2$ group (by 0.20 ppm) in (*E*)-**4a**, compared to (*Z*)-**4a**, due to mutual anisotropic shielding of these groups.

The strong upfield shift of the carbene carbon signal of **5a** (**5a**, δ = 176.9; **5a'**, δ = 190.8) and the bathochromic shift of the [ν(C≡O)] A_1- and E-bands in the IR spectrum of **5a** [**5a**, 2059.0 cm^{-1} (10%), 1917.8 (100); **5a'**, 2049.3 (20), 1925.9 (100)] relative to those of aminocarbene complexes indicate a strong influence of the zwitterionic structure **E** (Scheme 2).

Since only few examples of hydrazinocarbene complexes are known so far,[3,9] an X-ray structure analysis was carried out for (*E*)-**3a** and (*Z*)-**3c**. Figure 1 shows the molecular structure and Tables 5−7 give the experimental data for the crystal structure of the hydrazino alkynylcarbene complexes (*E*)-**3a**. The plane defined by N(2)−C(1)−C(6) approximately bisects the angle between two *cis*-CO groups at tungsten [C(16)−W−C(1)−N(2) = 41.3°]. The coordination geometry at N(2) is planar (sum of bond angles 360.0°). The lone

(5) The reaction of zwitterions $(CO)_5W^-N(Ph)N^+(Ph)$=C(OMe)Ph with iodine has been recently reported to give imidates: McGowan, P. C.; Massey, S. T.; Abboud, K. A.; McElwee-White, L. *J. Am. Chem. Soc.* **1994**, *116*, 7419−7420.

(6) Imidates were obtained from photochemical reactions of Fischer carbene chromium complexes and sulfilimines: Alcaide, B.; Cassarubios, L.; Domínguez, G.; Sierra, M. *J. Org. Chem.* **1993**, *58*, 3886−3894. Imidates were also obtained from reactions of Fischer carbene complexes with nitrosobenzene: Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83.

(7) Compounds of related type have been isolated and characterized by an X-ray analysis; see: Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Chem. Ber.* **1994**, *27*, 2475.

(8) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421−427.

(9) Ito, Y.; Hirao, T.; Saegusa, T. *J. Organomet. Chem.* **1977**, *131*, 121.

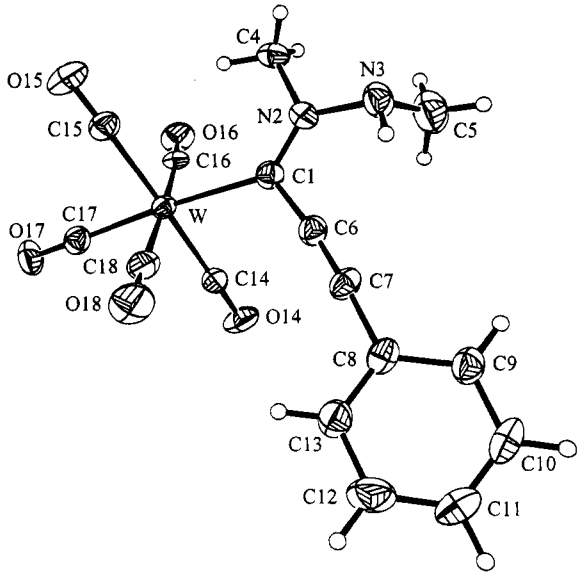


Figure 1. Molecular structure of hydrazinocarbene complex (*E*)-**3a**.

pair at N(2) is delocalized by virtue of the small interplanar angle C(6)−C(1)−N(2)−N(3) = −4.1(10)° and the short distance C(1)−N(2) = 1.307(9) Å. Due to the repulsive interaction of the lone pairs at the nitrogen atom N(3) with the adjacent delocalized π system, the interplanar angle C(1)−N(2)−N(3)−C(5) amounts to 96.3(10)°. A geometry similar to that of the hydrazino alkynylcarbene complexes (*E*)-**3a** has been found for a hydrazino alkenylcarbene complex.[3]

Regioselectivity of (Unsymmetrical) Methylhydrazine (2b)

The site of alkylation in methylhydrazine (**2b**) with most alkylating agents is the (more nucleophilic) substituted nitrogen atom,[10] while the position of acylation is very sensitive to the nature of the reagent used.[11] The addition of the ambident electrophile **1** to **2b** is very selective and occurs preferentially at the substituted nitrogen atom. Minor products (<10%) resulting from an attack of the unsubstituted nitrogen atom at **1** have been detected by NMR measurements, but they have not been fully characterized. Complexes (*E*/*Z*)-**3b**, (*E*/*Z*)-**4a**, **5b**, and **6b** are obtained as the main products (Scheme 3).

The reaction of **2b** with **1** (Scheme 3) follows a similar pattern as outlined in Scheme 1 for the reaction of **2a** with **1**. The product composition varies with the reaction temperature (Table 2). At −78 °C the 1-addition is favored over the 3-addition and leads to the formation of (*E*/*Z*)-**3b** and (*E*/*Z*)-**4a** *via* intermediates **F** and **G**. Cyclization to **5b** may involve the formation of intermediates **H** and **I**. Interestingly, the pyrazolinylidene complexes **5a**/**5a′** are stable thermally in C_6D_6 for at least 24 h at 80 °C, whereas the corresponding (*NH*) aminocarbene derivative **5b** rearranges quickly (*via* an intermediate **K**) to the pyrazole complex **6b** (Scheme 4). Furthermore, the tungsten compound **6b** is stable at 60 °C for several hours, but the corresponding chromium complex **6b′** is demetalated in C_6D_6 at 60 °C in 10 h to give the pyrazole **7b** together with $Cr(CO)_6$. The configurational assignment of **6b** and **6b′** is based on NOE experiments, which for each compound indicate a strong interaction between the NCH_3 group and the *o*-H's of the phenyl group.

(10) Butler, D. E.; Alexander, S. M.; McLean, J. M.; Strand, L. B. *J. Med. Chem.* **1971**, *14*, 1052.
(11) (a) Hinman, R. L.; Fulton, D. *J. Am. Chem. Soc.* **1958**, *80*, 1895. (b) Condon, F. E. *J. Org. Chem.* **1972**, *37*, 3615.

Scheme 3

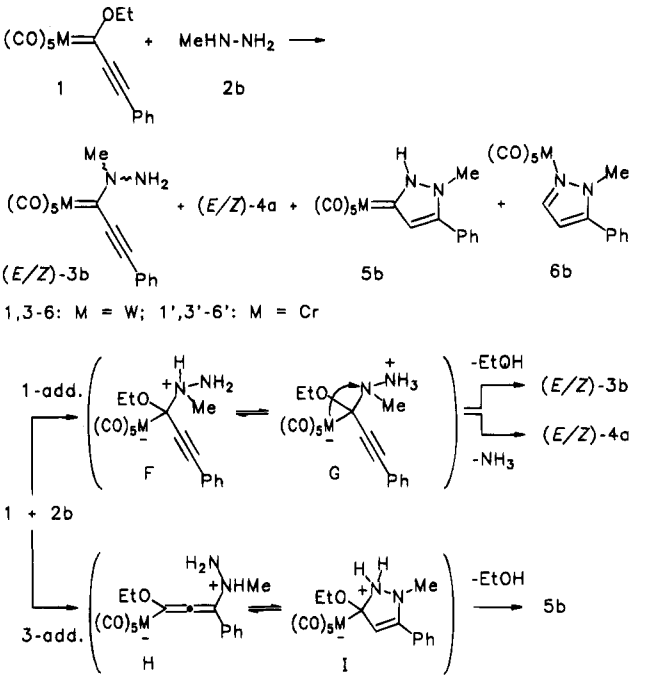


Table 2. Influence of Temperature on Product Composition in the Reaction of 2b with 1 (1′)

	M	(*E*)-**3**/(*Z*)-**3**/(*E*)-**4**/(*Z*)-**4**/**5**/**6**[a]	*b*	*c*
b	W	22/14/21/9/7/8	81	−78
b	W	0/0/8/3/26/39	76	20
b′	Cr	0/0/0/0/0/74	74	20

[a] Product ratio. [b] Total yield in %. [c] Reaction temperature in °C.

Table 3. Influence of Temperature on Product Composition in the Reaction of 2c with 1 (1′)

	M	(*Z*)-**3**/(*E*)-**3**/(*E*)-**4**/(*Z*)-**4**/**8**/**10**/**11**[a]	*b*	*c*
c	W	26/0/25/15/0/21/5	92	−78
c	W	0/0/33/7/5/3/39	84	20
c′	Cr	0/0/25/15/5/3/40	85	20

[a] Product ratio. [b] Total yield in %. [c] Reaction temperature in °C.

Table 4. Product Composition of the Reaction of 2d with 1′

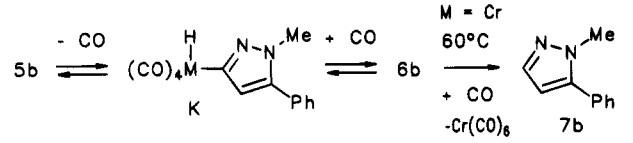
	M	(*E*)-**3**/(*Z*)-**3**/(*E*)-**4**/(*Z*)-**4**/**8**/**10**/**11**[a]	*b*	*c*
d′	Cr	0/0/24/16/7/25/10	82	20

[a] Product ratio. [b] Total yield in %. [c] Reaction temperature in °C.

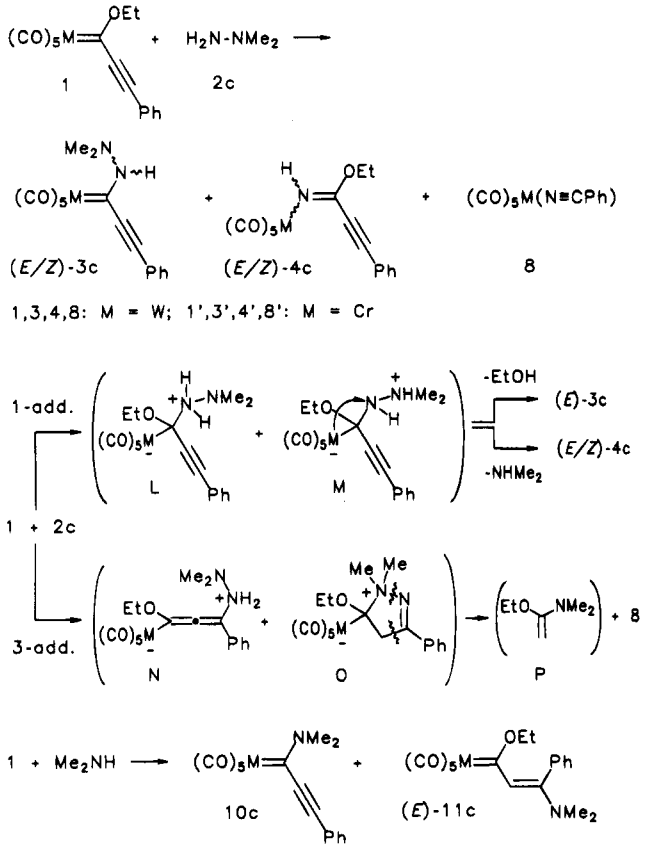
Fragmentation of (Unsymmetrical) 1,1-Dimethylhydrazine (2c)

All products from the reaction of 1,1-dimethylhydrazine (**2c**) with **1** seem to result from addition of the unsubstituted nitrogen atom. A hydrazinocarbene complexes (*Z*)-**3c** and imidates (*E*/*Z*)-**4c** are obtained, most probably, *via* intermediates **L** and **M** (Scheme 5). Interestingly, a benzonitrile complex **8** is formed instead

Scheme 4



Scheme 5



of a zwitterionic cyclization product related to **5**. Compound **8** is thus obtained from **2c** and **1** at 20 °C but not at −78 °C. The generation of a benzonitrile complex **8** is quite unexpected. It may result from 3-addition *via* intermediates **N** and **O**. A cycloreversion of **O** could possibly lead to formation of **8** together with a ketene semiaminal **P**. As a further peculiarity of the reaction of **2c** with **1** high amounts of (dimethylamino)carbene complexes **10c** and (*E*)-**11c** are obtained by 1- and 3-addition, respectively, of dimethylamine to **1**. Dimethylamine, which is eliminated from **M** while compound **4c** is formed, apparently reacts faster with **1** than does **2c**.

Figure 2 shows the molecular structure of (*Z*)-**3c**, and Tables 5, 6, and 8 give the experimental details of the crystal structure of this compound. The plane defined by N(2)−C(1)−C(6) approximately bisects the angle between two *cis*-CO groups at tungsten [C(24)−W−C(1)−N(2) = 46.6°], and the lone pair at N(2) is delocalized as indicated by the interplanar angle C(6)−C(1)−N(2)−N(3) = 176.9(6)° and the short distance C(1)−N(2) = 1.304(9) Å. N(3) has a tetrahedral configuration (sum of bond angles 329.5°).

A stereoisomer (*E*)-**3c** has not been detected in the reaction mixture of **1** with **2c**. This is possibly due to the thermal instability of such a compound.[2,3] From earlier studies (*E*)-**3c** is expected to afford the complex

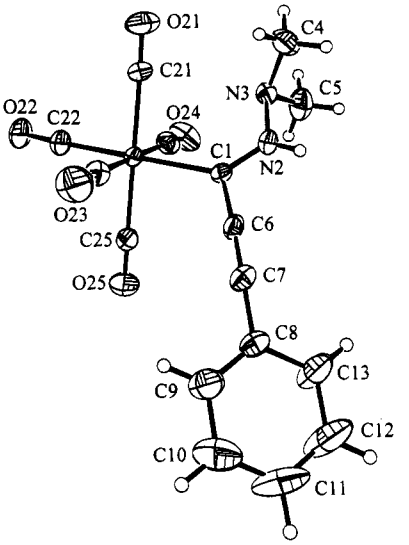
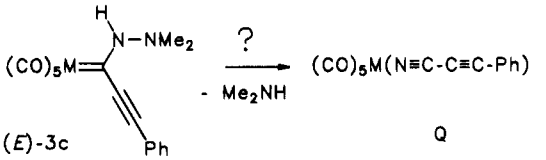


Figure 2. Molecular structure of hydrazinocarbene complex (*Z*)-**3c**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) of (*E*)-3a and (*Z*)-3c

	(*E*)-**3a**		(*Z*)-**3c**
W−C(1)	2.239(7)		2.210(6)
C(1)−N(2)	1.307(9)		1.304(9)
N(2)−N(3)	1.430(8)		1.409(8)
N(2)−C(4)	1.460(9)	N(3)−C(4)	1.463(10)
N(3)−C(5)	1.453(11)		1.446(11)
C(1)−C(6)	1.439(10)		1.427(9)
C(6)−C(7)	1.186(10)		1.197(10)
C(7)−C(8)	1.451(10)		1.433(10)
W−C(1)−N(2)	132.1(5)		128.6(5)
W−C(1)−C(6)	113.8(5)		118.7(5)
C(6)−C(1)−N(2)	114.1(6)		112.7(7)
C(1)−N(2)−N(3)	123.7(6)		123.2(6)
C(1)−N(2)−C(4)	124.6(6)	C(4)−N(3)−C(5)	111.3(7)
C(4)−N(2)−N(3)	111.7(6)	N(2)−N(3)−C(4)	109.3(6)
N(2)−N(3)−C(5)	111.1(6)		108.9(6)
C(1)−C(6)−C(7)	173.9(8)		172.5(8)
C(6)−C(7)−C(8)	175.2(8)		177.7(8)
C(1)−N(2)−N(3)−C(5)	96.3(10)		−120.9(8)
C(6)−C(1)−N(2)−N(3)	−4.1(10)		176.9(6)
C(16)−W−C(1)/ W−C(1)−N(2)	41.3	C(24)−W−C(1)/ W−C(1)−N(2)	46.6

Q by elimination of Me_2NH in a Beckmann-type rearrangement. Experimental evidence for the formation of **Q** is yet to be obtained.



(Unsubstituted) Hydrazine (2d)

The reaction of hydrazine (**2d**) with the chromium complex **1′** (Scheme 6) also corresponds to the reaction scheme outlined above. It leads to the formation of imidate complexes (*E*/*Z*)-**4c′** and of aminocarbene complexes **10d′** and (*Z*)-**11d′** as main reaction products. Small amounts of the (benzonitrile)$Cr(CO)_5$ (**8′**) are also obtained.

(Electron-Deficient) Acetylhydrazine (2e)

The smooth reaction of acetylhydrazine (**2e**) with chromium complex **1′** leads to formation of the *N*-

Table 6. Details of the X-ray Crystal Structures Analyses of (*E*)-3a and (*Z*)-3c: Data Collection and Structures Solution

	(*E*)-3a	(*Z*)-3c
formula	$C_{16}H_{12}N_2O_5W$	$C_{16}H_{12}N_2O_5W$
mol wt	496.13	496.13
cryst color	orange	red-orange
cryst system	triclinic	triclinic
space group (No.)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	8.501(2)	9.380(3)
b (Å)	9.645(2)	9.685(4)
c (Å)	11.860(2)	10.804(3)
α (deg)	103.56(2)	84.77(5)
β (deg)	95.59(2)	80.74(3)
γ (deg)	111.76(2)	66.47(3)
V (Å^3)	859.5(3)	887.8(5)
Z	2	2
D_{calc} (g cm^{-3})	1.917	1.856
μ (cm^{-1})	67.5	65.3
wavelength (Å)	0.710 73	0.710 73
F(000) (e)	472	472
diffractometer	Enraf-Nonius MACHIII	Enraf-Nonius MACHIII
scan mode	$\omega-2\theta$	$\omega-2\theta$
$[(\sin\theta)/\lambda]_{max}$ (Å^{-1})	0.62	0.62
T (°C)	−50	−50
abs corr	ψ-scan (empirical)	ψ-scan (empirical)
transm	69.2 ↔ 99.9%	71.1 ↔ 99.9%
no. of measd reflcns	3648 ($\pm h,\pm k,-l$)	3818 ($\pm h,+k,\pm l$)
no. of indep reflcns	3474	3596
no. of obsd reflcns [$>2\sigma(I)$]	3.49	3213
R_{av}	0.027	0.021
no. of refined params	222	222
R (all data)	0.043	0.036
wR^2 (all data)	0.083	0.086
resid elec dens (e Å^{-3})	2.11 (−1.84)	1.15 (−1.23)
H atoms	calculated	calculated
programs used	EXPRESS, MolEN, SHELX-86, SHELXL-93, ORTEX	

Table 7. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) of (*E*)-3a[a]

	x	y	z	U(eq)
W	7262(1)	4157(1)	1433(1)	31(1)
C(1)	6879(9)	3330(8)	3039(6)	37(2)
N(2)	6132(8)	1938(7)	3164(5)	42(1)
N(#)	6091(10)	1638(9)	4288(6)	50(2)
C(4)	5321(12)	497(9)	2186(7)	55(2)
C(5)	4484(14)	545(14)	4657(9)	75(3)
C(6)	7566(9)	4569(9)	4138(6)	40(2)
C(7)	8149(10)	5684(9)	4981(6)	40(2)
C(8)	8848(9)	7124(9)	5948(6)	40(2)
C(9)	8322(11)	7155(10)	7027(6)	47(2)
C(10)	8899(12)	8549(12)	7903(7)	59(2)
C(11)	10009(12)	9888(11)	7724(8)	60(2)
C(12)	10565(12)	9859(11)	6677(9)	67(3)
C(13)	9980(10)	8471(10)	5788(7)	52(2)
C(14)	6304(9)	5741(8)	2136(6)	39(2)
O(14)	5752(8)	6621(7)	2506(6)	60(2)
C(15)	8089(10)	2519(9)	601(7)	42(2)
O(15)	8469(8)	1615(7)	54(5)	62(2)
C(16)	4851(9)	2700(7)	463(6)	37(2)
O(16)	3561(7)	1918(7)	−148(5)	59(2)
C(17)	7683(9)	5060(9)	74(7)	42(2)
O(17)	7905(8)	5564(8)	−706(5)	60(2)
C(18)	9714(10)	5668(9)	2338(7)	44(2)
O(18)	11062(8)	6528(8)	2851(6)	71(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

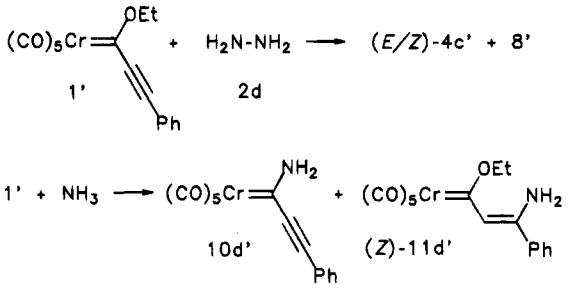
acetylpyrazole (12e) (75%) as the only organic product (Scheme 7). Since the nucleophilicity of the substituted nitrogen atom of **2e** is amide-like and therefore low, the addition of the NH_2 group of **2e** to **1′** becomes the main reaction pathway. It is initiated by a Michael-type addition and follows the principles outlined above.

Table 8. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) of (*Z*)-3c[a]

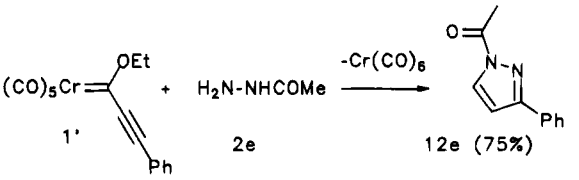
	x	y	z	U(eq)
W	550(1)	1616(1)	1886(1)	32(1)
C(1)	2943(7)	1392(7)	2079(6)	31(1)
N(2)	3766(7)	2103(7)	1450(6)	39(1)
N(3)	3219(7)	3175(7)	482(6)	40(1)
C(4)	3102(11)	4643(10)	837(9)	58(2)
C(5)	4287(11)	2681(12)	−664(9)	66(3)
C(6)	3780(7)	307(8)	2966(7)	36(2)
C(7)	4484(8)	−725(8)	3623(7)	41(2)
C(8)	5347(9)	−1998(9)	4368(7)	43(2)
C(9)	4613(12)	−2639(11)	5286(10)	66(3)
C(10)	5456(17)	−3914(13)	5961(11)	91(4)
C(11)	7053(17)	−4538(12)	5686(11)	95(5)
C(12)	7719(14)	−3891(16)	4772(12)	111(5)
C(13)	6958(11)	−2627(13)	4120(10)	79(3)
C(21)	−184(9)	3905(8)	1733(8)	44(2)
O(21)	−642(8)	5171(7)	1631(7)	75(2)
C(22)	−1595(9)	1819(9)	1690(9)	50(2)
O(22)	−2850(6)	1983(8)	1548(7)	70(2)
C(23)	42(9)	1712(9)	3791(8)	48(2)
O(23)	−227(9)	1756(8)	4861(6)	77(1)
C(24)	1167(10)	1512(9)	−14(8)	46(2)
O(24)	1499(9)	1443(8)	−1069(6)	71(2)
C(25)	1294(9)	−679(8)	2055(8)	43(2)
O(25)	1717(8)	−1948(6)	2157(7)	66(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

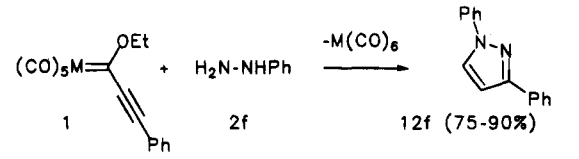
Scheme 6



Scheme 7



Scheme 8

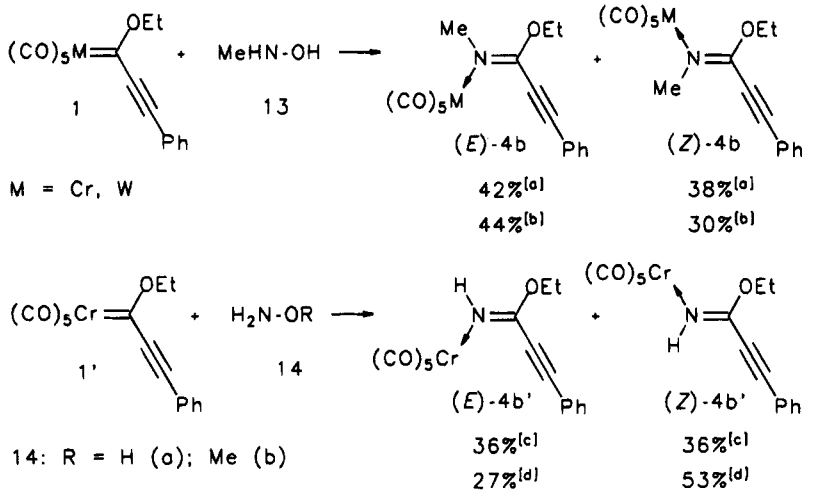


The configurational assignment of **12e** is based on the deshielding of 5-H (δ 8.10) by the anisotropic effect of the (N)C=O group and also on the deshielding of the *o*-H's of the phenyl group by the C=N unit. As expected, an NOE between the $COCH_3$ and the phenyl group was not observed.

Phenylhydrazine (2f)

The hydrazinolysis of **1** (or **1′**) with phenylhydrazine (**2f**) at 80 °C for 4 h affords the *N*-phenylpyrazole (**12f**)

Scheme 9



[a] obtained from 1, [b] obtained from 1', [c] obtained from 14a, [d] obtained from 14b

(Scheme 8) as the only isolated product. The reaction is initiated by a 3-addition of the unsubstituted nitrogen atom of **2f** to **1** and followed by a cyclization as outlined above.

Imidates 4 from Hydroxylamines 13 and 14

The formation of imidate complexes **4** from the reaction of hydrazines **2** with carbene complexes **1** involves the insertion of a NH fragment into the M=C bond of the carbene complexes. An insertion of similar type is also observed in reactions of hydroxylamines **13** or **14** with **1** (Scheme 9).[2] Apparently these reactions follow a similar pattern as is outlined above, but they give better yields of imidate complexes **4** than obtained with hydrazines **2**.

Experimental Section

All operations were performed under argon. Solvents were dried by distillation from sodium/benzophenone. Melting points are uncorrected. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were obtained with Bruker WM 300 and WP 360 spectrometers. Multiplicities 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 analyser; column chromatography, Merck-Kieselgel 100; TLC, Merck DC-Alufolien Kieselgel 60 F 254. R_f values refer to TLC tests.

Pentacarbonyl[1-(1,2-dimethylhydrazino)-3-phenylpropynylidene]tungsten [(*E*)-3a and (*Z*)-3a], Pentacarbonyl(ethyl *N*-methyl-3-phenylpropiolimidato-*N*)tungsten [(*E*)-4a and (*Z*)-4a], and Pentacarbonyl(1,2-dimethyl-3-phenyl-3-pyrazolin-5-ylidene)tungsten (5a). Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1**) (482 mg, 1.00 mmol) is added to a precooled solution of 1,2-dimethylhydrazine (**2a**) in 3 mL of diethyl ether [generated from 1,2-dimethylhydrazine dihydrochloride, 266 mg (2.00 mmol) and concentrated KOH/H_2O in diethyl ether/H_2O] with vigorous stirring at −78 °C within 5 min. After a few minutes a yellow solution is obtained, from which the solvent is removed in vacuo (20 °C, 15 Torr). According to the ^{1}H NMR spectrum (integration of the NCH_3 and OCH_2 groups) in C_6D_6 a mixture of (*E*)-**3a**:(*Z*)-**3a**:(*E*)-**4a**:(*Z*)-**4a**:**5a** = 3:2:4:2:4 is formed. Chromatography on silica gel with pentane/diethyl ether (2:1) affords a yellow band of (*E*/*Z*)-**4a** [173 mg, 34%, $R_f = 0.8$ in pentane/diphenyl ether (2:1), (*E*)-**4a**:(*Z*)-**4a** = 2:1; separation by fractional crystallization from 10 mL of pentane at −15 °C], a red band of (*E*/*Z*)-**3a** [139 mg, 28%, $R_f = 0.4$ in pentane/diethyl ether (2:1), (*E*)-**3a**:(*Z*)-**3a** = 3:2; fractional crystallization from 10 mL of pentane at −15 °C yields red platelets of the (*E*) isomer and red needle of the (*Z*) isomer (mp 112 °C)], and a pale yellow band of **5a** [114 mg, 23%, $R_f = 0.2$ in pentane/diethyl ether (2:1); yellowish crystals from pentane at −15 °C, mp 150 °C]. The reaction of **1** with **2a** at 20 °C yields (*E*)-**3a**:(*Z*)-**3a**:(*E*)-**4a**:(*Z*)-**4a**:**5a** = 3:2:0:0:48 according to the ^{1}H NMR spectrum. Chromatography affords **5a** [397 mg, 80%].

(*E*)-3a. ^{1}H NMR (C_6D_6): δ 7.40, 7.00 and 6.95 (2:1:2 H, *o*-:*m*-:*p*-H, Ph), 5.66 (1 H, q, $^2J = 6$ Hz, NH), 3.20 (3 H, s, 1-NCH_3), 1.95 (3 H, d, $^2J = 6$ Hz, 2-$NHCH_3$). ^{13}C NMR ($CDCl_3$): δ 212.3 (W=C), 202.9 and 198.9 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 131.8, 130.4, 129.0 (2:1:2, CH each, *o*-:*m*-:*p*-C, Ph), 123.1 and 121.4 [C(q) each, *i*-C Ph and C3], 89.1 [C(q), C2], 46.6 (1-NCH_3), 36.9 (2-NCH_3). IR (diffuse reflection) (cm^{-1}) (%): $\tilde{\nu} = 3304.3$ (10) [ν(N−H)], 2171.8 [ν(C≡C)], 2060.0 (20), 1895.0 (100) [ν(C≡O)]. IR (hexane): 2063.5 (20), 1975.4 (10), 1930.2 (100). MS (70 eV) [*m*/*z* (%)] (^{184}W): 496 (20), 468 (20), 440 (30), 412 (50), 384 (30), 356 (70) [M^+ − 5CO], 328 (100). Anal. Calcd for $C_{16}H_{12}N_2O_5W$ (496.1): C, 38.73; H, 2.44; N, 5.65. Found: C, 38.86; H, 2.56; N, 2.76.

(*Z*)-3a. ^{1}H NMR (C_6D_6): δ 7.35, 7.00 and 6.97 (2:1:2 H, *o*-:*m*-:*p*-H, Ph), 6.02 (1 H, q, $^2J = 6$ Hz, NH), 2.70 (3 H, s, 1-NCH_3), 2.10 (3 H, d, $^2J = 6$ Hz, 2-$NHCH_3$). ^{13}C NMR ($CDCl_3$): δ 212.1 (W=C), 203.8 and 197.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 131.7, 130.2, 129.0 (2:1:2, CH each, *o*-:*m*-:*p*-C, Ph), 122.5 and 122.0 [C(q) each, *i*-C Ph and C3], 91.6 [C(q), C2], 40.7 (1-NCH_3), 36.1 (2-NCH_3). IR (diffuse reflection) (cm^{-1}) (%): $\tilde{\nu} = 3295.3$ (5) [ν(N−H)], 2172.7 [ν(C≡C)], 2061.3 (40), 1901.8 (100) [ν(C≡O)]. MS (70 eV) [*m*/*e* (%)] (^{184}W): 496 [M^+].

(*E*)-4a. ^{1}H NMR (C_6D_6): δ, 7.50, 6.90 and 6.85 (2:1:2 H, *o*-:*m*-:*p*-H, Ph), 3.55 (2 H, q, OCH_2), 3.00 (3 H, s, NCH_3), 0.75 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 202.4 and 199.3 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 153.9 [C(q), C=N]; 132.3, 131.0, 128.9 (2:2:1, CH each, *o*-:*m*-:*p*-C, Ph); 119.5 [C(q), *i*-C, Ph], 102.0 [C(q), C3], 80.2 [C(q), C2], 68.2 (OCH_2), 46.5 (NCH_3), 14.3 (CH_3, Et). IR (hexane) (cm^{-1}) (%): $\tilde{\nu} = 2068.3$ (10), 1972.9 (10), 1928 (100), 1897.0 (30) [ν(C≡O)]. IR (diffuse reflection): 3309.6 (10) [ν(N−H)], 2217.9 [ν(C≡C], 2067.7 (20), 1973.3 (20), 1905.0 (100) [ν(C≡O)], 1603.3 (30) [ν(C=N)]. MS (70 eV) [*m*/*e* (%)] (^{184}W): 511 (10) [M^+], 483 (5), 455 (20), 427 (40), 399 (30), 371 (40) [M^+ − 5CO], 343 (50), 187 (100). Anal. Calcd for $C_{17}H_{13}NO_6W$ (511.1): C, 39.95; H, 2.56; N. 2.74. Found: C, 39.85; H, 2.67; N, 2.96.

(*Z*)-4a. ^{1}H NMR (C_6D_6): δ 7.05, 7.00 and 6.90 (2:1:2 H, *o*-:*m*-:*p*-H, Ph), 3.75 (2 H, q, OCH_2), 3.25 (3 H, s, NCH_3), 1.05 (3

H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 204.3 and 199.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 155.6 [C(q), C=N]; 132.2, 131.0, 128.9 (2:2:1, CH each, *o*-:*m*-:*p*-C, Ph); 119.0 [C(q), *i*-C, Ph], 102.0 [C(q), C3], 80.2 [C(q), C2], 67.8 (OCH_2), 50.2 (NCH_3), 14.3 (CH_3, Et). IR (hexane) (cm^{-1}) (%): $\tilde{\nu}$ = 2068.4 (10), 1972.6 (10), 1928.9 (100), 1894.0 (30) [ν(C≡O)]. IR (diffuse reflection): 3343.8 (10) [ν(N−H)], 2209.0 [ν(C≡C)], 2067.8 (20), 1973.8 (20), 1907.8 (100) [ν(C≡O)], 1587.7 (30) [ν(C=N)]. Anal. Calcd for $C_{17}H_{13}NO_6W$ (511.1): C, 39.95; H, 2.56; N, 2.74. Found: C, 39.89; H, 2.74; N, 3.02

5a. ^1H NMR (C_6D_6): δ 7.05 and 6.85 (3:2 H, Ph), 6.60 (1 H, s, 4-H), 3.20 (3 H, s, 1-NCH_3), 2.30 (3 H, s, 2-NMe). ^{13}C NMR ($CDCl_3$): δ 203.5 and 200.1 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 176.9 [C(q), C5], 145.9 [C(q), C3]; 130.0, 129.2 and 128.9 (1:2:2 C, CH each, Ph), 128.5 [C(q), *i*-C, Ph], 123.1 (CH, C4), 38.6 (1-NCH_3), 33.5 (2-NCH_3). IR (hexane) (%): $\tilde{\nu}$ = 2057.5 (10), 1978.7 (10), 1963.3 (5), 1917.8 (100) [ν(C≡O)]. MS (70 eV) [*m/e* (%)] (^{184}W): 496 (50) [M^+], 468 (40), 440 (40), 412 (20), 384 (50), 356 (80) [M^+ − 5CO], 91 (70), 86 (80), 51 (100). Anal. Calcd for $C_{16}H_{12}N_2O_5W$ (496.1): C, 38.73; H, 2.44; N, 5.65. Found: C, 39.01; H, 2.52; N, 5.66.

Pentacarbonyl(1,2-dimethyl-3-phenyl-3-pyrazolin-5-ylidene)chromium (5a′). Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1′**) (350 mg, 1.00 mmol) is added to 1,2-dimethylhydrazine (**2a**) in 3 mL of diethyl ether [generated from 1,2-dimethylhydrazine dihydrochloride, 266 mg (2.00 mmol), and concentrated KOH/H_2O in diethyl ether/H_2O] with vigorous stirring at −20 °C within 5 min. The reaction is slightly exothermic and yields a yellow solution, from which the solvent is removed in vacuo (20 °C, 15 Torr). Chromatography on silica gel with pentane/dichloromethane (10:1) affords a pale yellow band of **5a′** [299 mg, 81%, R_f = 0.3 in pentane/dichloromethane (2:1), yellowish crystals from pentane at −15 °C, mp 160 °C, dec]. ^1H NMR (C_6D_6): δ 7.15 and 6.95 (3:2 H, Ph), 6.50 (1 H, s, 4-H), 3.50 (3 H, s, 1-NCH_3), 2.35 (3, H, s, 2-NMe). ^{13}C NMR (C_6D_6): δ 224.3 and 220.5 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 190.8 [C(q), C5], 145.5 [C(q), C3]; 129.9, 129.2 and 128.8 (1:2:2 C, CH each, Ph), 128.6 [C(q), *i*-C, Ph], 121.9 (CH, C4), 37.8 (1-NCH_3), 33.9 (2-NCH_3). IR (hexane) (%): $\tilde{\nu}$ = 2049.3 (20), 1937.9 (10), 1925.9 (100) [ν(C≡O)]. MS (70 eV) [*m/e* (%)]: 364 (50) [M^+], 336 (40), 308 (40), 280 (30), 252 (50), 224 (80) [M^+ − 5CO], 172 (50) [224 − Cr], 171 [ligand − H], 93 (100), 91 (100). Anal. Calcd for $C_{16}H_{12}CrN_2O_5$ (364.3): C, 52.76; H, 3.32; N, 7.69. Found: C, 52.59; H, 3.47; N, 7.69.

Pentacarbonyl[1-(1-methylhydrazino)-3-phenylpropynylidene]tungsten [(*E*)-3b and (*Z*)-3b], Pentacarbonyl(ethyl *N*-methyl-3-phenylpropiolimidato-*N*)tungsten [(*E*)-4a and (*Z*)-4a], Pentacarbonyl(2-methyl-3-phenyl-3-pyrazolin-5-ylidene)tungsten (5b), and Pentacarbonyl(1-methyl-5-phenylpyrazole-*N*)tungsten (6b) from 1 and 2b. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1**) (482 mg, 1.00 mmol) is added to a precooled solution of methylhydrazine (**2a**) (138 mg, 3.00 mmol) in 3 mL of diethyl ether at −78 °C with vigorous within 5 min. A yellow solution is obtained, from which the solvent is removed (15 Torr, 20 °C). The ^1H NMR spectrum in C_6D_6 (360 MHz, integration of the NCH_3 and OCH_2 signals) shows (*E*)-**3b**:(*Z*)-**3b**:(*E*)-**4a**:(*E*)-**4a**:**5b**:**6b** = 3:2:3:1:1:1. Chromatography on silica gel with pentane/dichloromethane (10:1 to 2:1) affords a pale yellow band of **6b** [39 mg, 8%, R_f = 0.3 in pentane/dichloromethane (2:1), yellowish crystals from pentane at −15 °C], a yellow band with (*E*/*Z*)-**4a** [153 mg, 30%, R_f = 0.8 in pentane/diethyl ether (2:1), see above], a red band with (*E*/*Z*)-**3b** [174 mg, 36%, R_f = 0.4 in pentane/diethyl ether (2:1)], and a pale yellow band of **5b** [34 mg, 7%, R_f = 0.2 in pentane/diethyl ether (2:1)]. The reaction of **1** with **2b** at 20 °C affords (*E*)-**3b**:(*Z*)-**3b**:(*E*)-**4a**:(*Z*)-**4a**:**5b**:**6b** = 0:0:3:1:10:15, total yield 76%.

(*E*)-3b. ^1H NMR (C_6D_6): δ 7.35, 7.00 and 6.95 (2:1:2 H, *o*-:*m*-:*p*-H, Ph), 4.55 (2 H, s, NH_2), 2.95 (3 H, q, NCH_3). ^{13}C NMR ($CDCl_3$): δ 203.6 and 198.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 203.3 (W=C); 131.9, 130.5, 129.0 (2:1:2, CH each, *o*-:*m*-:*p*-C, Ph), 123.0 and 121.5 [C(q) each, *i*-C Ph and C3], 89.6 [C(q), C2], 49.4 (NCH_3). IR (diffuse reflection): $\tilde{\nu}$ = 3352.0 (10) [ν(N−H)], 2174.8 [ν(C≡C)], 2060.8 (20), 1972.2 (20), 1888.0 (100) [ν(C≡O)]. MS (70 eV) [*m/e* (%)] (^{184}W): 482 (20) [M^+], 454 (5), 426 (50), 398 (10), 370 (30), 342 (100). Anal. Calcd for $C_{15}H_{10}N_2O_5W$ (482.1): C, 37.37; H, 2.09; N, 5.81. Found: C, 37.51; H, 2.02; N, 6.07.

(*Z*)-3b. ^1H NMR (C_6D_6): δ 7.40, 7.00 and 6.98 (2:1:2 H, *o*-:*m*-:*p*-H, Ph), 4.80 (2 H, s, NH_2), 2.55 (3 H, q, NCH_3). ^{13}C NMR ($CDCl_3$): δ 202.2 and 198.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 203.6 (W=C); 131.7, 130.2, 128.9 (2:1:2, CH each, *o*-:*m*-:*p*-C, Ph), 124.5 and 122.0 [C(q) each, *i*-C Ph and C3], 91.2 [C(q), C2], 43.9 (NCH_3). IR (diffuse reflection): $\tilde{\nu}$ = 3354.3 (5) and 3278.8 (2) [ν(N−H)], 2175.6 [ν(C≡C)], 2060.9 (40), 1970.3 (50), 1940.0 (60), 1889.8 (100) [ν(C≡O)]. MS (70 eV) [*m/e* (%)] (^{184}W): 482 [M^+]. Anal. Calcd for $C_{15}H_{10}N_2O_5W$ (482.1): C, 37.37; H, 2.09; N, 5.81. Found: C, 37.43; H, 2.20; N, 5.93.

5b. ^1H NMR (C_6D_6): δ 7.05 and 6.98 (3:2 H, m and "d", Ph), 6.80 (1 H, s, 4-H), 6.60 (1 H, s, broad, NH), 2.20 (3 H, 2, 2-NMe).

6b. ^1H NMR (C_6D_6): δ 7.33 (1 H, d, ^3J = 2.5 Hz, 3-H), 7.05 and 6.75 (3:2 H, m and "d", Ph), 5.70 (1 H, d, ^3J = 2.5 Hz, 4-H), 3.32 (3 H, s, 1-NCH_3). ^{13}C NMR (C_6D_6): δ = 203.1 and 200.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 149.0 (CH, C3), 148.0 [C(q), C5], 131.0 [C(q), *i*-C, Ph]; 130.8, 130.3, 130.1 (2:2:1, CH each, *o*-:*m*-:*p*-C, Ph), 109.0 [C(q), C4], 39.6 (NCH_3). IR (diffuse reflection) (cm^{-1}) (%): $\tilde{\nu}$ = 2070.8 (50), 1975.1 (50), 1892.5 (100) [ν(C≡O)]. Anal. Calcd for $C_{15}H_{10}N_2O_5W$ (482.1): C, 37.37; H, 2.09; N, 5.81. Found: C, 37.54; H, 2.15; N, 6.02.

Pentacarbonyl(1-methyl-5-phenylpyrazole-N)chromium (6b′) from 1′ and 2b. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1′**) (350 mg, 1.00 mmol) in 4 mL of ethanol is added to methylhydrazine (**8b**) (138 mg, 3.00 mmol) in 1 mL of ethanol with vigorous stirring at 20 °C within 5 min. The reaction is slightly exothermic and yields a yellow solution. The ^1H NMR spectrum in C_6D_6 (360 MHz, integration of the OCH_2 signals) shows **6b′** as the main product. The solvent is removed in vacuo (20 °C, 15 Torr), and the yellow oily residue is crystallized from 10 mL of pentane at −78 °C [259 mg, 74%, R_f = 0.3 in pentane/dichloromethane (2:1), yellowish crystals from pentane at −15 °C].

6b. ^1H NMR (C_6D_6): δ 7.35 (1 H, d, ^3J = 2.5 Hz, 3-H), 7.03 and 6.72 (3:2 H, m and "d", Ph), 5.70 (1 H, d, ^3J = 2.5 Hz, 4-H), 3.13 (3 H, s, 1-NCH_3). IR (diffuse reflection) (cm^{-1}) (%): $\tilde{\nu}$ = 2067.5 (50), 1981.4 (50), 1898.5 (100) [ν(C≡O)]. Anal. Calcd for $C_{15}H_{10}CrN_2O_5$ (350.3): C, 51.44; H, 2.88; N, 8.00. Found: C, 51.65; H, 3.00; N, 8.13.

1-Methyl-5-phenylpyrazole (7b). Pentacarbonyl(1-methyl-5-phenylpyrazole-N)chromium (**6b′**) in C_6D_6 is heated to 60 °C for 10 h. The ^1H NMR of the solution shows signals of **6b′** and **7b** in a ratio of 1:5, but after 20 h at 60 °C signals of **7b** only are detected. ^1H NMR (C_6D_6): δ 7.53 (1 H, s, broad, 3-H), 7.05 (5 H, m, Ph), 6.10 (1 H, s broad, 4-H), 3.40 (N-CH_3).

Pentacarbonyl[1-(2′,2′-dimethylhydrazino)-3-phenylpropynylidene]tungsten [(*Z*)-4c and (*Z*)-4c], (Benzonitrile)pentacarbonyltungsten (8), Pentacarbonyl[(2*E*)-1-ethoxy-3-(dimethylamino)-3-phenyl-2-propenylidene]tungsten (10c), and Pentacarbonyl[(2*E*)-1-(dimethylamino)-3-phenyl-2-propynylidene]tungsten (11c) from 1 and 2c. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1**) (482 mg, 1.00 mmol) is added to a precooled solution of 1,1-dimethylhydrazine (**2c**) (180 mg, 3.00 mmol) in 3 mL of diethyl ether with vigorous stirring at −78 °C within 5 min. After a few minutes a yellow solution is obtained, from which the solvent is removed in vacuo (20 °C, 15 Torr). According to the ^1H NMR spectrum (integration of the NCH_3 and OCH_2 groups) in C_6D_6 a mixture of (*Z*)-**3c**:(*E*)-**3c**:(*E*)-**4c**:(*Z*)-**4c**:**8**:**10c**:**11c** = 6:0:6:4:0:5:1 is formed. Chromatography on silica gel with pentane/diethyl ether (2:1) affords a yellow band of (*E*/*Z*)-**4c** [169 mg, 34%, R_f = 0.8 in pentane/diethyl ether (2:1), (*E*)-**4c**:(*Z*)-**4c** = 6:1; separation by fractional crystallization from 10 mL of pentane at −15 °C], a red band of (*Z*)-**3c** [199 mg, 40%, R_f = 0.4 in pentane/diethyl ether (2:

1); red platelets from 10 mL of pentane at −15 °C, mp 88 °C], and a pale yellow band of **10c** [110 mg, 21%, R_f = 0.3 in pentane/diethyl ether (1:1)].[12] The reaction of **1** with **2c** at 20 °C yields (*Z*)-**3c**:(*e*)-**3c**:(*E*)-**4c**:(*Z*)-**4c**:**8**:**10c**:(*E*)-**11c** = 0:0:6:1:1:1:7 according to the ^{1}H NMR spectrum. Chromatography affords **8** [38 mg, 9%, R_f = 0.80 in pentane/dichloromethane (4:1), yellow crystals][13] and (*E*)-**11c** [205 mg, 39%, R_f = 0.2 in pentane/diethyl ether (1:1)].[12]

(*Z*)-3c. ^{1}H NMR (C_6D_6): δ 7.85 (1 H, s broad, NH), 7.60 and 6.95 (2:3 H, "d" and m, Ph), 2.00 [6 H, s, $N(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 229.9 (W=C); 206.4 and 199.6 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 132.3, 130.5, 129.1 (2:1:2, CH each, *o*-:*m*-:*p*-C, Ph), 122.6 and 118.5 [C(q) each, *i*-C Ph and C3], 93.3 [C(q), C2], 46.9 (NCH_3). IR (diffuse reflection): $\tilde{\nu}$ = 3226.0 (10), [ν(N−H)], 2182.4 [ν(C≡C)], 2061.3 (20), 1975.7 (20), 1911.7 (100) [ν(C≡O)]. MS (70 eV) [*m/e* (%)] (^{184}W): 496 (20) [M^+], 468 (25), 440 (30), 412 (30), 384 (30), 356 (80), 127 (100). Anal. Calcd for $C_{16}H_{12}N_2O_5W$ (496.1): C, 38.73; H, 2.44; N, 5.65. Found: C, 38.85; H, 2.39; N, 5.67.

(*E*)-4c. ^{1}H NMR (C_6D_6): δ 7.60, 7.15 and 7.05 (2:1:2 H, *o*-:*m*-:*p*-H, Ph), 6.50 (1 H, s broad, NH), 3.30 (2 H, q, OCH_2), 0.90 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 202.4 and 197.9 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 158.8 [C(q), C=N]; 132.9, 131.4, 129.9 (2:2:1, CH each, *o*-:*m*-:*p*-C, Ph); 118.9 [C(q), *i*-C, Ph], 102.0 [C(q), C3], 78.4 [C(q), C2], 67.7 (OCH_2), 15.1 (CH_3). IR (hexane) (cm^{-1}) (%): $\tilde{\nu}$ = 2068.3 (10), 1972.9 (10), 1928.1 (100), 1897.0 (30) [ν(C≡O)]. IR (diffuse reflection): 3309.6 (10) [ν(N−H)], 2217.9 [ν(C≡C)], 2067.7 (20), 1973.3 (20), 1905.0 (100) [ν(C≡O)], 1603.3 (30) [ν(C=N)]. MS (70 eV) [*m/e* (%)] (^{184}W): 497 (10) [M^+], 469 (5), 441 (20), 413 (20), 385 (20), 357 (20) [M^+ − 5CO], 127 (100) [N≡CC≡CPh$^+$]. Anal. Calcd for $C_{16}H_{11}NO_6W$ (497.1): C, 38.66; H, 2.23; N, 2.82. Found: C, 38.94; H, 2.38; N, 3.10.

(*Z*)-4c. ^{1}H NMR (C_6D_6): δ 7.20, 7.10 and 7.08 (2:1:2 H, *o*-:*m*-:*p*-H, Ph), 7.05 (1 H, s broad, NH), 3.80 (2 H, q, OCH_2), 1.05 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 208.6 and 197.6 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 159.6 [C(q), C=N]; 132.6, 131.4, 128.8 (2:1:2, CH each, *o*-:*m*-:*p*-C, Ph); 118.6 [C(q), *i*-C, Ph], 98.1 [C(q), C3], 76.3 [C(q), C2], 68.8 (OCH_2), 14.6 (CH_3). IR (hexane) (cm^{-1}) (%): $\tilde{\nu}$ = 2068.4 (10), 1972.6 (10), 1928.9 (100), 1894.0 (30) [ν(C=O)]. IR (diffuse reflection): 3343.8 (10) [ν(N−H)], 2209.0 [ν(C≡C)], 2067.8 (20), 1973.8 (20), 1907.8 (100) [ν(C≡O)], 1587.7 (30) [ν(C=N)]. Anal. Calcd for $C_{16}H_{11}NO_6W$ (497.1): C, 38.66; H, 2.23; N, 2.82. Found: C, 38.85; H, 2.27; N, 3.05. Found: C, 38.89; H, 2.34; N, 3.12.

Pentacarbonyl(ethyl 3-phenylpropiolimidato-*N*)chromium [(*E*)-4c′ and (*Z*)-4c′], Pentacarbonyl[(2E)-1-ethoxy-3-(dimethylamino)-3-phenyl-2-propenylidene]chromium (10′), and (Benzonitrile)(pentacarbonyl)chromium (8′) from 1′ and 2c. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1′**) (350 mg, 1.00 mmol) in 3 mL of dichloromethane is added dropwise to 1,1-dimethylhydrazine (**2c**) (180 mg, 3.00 mmol) in 1 mL of ethanol at 20 °C within 5 min with vigorous stirring. The reaction is slightly exothermic and yields a yellow solution. After the solvent has been removed in vacuo (20 °C, 15 Torr), a yellow oil is obtained. The ^{1}H NMR spectrum in C_6D_6 (360 MHz, integration of the OCH_2 signals) shows (*E*)-**4c′**:(*Z*)-**4c′**:**8′** = 5:3:8. Chromatography on silica gel with pentane/dichloromethane (10:1) affords a small bright yellow band with **8′** [15 mg, 5%, R_f = 0.80 in pentane/dichloromethane (4:1), yellow crystals].[13] The second yellow band contains (*E*)-**4c′** [91 mg, 25%, R_f = 0.50 in pentane/dichloromethane (4:1), yellow spherical crystals from pentane at −15 °C] and (*Z*)-**4c′** [55 mg, 15%, R_f = 0.55 in pentane/dichloromethane (4:1), yellow needles from pentane at −15 °C, mp 81 °C]. The compounds (*E*)-**4c′** and (*Z*)-**4c′** are separated by fractional crystallization from pentane at −15 °C. A third yellow fraction contains **10′** [160 mg, 40%, R_f = 0.3 in pentane/diethyl ether (1:1), yellow crystals].[12]

(*E*)-4c′. ^{1}H NMR (C_6D_6): δ 7.50, 7.15 and 7.10 (2:1:2 H, *o*-:*m*-:*p*-H, Ph), 6.40 (1 H, s broad, NH), 3.80 (2 H, q, OCH_2), 1.10 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 220.8 and 214.9 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 165.6 [C(q), C=N]; 132.7, 131.3, 129.0 (2:2:1, CH each, *o*-:*m*-:*p*-C, Ph); 119.5 [C(q), *i*-C, Ph], 100.2 [C(q), C3], 78.8 [C(q), C2], 66.9 (OCH_2), 14.6 (CH_3). IR (hexane) (cm^{-1}) (%): $\tilde{\nu}$ = 2219.2 (5) [ν(C≡C)], 2064.3 (10), 1975.2 (10), 1936.9 (100), 1912.5 (30) [ν(C≡O)]. IR (diffuse reflection): 3308.5 (10) [ν(N−H)], 2221.1 [ν(C≡C)], 2065.7 (20), 1982.1 (20), 1917.6 (100) [ν(C≡O)], 1608.4 (30) [ν(C=N)]. MS (70 eV) [*m/e* (%)]: 365 (50) [M^+], 337 (30), 309 (20), 281 (40), 253 (50), 225 (60) [M^+ − 5CO], 196 (50), 173 (30) [225 − Cr], 172 [ligand − H], 153 (70), 128 (80), 127 (80), 123 (70), 101 (80), 77 (100). Anal. Calcd for $C_{16}H_{11}CrNO_6$ (365.3): C, 52.61; H, 3.04; N, 3.83. Found: C, 52.94; H, 3.23; N, 4.05.

(*Z*)-4c′. ^{1}H NMR (C_6D_6): δ 7.35, 7.18 and 7.15 (2:2:1 H, *o*-:*m*-:*p*-H, Ph), 7.00 (2 H, s broad, NH), 4.10 (2 H, q, OCH_2), 135 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 222.0 and 215.4 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 166.1 [C(q), C=N]; 132.4, 131.3, 128.3 (2:1:2, CH each, *o*-:*m*-:*p*-C, Ph); 119.2 [C(q), *i*-C, Ph], 96.9 [C(q), C3], 77.0 [C(q), C2], 66.4 (OCH_2), 14.6 (CH_3). IR (hexane) (cm^{-1}) (%): $\tilde{\nu}$ = 2209.4 (5) [ν(C≡C)], 2064.6 (10), 1978.3 (10), 1938.3 (100), 1911.2 (30) [ν(C≡O)]. IR (diffuse reflection): 3350.3 (10) [ν(N−H)], 2215.7 [ν(C≡C)], 2064.2 (20), 1979.5 (30), 1930.1 (100) [ν(C≡O)], 1591.8 (20) [ν(C=N)]. Anal. Calcd for $C_{16}H_{11}CrNO_6$ (365.3): C, 52.61; H, 3.04; N, 3.83. Found: C, 52.78; H, 3.12; N, 3.76.

8′. ^{1}H NMR (C_6D_6/CS_2 1:1, 25 °C): δ 7.30 and 6.90 (3:2 H, m each, C_6H_5), 6.60 (1 H, s, 2-H), 4.40 (2H, q broad, OCH_2), 2.80 and 2.20 (3 H each, s broad each, NMe_2), 0.60 (3 H, t, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 20 °C): δ 293.7 (Cr=C), 224.8 and 219.5 [1:4C, *trans*- and *cis*-CO $Cr(CO)_5$], 156.2 [C(q), C3), 137.7 [C(q), *i*-C, Ph]; 128.9, 128.8 and 128.6 (1:2:2 C, CH each, Ph), 118.8 (CH, C2), 73.2 (OCH_2), 41.4 (2 C, broad, NMe_2), 14.2 (CH_3, Et). IR (hexane) (cm^{-1}) (%): $\tilde{\nu}$ = 2048.0 (20), 1982.1 (5), 1928.2 (100) [ν(C≡O)]. MS (70 eV) [*m/e* (%)]: 395 (20) [M^+], 367 (20), 339 (10), 311 (50), 283 (30), 255 (100) [M^+ − 5CO], 227 (80), 184 (60), 158 (80), 155 (60).

Pentacarbonyl(ethyl 3-phenylpropiolimidato-*N*)chromium [(*E*)-4c′ and (*Z*)-4c′], Pentacarbonyl[1-amino-3-phenyl-2-propynylidene]chromium (10d′), Pentacarbonyl-[(2*Z*)-1-ethoxy-3-amino-3-phenyl-2-propenylidene]-chromium [(*Z*)-11d′], and (Benzonitrile)(pentacarbonyl)-chromium (8′) from 1′ and 2d. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1′**) (350 mg, 1.00 mmol) and hydrazine monohydrate (**2d**) (150 mg, 3.00 mmol) are reacted as described above in EtOH at 20 °C. The ^{1}H NMR spectrum in C_6D_6 (360 MHz, integration of the OCH_2 signals) shows (*E*)-**4c**:(*Z*)-**4c**:**8′**:**10d′**:(*Z*)-**11d′** = 3:2:1:2:1. Chromatography on silica gel yields **8′** [20 mg, 7%, R_f = 0.80 in pentane/dichloromethane (4:1), yellow crystals, literature ref 8], (*E*)-**4c′** (88 mg, 24%, see above) together with (*Z*)-**4c′** (58 mg, 16%, see above), **10d′** (92 mg, 25%, red crystals),[8] and **11d′** (37 mg, 10%, yellow crystals).[8]

1-Acetyl-3-phenylpyrazole (12e) from 1′ and 2e. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1′**) (350 mg, 1.00 mmol) and acetylhydrazine (**2e**) (74 mg, 1.00 mmol) are reacted in 3 mL of dichloromethane for 2 h at 20 °C. After the mixture has turned yellow the solvent is removed in vacuo (20 °C, 15 Torr). Chromatography on silica gel with pentane/dichloromethane (10:1) affords colorless $Cr(CO)_6$ and a pale yellow band of **12e** [140 mg, 75%, R_f = 0.2 in pentane/dichloromethane (2:1), yellowish crystals from pentane at −15 °C, mp 58 °C]. ^{1}H NMR (C_6D_6): δ 8.10 (1 H, d, ^3J = 3 Hz, 5-H), 7.80 and 7.10 (2:3 H, "d" and m, Ph), 6.20 (1 H, d, ^3J = 3 Hz, 4-H), 2.50 (3 H, s, $COCH_3$). ^{13}C NMR ($CDCl_3$): δ 169.3 [C(q), NC=O], 155.6 [C(q), C3], 133.0 [C(q), *i*-C, Ph]; 129.7, 129.4 and 128.7 (1:2:2 C, CH each, Ph), 107.9 and 107.3 (CH each, C4 and C5), 21.7 (CH_3). IR (diffuse reflection (cm^{-1})

(12) For spectroscopic data see: (a) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47−C52. (b) Aumann, R. *Chem. Ber.* **1993**, *126*, 1867−1872. (c) Duetsch, M.; Stein, F.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1993**, *126*, 2535−2541.

(13) Aumann, R.; Althaus, S.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 357−364.

(%): ν = 1732.6 (90) [ν(NC=O)], 1539.3 (30) and 1503.8 (20) [ν(C=N)] and [ν(C=C)]. MS (70 eV) [*m/e* (%)]: 186 (60) [M^+], 145 (60), 144 (100) [$M^+ - O{=}C{=}CH_2$], 117 (60), 115 (60). Anal. Calcd for $C_{11}H_{10}N_2O$ (186.2): C, 70.95; H, 5.41; N, 15.04. Found: C, 70.65; H, 5.38; N, 14.96.

1-Phenyl-3-phenylpyrazole (12f) from 1 or 1′ and 2f. Pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1**) (482 mg, 1.00 mmol) [or pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1′**) (350 mg, 1.00 mmol)] and phenylhydrazine (**2f**) (108 mg, 1.00 mmol) in 3 mL of toluene are heated for 4 h at 80 °C. It is shown by TLC that **1** has been consumed completely. Chromatography on silica gel with pentane/dichloromethane (10:1) affords colorless $W(CO)_6$ [$Cr(CO)_6$] and a pale yellow band of **12f** [165 (198) mg, 75 (90)%, R_f = 0.5 in pentane/dichloromethane (3:1), colorless felty crystals from pentane at −15 °C, mp 80 °C]. ^{1}H NMR (C_6D_6): δ 8.05 and 7.60 (2:2 H, "d" each, *o*-H of Ph each), 7.33 (1 H, d, ^3J = 3 Hz, 3-H), 7.20 and 7.05 (2:2 H, "t" each, *m*-H of Ph each), 7.12 and 6.85 (1:1 H, "t" each, *p*-H of Ph each), 6.40 (1 H, d, ^3J = 3 Hz, 4-H). ^{13}C NMR (C_6D_6): δ 152.9 [C(q), C3], 140.4 [C(q), *i*-C, 1-Ph], 133.7 [C(q), *i*-C, 3-Ph]; 129.7, 129.0 and 128.6 (2:2:1 C, CH each, 3-Ph); 126.1, 126.0 and 119.1 (2:1:2 C, CH each, 1-Ph); 118.9 and 105.0 (CH each, C4 and C5). MS (70 eV) [*m/e* (%)]: 220 (100) [M^+], 192 (20), 178 (5), 165 (10), 143 (5), 116 (10), 89 (30), 77 (50). Anal. Calcd for $C_{15}H_{12}N_2$ (220.3): C, 81.79; H, 5.49; N, 12.72. Found: C, 82.00; H, 5.64; N, 13.01.

Pentacarbonyl(ethyl *N*-methyl-3-phenylpropiolimidato-*N*)tungsten [(*E*)-4a and (*Z*)-4a] from 1 and 13. Triethylamine (101 mg, 1.00 mmol) in 2 mL of ethanol is added to pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)tungsten (**1**) (482 mg, 1.00 mmol) and *N*-methylhydroxylamine hydrochloride (166 mg, 2.00 mmol) in 3 mL of ethanol with vigorous stirring at 20 °C within 5 min. A yellow solution is obtained from which the solvent is removed in vacuo (20 °C, 15 Torr). According to the ^{1}H NMR spectrum in C_6D_6 of the pentane extract, (*E*)-**4a**:(*Z*)-**4a** = 1:1 is obtained. Fractional crystalization from 10 mL of pentane at −15 °C yields (*E*)-**4a** (215 mg, 42%) and (*Z*)-**4a** (194 mg, 38%).

Pentacarbonyl(ethyl *N*-methyl-3-phenylpropiolimidato-*N*)chromium [(*E*)-4a′ and (*Z*)-4a′] from 1′ and 13. Triethylamine (101 mg, 1.00 mmol) in 2 mL of ethanol is added to a solution of pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1′**) (350 mg, 1.00 mmol) and *N*-methylhydroxylamine hydrochloride (166 mg, 2.00 mmol) in 3 mL of ethanol with vigorous stirring at 20 °C within 5 min. A yellow solution is obtained from which the solvent is removed in vacuo (20 °C, 15 Torr). According to the ^{1}H NMR spectrum in C_6D_6 of the pentane extract, (*E*)-**4a′**:(*Z*)-**4a′** = 3:2 is obtained. Fractional crystallization from 10 mL of pentane at −15 °C yields (*E*)-**4a′** (168 mg, 44%) and (*Z*)-**4a′** (112 mg, 30%).

Pentacarbonyl(ethyl 3-phenylpropiolimidato-*N*)chromium [(*E*)-4c′ and (*Z*)-4c′] from 1′ and 14a. Triethylamine (101 mg, 1.00 mmol) in 2 mL of ethanol is added to a solution of pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1′**) (350 mg, 1.00 mmol) and hydroxylamine hydrochloride (138 mg, 2.00 mmol) in 3 mL of ethanol with vigorous stirring at 20 °C within 5 min. A yellow solution is obtained from which the solvent is removed in vacuo (20 °C, 15 Torr). The residue is extracted with pentane. It is shown by TLC and a ^{1}H NMR spectrum in C_6D_6 that a mixture of (*E*)-**4c′**:(*Z*)-**4c′** = 1:1 is obtained, which can be crystallized from 10 mL of pentane to give yellow crystals (263 mg, 72%).

Pentacarbonyl(ethyl 3-phenylpropiolimidato-*N*)chromium [(*E*)-4c′ and (*Z*)-4c′] from 1′ and 14b. Triethylamine (101 mg, 1.00 mmol) in 2 mL of ethanol is added to a solution of pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium (**1′**) (350 mg, 1.00 mmol) and *O*-methylhydroxylamine hydrochloride (83 mg, 1.00 mmol) in 3 mL of ethanol with vigorous stirring at 20 °C within 5 min. A yellow solution is obtained from which the solvent is removed in vacuo (20 °C, 15 Torr). The residue is extracted with pentane. It is shown by TLC and a ^{1}H NMR spectrum in C_6D_6 that a mixture of (*E*)-**4c′**:(*Z*)-**4c′** = 1:2 is obtained, which can be crystallized from 10 mL of pentane to give yellow crystals (292 mg, 80%).

Acknowledgment. This work was supported by the *Volkswagen-Stiftung* and by the *Fonds der Chemischen Industrie*.

Supplementary Material Available: Tables of positional and displacement parameters and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

OM9409682