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Stereochemistry of 4-(*NH*-amino)-1-metalla-1,3-dienes $(CO)_5M{=}C(OEt){-}CH{=}C(NHR)Ph$ (M = Cr, W)[1]

Rudolf Aumann *, Klaus B. Roths, Michael Kößmeier, Roland Fröhlich

Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, D-48149, Münster, Germany

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Abstract

Structures of 4-(*NH*-amino)-1-metalla-1,3-dienes [= (enamino)carbene complexes] $(CO)_5M{=}C(OEt){-}CH{=}C(NHR)Ph$ **6a**–**d** (M = Cr, W; R = H, CH_2Ph, Ph) have been studied in solid state and in solution. It was shown by X-ray analyses that compounds **6a**, **6b** (M = Cr; R = H, Ph) and **6d** (M = W; R = CH_2Ph) adopt (*Z*) configuration in solid state, in contrast to compound $(CO)_5Cr{=}C(OEt){-}CH{=}C(NC_4H_8)Ph$ **6e**, for which (*E*) configuration was found. A (*Z*/*E*) equilibrium of compounds **6** is established in solution. It was shown by NMR techniques that the (*Z*/*E*) interconversion of the *NH*-derivative **6b** is fast on the NMR time-scale, but the equilibrium in solution is shifted to predominance of the stereoisomer (*Z*)-**6b**. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Aminocarbene complexes; Carbene complexes; Chromium and tungsten complexes; 4-Amino-1-metalla-1,3-dienes; Enamines

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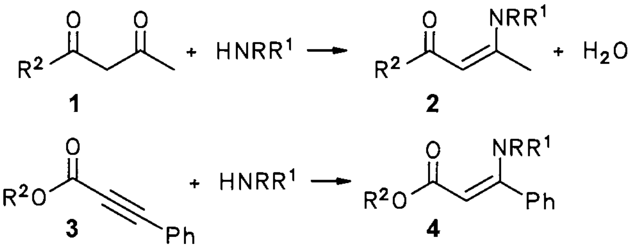
1. Introduction

Enamines are widely used in organic synthesis as synthetic equivalents of organic carbonyl compounds. Enamines with electron-withdrawing groups in conjugation to the C=C(N) bond, like enaminones **2** or enamino esters **4**, are structurally related to 1,3-dicarbonyl compounds and may be derived from 1,3-dicarbonyl compounds **1** by condensation with an amine, and e.g. from a propargylic ester **3** by addition of an amine to the C≡C bond, respectively (Scheme 1) [1].

The latter reaction has been extended to the formation of (enamino)carbene complexes $(CO)_5M{=}C(OEt){-}CH{=}CPh(NRR^1)$ **6** by addition of an amine $HNRR^1$ to the C≡C of (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt){-}C{\equiv}CPh$ **5** (M = Cr, W). Addition of amines to compounds **5** can be highly regio- and stereoselective such that under an appropriate set of conditions, a single product is obtained. Thus, secondary alkyl amines $HN(Alkyl)_2$ (e.g. dimethylamine, pyrrolidine or morpholine) at 20°C produce 4-amino-1-metalla-1,3-dienes **6**, which have an (*E*)-configurated C=C(N) double bond in virtually quantitative yield [3]d. Furthermore, addition of primary aryl amines H_2NAr to compounds **5** is also highly regio- and stereoselective but yields complexes **6** in (*Z*)-configuration only (Scheme 2) ([2]k). Two side reactions must be encountered, which



Scheme 1. Common routes to enaminones **2**, and enamino esters **4**, respectively.

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* Corresponding author. Fax: + 49 251 8339772.

[1] Part 94 of the series: Organic Synthesis of Transition Metal Compounds. For preceeding paper see: R. Aumann, K. Roths, R. Fröhlich, Organometallics, (1998) submitted.

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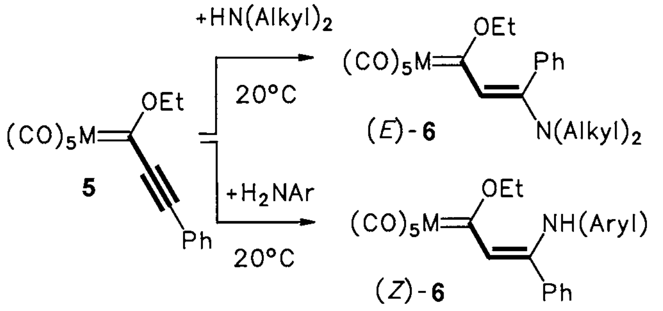


Scheme 2. Formation of 4-amino-1-metalla-1,3-dienes in (*E*)-, and (*Z*) configuration, respectively, with high regio- and stereoselectivity

lead to formation of 1-substitution products $(CO)_5M{=}C(NRR^1){-}C{\equiv}CPh$ **7**, and allenylidene complexes $(CO)_5M{=}C{=}C{=}CPh(NRR^1)$ **8**, respectively [2,3].

Whilst enaminones **2** and enamino esters **4** have become common reagents in organic synthesis [4], the synthetic potential of (enamino)carbene complexes **6** is currently in an early stage of investigation [3]. Transformations studied so far, include addition of alkynes to give cyclopentadienes ([2]c,e; [5]) or pyridines [6], and addition of isocyanides to give amino pyrroles ([2]m,o) or amino naphthalenes ([2]l,p).

Though (enamino)carbene complexes **6** are structurally related to enamino esters **4** with respect to the basic carbon skeleton, it should be noted that most reaction patterns of compounds **6** find no parallel with compounds **4**. This may at least partially be attributed to the high propensity of the $(CO)_5M$ unit to stabilize negative charge, thus that highly polarized adducts are readily formed.

(Enamino)carbene complexes $(CO)_5M{=}C(OEt){-}CH{=}CPh(NRR^1)$ **6** which have a *NH* functional group ($R^1 = H$) are most easily modified by substitution of the hydrogen atom ([2]k,l,o,p) and for this reason deserve special attention with respect to synthetic application. Since the stereochemistry of such compounds was found to have a strong influence on the overall reaction course, we wish to report on structural investigations of compounds **6a**–**6e**. Though on first sight there are eight planar stereoisomers of compounds **4** and **6**, which should be encountered: *cis*/*trans* isomers with respect to the C=C bond, *s-cis*/*s-trans* isomers with respect to the X=C–C=C system [7] and *syn*/*anti* isomers with respect to the arrangement of the N–R group (Scheme 3), it is quite obvious that the number of planar stereoisomers of metal complexes **6** is restricted by steric interaction of the bulky $M(CO)_5$ group. Stereoisomers with non-planar zwitterionic iminium carbonylmetalate units $(^-OC)_5M{-}C{=}C{-}C{=}N^+$ are obtained instead of planar (enamino)carbene moieties $(OC)_5M{=}C{-}C{=}C{-}N$.

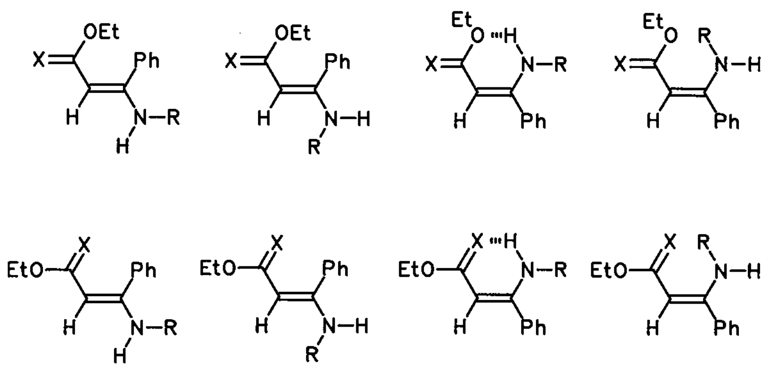
2. Results and discussion

Concern over the structure of compound **6b** was raised by controversial reports, in which (*Z*) configuration ([2]k) as well as (*E*) configuration were suggested for this compound ([2]i; [8]) In order to unravel this entanglement, we investigated solid state structures of (*NH*-enamino)carbene complexes and compared the results with NOE measurements in solution.

2.1. X-Ray structure analyses of (NH-enamino)carbene complexes

Crystal structure analyses were performed of the (*NH*-enamino)carbene complexes **6a**, **6b** and **6d** (see Section 3 for experimental data). It could be unambiguously demonstrated that in all crystals collected of these three compounds only (*Z*) stereoisomer were present (Figs. 1–3).

Common to the *M,C,C,C(NH)* backbone of compounds **6a**, **6b** and **6d** is an almost planar *s-trans* conformation [e.g. **6a**: Cr1–C4–C5–C6 −173.5(0.3)°, C4–C5–C6–N7 −7.2(0.6); **6b**: Cr–C2–C3–C4 169.9 (0.2), C2–C3–C4–N1 −179.1 (0.3)] and equalized bond distances C2–C3 [e.g. **6d**: 1.408 (8) Å] and C3–C4 [e.g. **6d**: 1.406 (8) Å] (Table 1) attributed to the influence of zwitterionic structures $(^-OC)_5M{-}C(OEt){=}CH{-}CPh({=}N^+HR)$ on the 4-amino-1-metalla-1,3-diene structure $(OC)_5M{=}C(OEt){-}CH{=}CPh(NHR)$. The im-



Scheme 3. Planar configurations of (*NH*-enamino)carbene complexes **6** [X = $Cr(CO)_5$, $W(CO)_5$] and *NH*-enamino esters **4** (X = O).

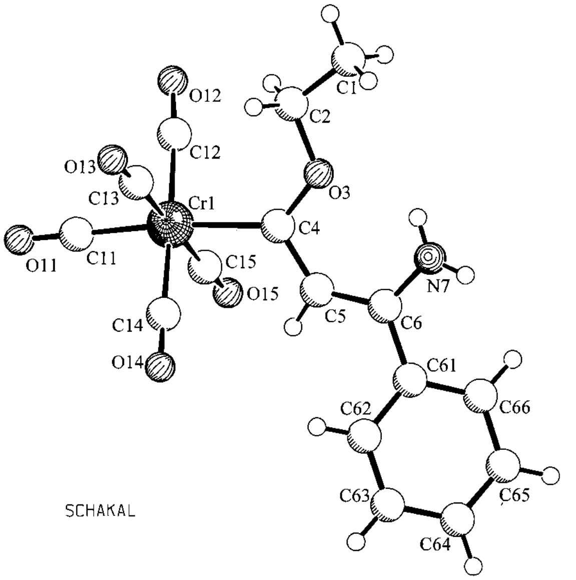


Fig. 1. Molecular structure of (NH_2-enamino)carbene complex (*Z*)-**6a**.

portance of the zwitterionic structure is indicated also by the long M–$C_{carbene}$ distance [e.g. **6d**: 2.256 (6) Å], as well as by the short distance C4–N [e.g. **6d**: 1.328 (8) Å] and an essentially planarized nitrogen atom [sum of valence angles of e.g. **6d**: C4–N1–C5 123.6 (2)° + C4–N1–C8 125.5 (2) + C5–N1–C8 110.7 (2) = 359.5]. The bond distances O3...H7 [e.g. **6a**: 2.07 Å, Fig. 1] and bond angles O3...H7–N [e.g. **6a**: 129°] are in line with the assumption of a hydrogen bridge between the N–H function and the OCH_2 group, by which the (*Z*) configuration of these compounds could be stabilized.

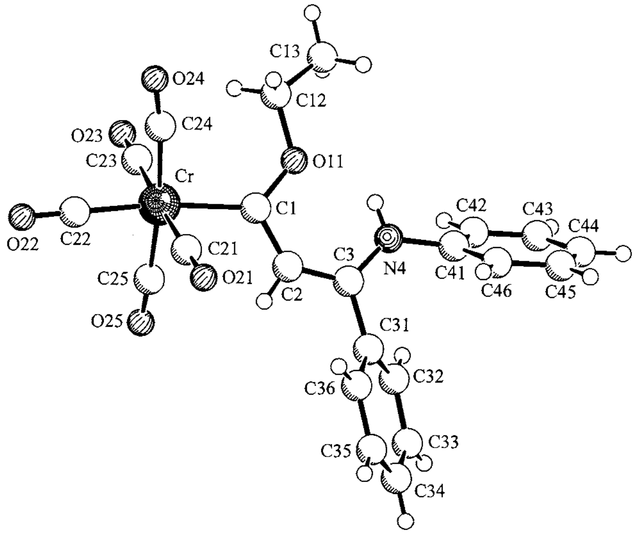


Fig. 2. Molecular structure of the 4-anilino-chroma-1,3-diene (*Z*)-**6b**.

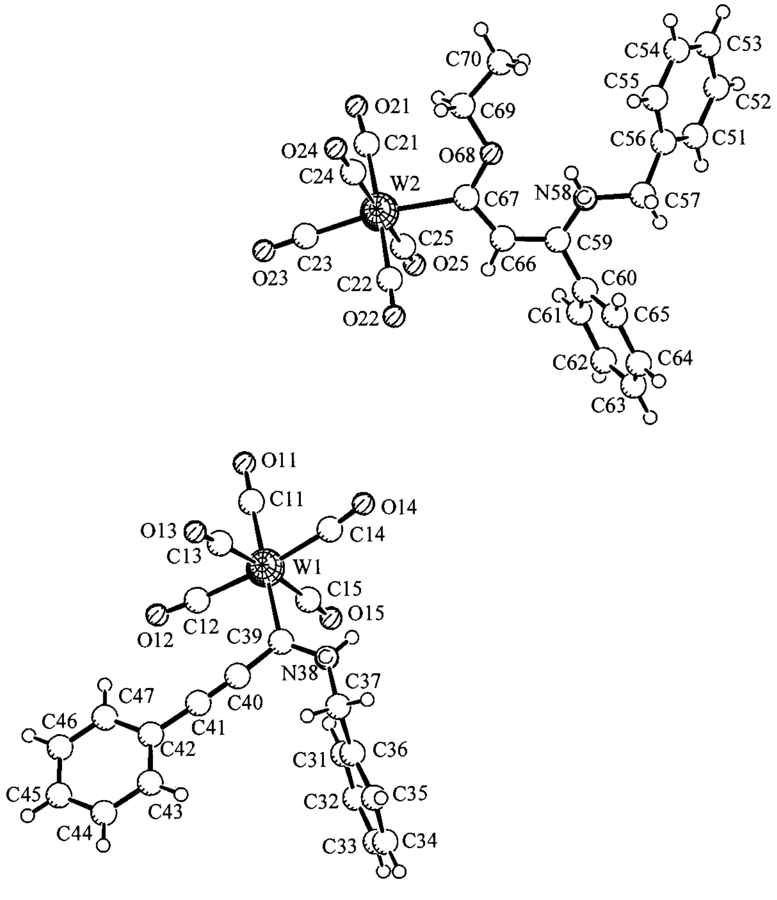


Fig. 3. Molecular structures of 4-benzylamino-1-tungsta-1,3-diene (*Z*)-**6d** together with (1-alkynyl)carbene complex **7d** (in the same crystal).

Table 1
Selected bond lengths of (enamino)carbene complexes **6a**–**f** [Å]

6	M	R	R[1]	[a]	M–C2	C2–C3	C3–C4	C4–N	Lit.[b]	Lit.[c]
a	Cr	H	H	Z	2.108(3)	1.416(4)	1.384(4)	1.332(4)	[6]d	[d]
b	Cr	Ph	H	Z	2.103(2)	1.404(3)	1.389(3)	1.333(3)	[3]k	[d]
c	W	Ph	H	Z	—[e]	—[e]	—[e]	—[e]	[3]m	—
d	W	CH_2Ph	H	Z	2.256(6)	1.408(8)	1.406(8)	1.328(8)	[d]	[d]
e	Cr	$-(CH_2)_4-$		E	2.111(3)	1.413(3)	1.396(3)	1.331(3)	[3]d	[d]
f	W	$-CH_2)_4-$		E	2.250(4)	1.407(5)	1.400(6)	1.328(4)	[3]h	[3]h

[a] Configuration of the C=C(N) bond.

[b] Reference for preparation of this compound.

[c] Reference of X-ray structure.

[d] This paper.

[e] Not determined.

2.2. NMR investigation of (NH-enamino)carbene complex 6c

As indicated in Table 1, *tertiary* (enamino)carbene complexes **6e** and **6f** adopt (*E*) configuration, whilst *primary* and *secondary* (enamino)carbene complexes **6a**–**d** exhibit (*Z*) configuration. Chemical shifts of signal 3-H have been used as rough means for configurational assignment of the structurally related 4-Ph compounds **6a**–**f** (Table 1) ([5]d). A more sophisticated configurational analysis refers to the low-field shift of N–H signals in (*Z*)-**6a**–**d** [e.g. (*Z*)-**6c** 10.59], infering the presence of a hydrogen bridge between the N–H and OEt group as indicated also be bond angles and bond distances in solid state structures (v.s.). Though the configuration of (enamino)carbene complexes **6** is expected to be easily determined by NOE measurements, involving signal 3-H and hydrogen atoms attached to substitutents at C4, we wish to exemplify that this is not the case: In NOESY experiments with compound (*Z*)-**6c** cross-peaks are found both between proton signals of N–H and 3-H as well as between N–H and OCH_2. Obviously, these results are contradictory, since the first effect would indicate (*E*)-, but the latter effect (*Z*) configuration for compound (*Z*)-**6**. A similar ambiguity is observed in ^1H NOE difference experiments. A more sophisticated analysis of the NOE difference spectra reveals that irradiation of signal N–H of (*Z*)-**6c** (signal A, Fig. 4) leads to production of a small negative signal (signal B, Fig. 4), which is shifted strongly up-field compared to the N–H signal of (*Z*)-**6c**, which could be attibuted to a stereoisomer which does not have a hydrogen bridge to the N–H group. Furthermore, irradiation of signal OCH_2 (signal C, Fig. 4) generates a small negative signal, which is shifted up-field (signal D). The new signals B and D quite obviously result from spin saturation-transfer between the OCH_2–, and N–H groups, respectively, between rapidly equilibrating (*Z*/*E*) stereoisomers of compound **6c**. Based on chemical shift differences expected from the anisotropic influence of a neighboring phenyl group, signal D is assigned to the OCH_2 group of the stereoisomer (*E*)-**6c**, which has not been detected before. The experiments indicate that—other than in solid state (v.s.)—there is rapid equilibration of stereoisomers (*Z*)-**6c** and (*E*)-**6c** in solution, but formation of stereoisomer (*Z*)-**6c** is energetically more favorable than of stereoisomer (*E*)-**6c**. The apparently low activation energy for the (*Z*/*E*) isomerization is attributed to the influence of a zwitterionic iminium carbonylmetalate ($^-OC)_5M-C(OEt)=CH-CPh(=N^+HPh)$ structure (v.s. X-ray data of e.g. compound **6d**).

(*NH*-Enamino)carbene complexes (*Z*)-**6a**–**d** readily adopt (*Z*) configuration in solid state as well as in solution. Based on bond distances as well as on proton shifts of the N–H group, the (*Z*) configuration is assumed to be stabilized by a hydrogen bridge (v.s.). Minimization of steric repulsion may be considered another driving force for preferential formation of the (*Z*) configuration. This effect may at least be important in adducts $(CO)_5M=C(OEt)-CH=CPh(OAr)$ obtained by addition of phenols HO–Ar to (1-alkynyl)carbene complexes **5** (in kinetical controlled reaction) as (*E*) stereoisomers, but which readily undergo (*E*/*Z*) isomerization in solution to give (*Z*) stereoisomers apparently for steric reasons [9].

If the hydrogen atom of the N–H group of a (*NH*-enamino)carbene complex **6a**–**d** is replaced by an alkyl substituent R, such that compounds (*NR*$_2$-enamino)carbene complexes are generated, a strong steric interaction of the *NR*$_2$ unit with the 2-OEt group is expected if the enamino unit is planarized by the influences of a zwitterionic structure ($^-OC)_5M-C2=C3-C4=N^+R_2$. This may explain, why zwitterionic compounds **6e**,**f** adopt (*E*) configuration (Fig. 5) in solid state as well as in solution. Interesting to note that in less polarized (*N-acyl*-enamino)carbene complexes, like $(OC)_5Cr=C(OEt)-CH=CPh[NPh(COPh)]$[3p] (*Z*) configuration is achieved due to the electron-withdrawing influence of the COPh group and a strong distortion of the NPh(COPh) group out of plane resulting thereof. Strong distortions from planarity are also

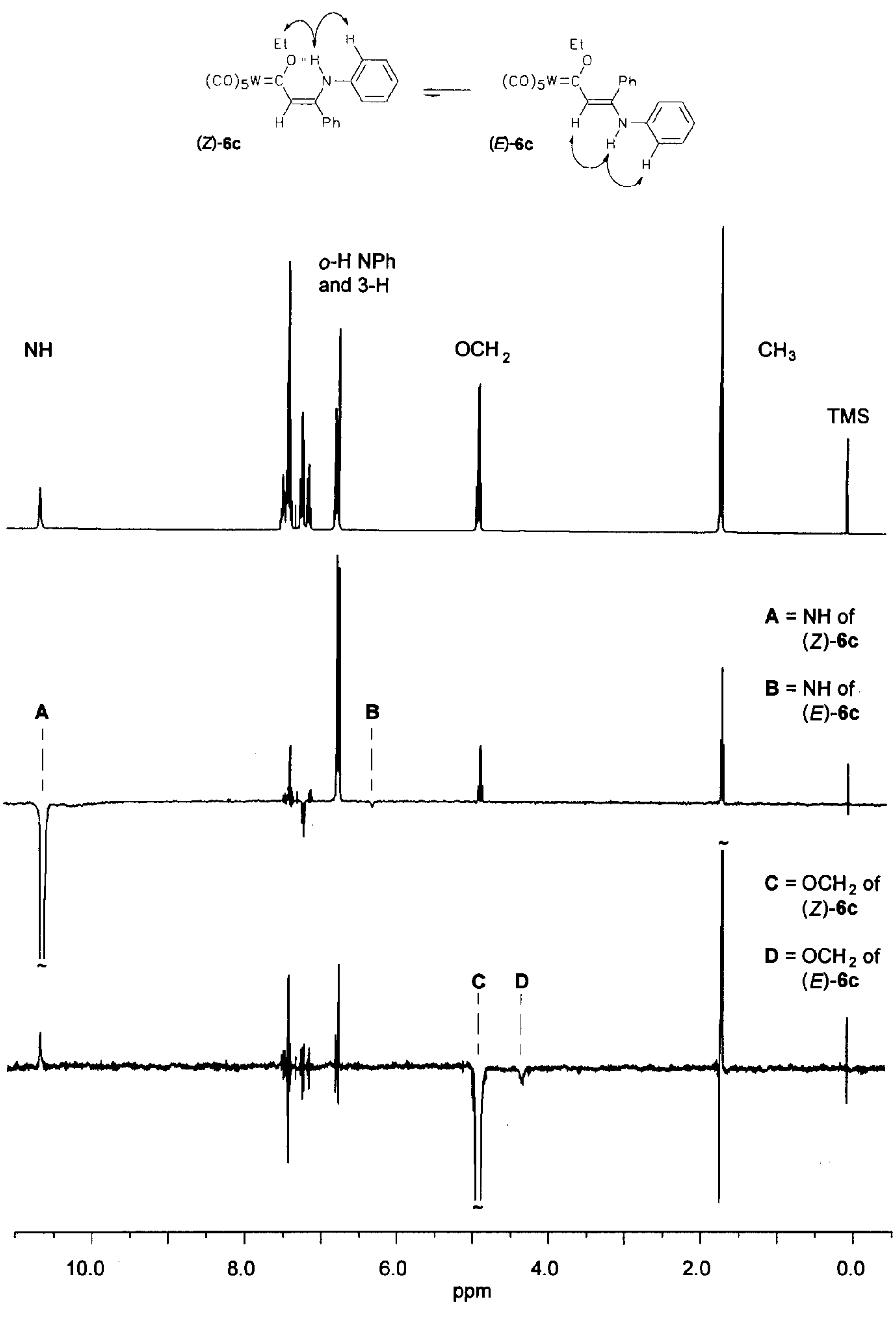


Fig. 4. Selected NOE difference spectra of (*NH*-enamino)carbene complex **6c**.

achieved if bulky substituents are attached to the C=C–C(N) skeleton of an (enamino)carbene complex **1**.

3. Experimental section

All X-ray data sets were collected with an Enraf Nonius CAD4 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92. Further information about the X-ray crystal structure analyses can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD 408299 for compounds **6d** and **7d**, CSD 408298 for **6b**, CSD 408297 for **6e** and CSD 408328 for **6a**, the names of the authors, and the journal citation Tables 2–9.

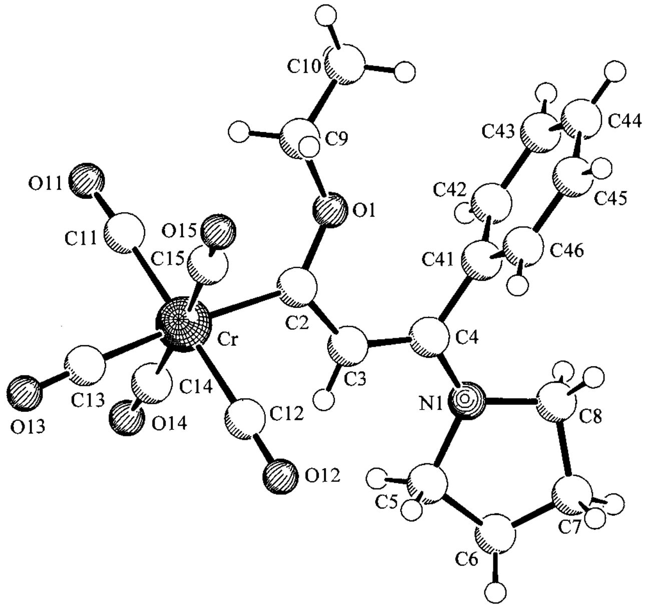


Fig. 5. Molecular structure of 4-pyrrolino-1-chroma-1,3-diene (*E*)-**6d**.

3.1. *Pentacarbonyl[3-amino-1-ethoxy-3-phenyl)-2-propenylidene]chromium (**6a**)*

Prepared according to lit. ([5]d). X-ray crystal structure analysis of **6a**: formula $C_{16}H_{13}CrNO_6$, $M = 367.27$, $0.20 \times 0.20 \times 0.10$ mm, $a = 10.472(2)$, $b = 12.094(2)$, $c = 15.448(2)$ Å, $\alpha = 81.02(1)$, $\beta = 72.10(2)$, $\gamma = 67.51(2)°$, $V = 1718.5(5)$ Å^3, $\rho_{calc} = 1.420$ g cm^{-3}, $\mu = 6.95$ cm^{-1}, empirical absorption correction via scan data ($0.934 \leq C \leq 0.995$), $Z = 4$, triclinic, space group P-1 (No. 2), $\lambda = 0.71073$ Å, $T = 293$ K, $\omega/2$ scans, 7215 reflections collected ($\pm h$, $\pm k$, $+l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 6948 independent and 4476 observed reflections $[I \geq 2\sigma(I)]$, 447 refined parameters, $R = 0.043$, $wR^2 = 0.107$, max. residual electron density 0.34 (-0.32) e Å^{-3}, hydrogens calculated and refined as riding atoms.

3.2. *Pentacarbonyl[1-ethoxy-3-phenyl-3-(phenylamino) 2-propenylidene]chromium (**6b**)*

Prepared according to lit ([2]m). X-ray crystal structure analysis of **6b**: formula $C_{22}H_{17}CrNO_6$, $M = 443.37$, $0.20 \times 0.15 \times 0.10$ mm, $a = 8.484(1)$, $b = 22.137(3)$, $c = 11.576(2)$ Å, $\beta = 94.09(1)$, $V = 2168.6(5)$ Å^3, $D_{calc.} = 1.358$ g cm^{-3}, $\mu = 5.64$ cm^{-1}, no absorption correction ($0.992 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 293$ K, $\omega/2\theta$ scans, 4711 reflections collected ($-h$, $+k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 4414 independent and 2602 observed reflections $[I \geq 2\sigma(I)]$, 275 refined parameters, $R = 0.039$, $Rw_2 = 0.087$, max residual electron density 0.11 (-0.29) e Å^{-3}, H-atoms were calculated and refined as riding atoms.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) for **6a**

Atom	x	y	z	U_{eq}^a
Cr(1)	690(1)	7546(1)	5094(1)	45(1)
C(1)	2998(6)	3341(3)	6057(4)	98(2)
C(2)	2286(6)	4542(3)	5714(3)	86(1)
O(3)	2747(3)	5371(2)	6001(2)	63(1)
C(4)	2243(4)	6552(3)	5795(2)	48(1)
C(5)	2929(3)	7146(3)	6116(2)	50(1)
C(6)	4055(3)	6691(3)	6514(2)	49(1)
N(7)	4624(4)	5539(3)	6755(3)	73(1)
C(61)	4711(3)	7496(3)	6672(2)	47(1)
C(62)	4840(4)	8442(3)	6064(2)	60(1)
C(63)	5484(5)	9180(4)	6191(3)	72(1)
C(64)	6008(4)	8993(4)	6935(3)	69(1)
C(65)	5878(4)	8081(4)	7545(3)	67(1)
C(66)	5237(4)	7326(3)	7425(2)	57(1)
C(11)	−693(4)	8597(3)	4529(2)	56(1)
O(11)	−1562(3)	9247(3)	4203(2)	81(1)
C(12)	−586(4)	6722(3)	5654(2)	58(1)
O(12)	−1405(3)	6268(3)	5960(2)	89(1)
C(13)	1509(4)	6551(3)	4086(3)	53(1)
O(13)	1985(3)	6008(2)	3448(2)	75(1)
C(14)	1964(4)	8371(3)	4495(2)	50(1)
O(14)	2744(3)	8844(2)	4137(2)	74(1)
C(15)	−99(4)	8534(3)	6097(2)	50(1)
O(15)	−544(3)	9113(2)	6717(2)	67(1)
Cr(2)	3326(1)	7837(1)	1009(1)	46(1)
C(21)	2689(6)	10938(4)	−1476(3)	91(2)
C(22)	2848(5)	10119(3)	−668(3)	71(1)
O(23)	2258(3)	9220(2)	−680(2)	59(1)
C(24)	2391(4)	8264(3)	−95(2)	49(1)
C(25)	1821(4)	7498(3)	−314(2)	55(1)
C(26)	1303(4)	7551(3)	−1055(2)	51(1)
N(27)	1099(4)	8473(3)	−1651(2)	70(1)
C(261)	947(4)	6540(3)	−1213(2)	52(1)
C(262)	1751(5)	5376(3)	−1022(3)	76(1)
C(263)	1434(6)	4436(4)	−1172(4)	96(2)
C(264)	311(5)	4637(4)	−1524(3)	80(1)
C(265)	−513(5)	5784(4)	−1715(3)	75(1)
C(266)	−198(4)	6734(3)	−1562(3)	64(1)
C(31)	4135(4)	7365(3)	1978(2)	55(1)
O(31)	4662(3)	7069(3)	2569(2)	78(1)
C(32)	3625(5)	6194(4)	983(3)	70(1)
O(32)	3832(5)	5199(3)	1027(3)	114(1)
C(33)	3126(4)	9389(3)	1227(3)	63(1)
O(33)	3076(4)	10282(3)	1429(2)	99(1)
C(34)	1445(5)	8118(4)	1767(3)	68(1)
O(34)	310(4)	8307(4)	2216(2)	119(1)
C(35)	5155(5)	7594(4)	199(3)	66(1)
O(35)	6285(4)	7439(3)	−260(2)	108(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.3. *Pentacarbonyl[(3-benzylamino-1-ethoxy-3-phenyl)propenylidene]tungsten (**6d**) and pentacarbonyl(1-benzylamino-3-phenyl-2-propin-1-ylidene)tungsten (**7d**)*

A 482 mg (1.00 mmol) sample of pentacarbonyl(3-amino-1-ethoxy-3-phenyl)propenylidene]tungsten (**5b**) in 4 ml of dry diethyl ether is reacted with 108 mg (1.00

Table 3
Selected bond lengths [Å] and angles [°] for **6a**

Cr(1)–C(4)	2.108(3)	O(3)–C(2)–C(1)	109.0(3)
C(1)–C(2)	1.456(5)	C(4)–O(3)–C(2)	122.0(3)
C(2)–O(3)	1.441(4)	O(3)–C(4)–C(5)	110.3(3)
O(3)–C(4)	1.343(4)	O(3)–C(4)–Cr(1)	130.1(2)
C(4)–C(5)	1.416(4)	C(5)–C(4)–Cr(1)	119.6(2)
C(5)–C(6)	1.384(4)	C(6)–C(5)–C(4)	130.5(3)
C(6)–N(7)	1.332(4)	N(7)–C(6)–C(5)	123.9(3)
C(6)–C(61)	1.473(4)	N(7)–C(6)–C(61)	116.4(3)
		C(5)–C(6)–C(61)	119.7(3)

Table 5
Selected bond lengths [Å] and angles [°] for **6b**

Cr(1)–C(1)	2.103(2)	O(11)–C(1)–C(2)	110.2(2)
C(21)–O(21)	1.140(4)	O(11)–C(1)–Cr(1)	129.1(2)
C(22)–O(22)	1.152(4)	C(2)–C(1)–Cr(1)	120.6(2)
C(23)–O(23)	1.142(3)	C(3)–C(2)–C(1)	130.8(2)
C(24)–O(24)	1.137(3)	N(4)–C(3)–C(2)	123.5(2)
C(25)–O(25)	1.141(3)	N(4)–C(3)–C(31)	118.3(2)
C(1)–O(11)	1.347(3)	C(2)–C(3)–C(31)	118.1(2)
C(1)–C(2)	1.404(3)	C(32)–C(31)–C(3)	121.4(2)
O(11)–C(12)	1.444(3)	C(36)–C(31)–C(3)	119.6(2)
C(12)–C(13)	1.444(4)	C(3)–N(4)–C(41)	128.7(2)
C(2)–C(3)	1.389(3)	C(42)–C(41)–N(4)	118.5(2)
C(3)–N(4)	1.333(3)	C(46)–C(41)–N(4)	120.9(2)
N(4)–C(41)	1.427(3)	C(3)–C(31)	1.487(3)

mmol) of benzylamine in 2 ml of diethyl ether. A yellow precipitate is removed after 1 h at 20°C and recrystallized from chloroform/pentane at −20°C to give orange crystals of a 1:1 mixture of **6d** and **7d** (m.p. 95°C, $R_f = 0.7$ in diethyl ether/petrolether 1:1). ^{1}H-NMR (CDCl$_3$) **6d** {**7d**}: δ{9.22 (1 H, t br, *syn*-NH)}, 8.60 (1 H, s br, NH)], {7.40–7.00 (20 H, m, 2 Ph of **6d** and **7d**}, 6.21 (1 H, s, 3-H), {4.69 (2 H, d, $^{3}J = 4.5$ Hz, *anti*-CH$_2$C$_6$H$_5$)}, 4.43 (2 H, q, $^{3}J = 7$ Hz, OCH$_2$), 4.14 (2 H, AB system of CH$_2$Ph, 1.10 (3 H, t, $^{3}J = 7$ Hz, OCH$_2$C*H*$_3$. ^{13}C-NMR (CDCl$_3$) **6d** {**7d**}: δ 270.8 (W=C), {232.8 (W=C)}, 203.8 and 198.3 [*trans*- and *cis*-CO, W(CO)$_5$)], {203.6 and 199.3 (*trans*- and *cis*-CO, W(CO)$_5$)}, 157.4 (Cq, C4), 136.3 and 134.3 (Cq each, *i*-Ph), {134.4 and 129.3 (Cq each, *i*-Ph}, {123.4, 130.9, 130.3, 129.3, 129.1, 128.7, 128.4, 127.7, 127.6, and 127.5 (CH each, Ph of **6d** and **7d**)}, 122.1 (CH, C3), {121.3 (Cq, C4), 91.7 (Cq, C2)}, 76.5 (OCH$_2$), {56.7 (NCH$_2$)}, 50.2 (NCH$_2$), 15.1 (OCH$_2$*C*H$_3$). IR (diffuse refexion), cm^{-1}: 2171.0 [ν(C≡C)]; 2057.2, 1993.3, 1878.2, 1960.1, 1940.3, 1937.9, 1924.8, 1880.3, 1879.8 and 1866.2 [ν(C≡O)]. MS (70 eV), ^{184}W, *m*/*e* (%) **6d**: 588 (20) [M^{+}-1], 561 (20) [M^{+}-CO], 533 (20) [M^{+}-2CO], 505 (20) [M^{+}-3CO], 477 (20) [M^{+}-4CO], 449 (20) [M^{+}-5CO] (20), 265 (40) [ligand^{+}] (40)]. **7d**: 543 (20) [M^{+}], 515 (5) [M^{+}-CO], 487 (30) [M^{+}-2CO], 459 (20) [M^{+}-3CO], 431 (20) [M^{+}-4CO], 219 (20) [ligand^{+}]. Anal. Calc. for C$_{44}$H$_{31}$N$_2$O$_{11}$W$_2$: C, 46.67; H, 2.85; N, 2.47. Found: C, 46.45; H, 2.85; N, 2.68%.

X-ray crystal structure analysis of **6d** and **7d**: formula C$_{44}$H$_{32}$N$_2$O$_{11}$W$_2$, $M = 1132.42$, $0.4 \times 0.25 \times 0.2$ mm, $a = 10.758(1)$, $b = 29.563(3)$, $c = 13.915(1)$ Å, $\beta = 109.03(1)$, $V = 4183.6(6)$ Å^3, $D_{\text{calc.}} = 1.798$ g cm^{-3}, $\mu = 55.57$ cm^{-1}, empirical absorption correction via ϕ scan data ($0.951 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 8948 reflections collected ($-h$, $+k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 8491 independent and 5996 observed reflections [$I \geq 2\sigma(I)$], 539 refined parameters, $R = 0.031$, $Rw_2 = 0.081$, max residual electron density 1.00 (−0.94) e Å^{-3}, H-atoms were calculated and refined as riding atoms.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) for **6b**

Atom	*x*	*y*	*z*	U_{eq}^{a}
Cr(1)	2247(1)	181(1)	2307(1)	55(1)
C(21)	2314(4)	−119(1)	772(3)	81(1)
O(21)	2371(4)	−289(1)	−154(3)	132(1)
C(22)	498(4)	−295(2)	2548(3)	89(1)
O(22)	−591(3)	−591(1)	2685(3)	135(1)
C(23)	2257(3)	509(1)	3804(3)	67(1)
O(23)	2220(3)	715(1)	4707(2)	107(1)
C(24)	3488(4)	−471(1)	2904(3)	70(1)
O(24)	4116(3)	−878(1)	3325(2)	108(1)
C(25)	855(3)	810(1)	1843(3)	70(1)
O(25)	−11(3)	1195(1)	1628(2)	111(1)
C(1)	4074(3)	754(1)	1840(2)	48(1)
O(11)	5489(2)	862(1)	2404(1)	57(1)
C(12)	6069(4)	519(2)	3408(3)	80(1)
C(13)	7458(4)	819(2)	3924(3)	99(1)
C(2)	3879(3)	1115(1)	843(2)	48(1)
C(3)	4852(3)	1554(1)	415(2)	44(1)
C(31)	4288(3)	1876(1)	−664(2)	43(1)
C(32)	4255(3)	2502(1)	−719(2)	53(1)
C(33)	3606(3)	2786(1)	−1706(2)	61(1)
C(34)	3010(3)	2456(2)	−2636(2)	65(1)
C(35)	3043(3)	1842(1)	−2598(2)	64(1)
C(36)	3662(3)	1547(1)	−1611(2)	53(1)
N(4)	6224(3)	1724(1)	951(2)	55(1)
C(41)	7400(3)	2115(1)	544(2)	49(1)
C(42)	7847(3)	2608(1)	1195(3)	66(1)
C(43)	9047(4)	2977(1)	856(3)	84(1)
C(44)	9793(4)	2838(2)	−115(3)	85(1)
C(45)	9350(4)	2348(2)	−760(3)	81(1)
C(46)	8143(3)	1979(1)	−433(2)	65(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **6d** and **7d**

Atom	x	y	z	U_{eq}[a]
W(1)	2674(1)	5181(1)	2993(1)	31(1)
C(11)	3104(7)	5211(2)	4502(5)	44(2)
O(11)	3371(6)	5222(2)	5375(4)	66(2)
C(12)	1814(7)	5808(2)	2875(5)	41(2)
O(12)	1274(5)	6140(2)	2844(4)	63(2)
C(13)	845(7)	4926(2)	2791(5)	42(2)
O(13)	−180(5)	4783(2)	2632(4)	66(2)
C(14)	3480(6)	4550(2)	3225(5)	39(2)
O(14)	3923(5)	4203(2)	3445(4)	62(1)
C(15)	4437(7)	5473(3)	3074(5)	47(2)
O(15)	5390(5)	5644(2)	3105(5)	72(2)
C(31)	3981(7)	5576(2)	−113(5)	42(2)
C(32)	4648(8)	5878(3)	−525(6)	57(2)
C(33)	4642(7)	5831(3)	−1499(6)	51(2)
C(34)	3984(7)	5478(3)	−2075(5)	50(2)
C(35)	3319(6)	5165(2)	−1673(5)	43(2)
C(36)	3305(6)	5216(2)	−684(5)	34(1)
C(37)	2514(6)	4883(2)	−289(5)	37(1)
N(38)	2793(5)	4905(2)	811(4)	36(1)
C(39)	2212(6)	5155(2)	1317(5)	32(1)
C(40)	1194(6)	5442(2)	716(4)	31(1)
C(41)	370(6)	5718(2)	295(5)	34(1)
C(42)	−590(6)	6055(2)	−171(5)	35(1)
C(43)	−1061(6)	6101(2)	−1220(5)	41(2)
C(44)	−1992(7)	6431(2)	−1669(5)	49(2)
C(45)	−2433(7)	6712(3)	−1057(6)	52(2)
C(46)	−1974(7)	6659(3)	−27(6)	55(2)
C(47)	−1060(7)	6341(2)	427(5)	47(2)
W(2)	4570(1)	2952(1)	8179(1)	31(1)
C(21)	5014(6)	2969(2)	9709(5)	36(1)
O(21)	5205(5)	2991(2)	10570(3)	50(1)
C(22)	4021(7)	2931(2)	6624(5)	43(2)
O(22)	3680(6)	2916(2)	5759(4)	69(2)
C(23)	3355(7)	3484(2)	8039(5)	39(2)
O(23)	2715(5)	3798(2)	7969(4)	61(2)
C(24)	3057(7)	2527(2)	8155(5)	38(2)
O(24)	2214(5)	2313(2)	8207(4)	58(1)
C(25)	6094(7)	3395(2)	8335(5)	45(2)
O(25)	6915(6)	3645(2)	8440(5)	75(2)
C(51)	11112(7)	1325(3)	9306(6)	58(2)
C(52)	11765(8)	1094(3)	10193(6)	66(2)
C(53)	11125(8)	770(3)	10555(6)	63(2)
C(54)	9840(8)	679(3)	10044(6)	59(2)
C(55)	9184(7)	908(2)	9160(6)	51(2)
C(56)	9808(6)	1235(2)	8774(5)	41(2)
C(57)	9132(7)	1463(3)	7791(5)	49(2)
N(58)	8142(6)	1787(2)	7882(4)	41(1)
C(59)	7842(6)	2186(2)	7430(4)	34(1)
C(60)	8523(6)	2341(2)	6716(5)	36(1)
C(61)	9166(7)	2748(3)	6878(6)	50(2)
C(62)	9773(8)	2904(3)	6195(7)	65(2)
C(63)	9733(8)	2647(3)	5362(6)	65(2)
C(64)	9087(8)	2247(3)	5193(6)	57(2)
C(65)	8472(6)	2084(3)	5873(5)	44(2)
C(66)	6905(6)	2480(2)	7596(4)	34(1)
C(67)	6065(6)	2418(2)	8178(4)	34(1)
O(68)	6313(4)	2020(1)	8682(3)	40(1)
C(69)	5614(9)	1891(3)	9364(7)	63(2)
C(70)	6263(7)	1492(3)	9942(6)	60(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 7
Selected bond lengths [Å] and angles [°] for **6d** and **7d**

W(1)–C(39)	2.221(6)	C(31)–C(36)–C(37)	122.8(5)
C(11)–O(11)	1.155(8)	C(35)–C(36)–C(37)	118.6(6)
C(12)–O(12)	1.133(7)	N(38)–C(37)–C(36)	113.8(5)
C(13)–O(13)	1.133(8)	C(39)–N(38)–C(37)	128.1(5)
C(14)–O(14)	1.132(8)	N(38)–C(39)–C(40)	115.5(5)
C(15)–O(15)	1.132(8)	N(38)–C(39)–W(1)	126.9(4)
C(37)–N(38)	1.462(8)	C(40)–C(39)–W(1)	117.5(4)
N(38)–C(39)	1.310(8)	C(41)–C(40)–C(39)	172.9(6)
C(39)–C(40)	1.423(8)	C(40)–C(41)–C(42)	177.9(6)
C(40)–C(41)	1.206(8)	C(43)–C(42)–C(47)	119.4(6)
C(41)–C(42)	1.429(9)	C(43)–C(42)–C(41)	120.5(6)
W(2)–C(67)	2.256(6)	C(47)–C(42)–C(41)	120.1(6)
C(56)–C(57)	1.486(9)	C(55)–C(56)–C(57)	121.5(7)
C(57)–N(58)	1.467(8)	C(51)–C(56)–C(57)	120.7(7)
N(58)–C(59)	1.328(8)	N(58)–C(57)–C(56)	111.6(5)
C(59)–C(66)	1.406(8)	C(59)–N(58)–C(57)	127.5(6)
C(59)–C(60)	1.485(8)	N(58)–C(59)–C(66)	123.2(6)
C(66)–C(67)	1.408(8)	N(58)–C(59)–C(60)	119.6(5)
C(67)–O(68)	1.351(7)	C(66)–C(59)–C(60)	117.2(5)
O(68)–C(69)	1.442(8)	C(61)–C(60)–C(65)	119.9(6)
C(69)–C(70)	1.471(10)	C(61)–C(60)–C(59)	119.5(6)
		C(65)–C(60)–C(59)	120.5(6)
		C(59)–C(66)–C(67)	130.0(6)
		O(68)–C(67)–C(66)	110.9(5)
		O(68)–C(67)–W(2)	129.1(4)
		C(66)–C(67)–W(2)	120.0(4)
		C(67)–O(68)–C(69)	121.0(5)
		O(68)–C(69)–C(70)	108.4(6)

*3.4. Pentacarbonyl[1-ethoxy-3-phenyl-3-(1-pyrrolidino)-2-propenylidene]chromium (**6e**)*

Prepared according to lit. ([2]d). X-ray crystal structure analysis of **6e**: formula $C_{20}H_{19}CrNO_6$, $M = 421.36$, $0.45 \times 0.25 \times 0.15$ mm, $a = 10.018(2)$, $b = 10.670(2)$, $c = 11.410(3)$ Å, $\alpha = 64.84(2)$, $\beta = 77.45(2)$, $\gamma = 67.74(2)°$, $V = 1019.3(4)$ Å^3, $D_{calc.} = 1.373$ g cm^{-3}, $\mu = 5.96$ cm^{-1}, empirical absorption correction via scan data ($0.960 \leq C \leq 0.999$), $Z = 2$, triclinic, space group P-1 (No. 2), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4368 reflections collected ($\pm h$, $+k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 4138 independent and 3186 observed reflections [$I \geq 2\sigma(I)$], 254 refined parameters, $R = 0.054$, $Rw_2 = 0.119$, max. residual electron density 0.32 (−0.30) e Å^{-3}, H-atoms were calculated and refined as riding atoms.

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Table 8
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) for **6e**

Atom	x	y	z	$U_{\mathrm{eq}}^{\mathrm{a}}$
Cr	2152(1)	1767(1)	4600(1)	32(1)
C(11)	3769(3)	2085(3)	3449(3)	43(1)
O(11)	4723(3)	2354(3)	2767(3)	72(1)
C(12)	455(3)	1589(3)	5688(3)	40(1)
O(12)	−558(3)	1497(3)	6355(2)	62(1)
C(13)	3153(3)	1207(3)	6040(3)	42(1)
O(13)	3734(3)	892(3)	6939(2)	63(1)
C(14)	1671(3)	3725(3)	4425(3)	35(1)
O(14)	1471(2)	4890(2)	4343(2)	51(1)
C(15)	2752(3)	−244(3)	4835(3)	37(1)
O(15)	3137(3)	−1467(2)	5049(2)	56(1)
C(2)	885(3)	2485(3)	3038(2)	29(1)
O(1)	1244(2)	2150(2)	1978(2)	40(1)
C(9)	2535(3)	1016(4)	1826(3)	57(1)
C(10)	2645(4)	1070(5)	507(4)	68(1)
C(3)	−536(3)	3479(3)	2993(2)	31(1)
C(4)	−1605(3)	3920(3)	2161(2)	30(1)
C(41)	−1450(3)	3295(3)	1172(2)	30(1)
C(42)	−1160(3)	4050(3)	−126(3)	45(1)
C(43)	−1020(4)	3440(4)	−1017(3)	56(1)
C(44)	−1205(4)	2107(4)	−631(3)	54(1)
C(45)	−1526(4)	1370(4)	657(3)	50(1)
C(46)	−1643(3)	1955(3)	1555(3)	40(1)
N(1)	−2889(2)	4895(2)	2260(2)	38(1)
C(8)	−4151(3)	5318(4)	1540(4)	53(1)
C(7)	−5372(4)	5986(7)	2345(7)	123(2)
C(6)	−4835(4)	6570(6)	2960(6)	100(2)
C(5)	−3276(3)	5596(4)	3209(4)	55(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 9
Selected bond lengths [Å] and angles [°] for **6e**

Cr–C(2)	2.111(3)	O(1)–C(2)–C(3)	110.3(2)
C(2)–O(1)	1.343(3)	O(1)–C(2)–Cr	128.7(2)
C(2)–C(3)	1.413(3)	C(2)–O(1)–C(9)	123.4(2)
C(7)–C(6)	1.401(6)	O(1)–C(9)–C(10)	108.1(3)
C(6)–C(5)	1.521(5)	C(4)–C(3)–C(2)	129.6(2)
O(1)–C(9)	1.435(3)	N(1)–C(4)–C(3)	120.8(2)
C(9)–C(10)	1.462(4)	N(1)–C(4)–C(41)	115.2(2)
C(3)–C(4)	1.396(3)	C(3)–C(4)–C(41)	123.9(2)
C(4)–N(1)	1.331(3)	C(42)–C(41)–C(4)	121.1(2)
C(4)–C(41)	1.493(4)	C(46)–C(41)–C(4)	119.6(2)
N(1)–C(5)	1.473(4)	C(4)–N(1)–C(5)	123.6(2)
N(1)–C(8)	1.476(3)	C(4)–N(1)–C(8)	125.5(2)
C(8)–C(7)	1.502(5)	C(5)–N(1)–C(8)	110.7(2)
		N(1)–C(8)–C(7)	101.9(3)
		C(6)–C(7)–C(8)	108.4(4)
		C(7)–C(6)–C(5)	105.9(3)
		N(1)–C(5)–C(6)	103.6(3)
		C(3)–C(2)–Cr	121.0(2)

References

[1] (a) O. Cervinka, in: Z. Rappoport (Ed.), The Chemistry of Enamines 1, John Wiley and Sons, Chichester, 1994, pp. 219–254. (b) J.L. Chiara, A. Gómez-Sánchez, in: Z. Rappoport (Ed.), The Chemistry of Enamines 1, John Wiley and Sons, Chichester, 1994, pp. 287–405. (c) H. Kropf, E. Schaumann, in P. Rademacher (Ed.), Houben-Weyl, 4th edn., vol. E15; Thieme: Stuttgart, 1993, pp. 604–717.

[2] (a) E.O. Fischer, F.R. Kreissl, J. Organomet. Chem. 35 (1972) C47. (b) E.O. Fischer, H.J. Kalder, J. Organomet. Chem. 131 (1977) 57. (c) M. Duetsch, R. Lackmann, F. Stein, A. de Meijere, Synlett (1991) 324. (d) M. Duetsch, F. Stein, R. Lackmann, E. Pohl, R. Herbst-Irmer, A. de Meijere, Chem. Ber. 125 (1992) 2051. (e) F. Stein, M. Duetsch, M. Noltemeyer, A. de Meijere, Synlett (1993) 486. (f) F. Stein, M. Duetsch, E. Pohl, R. Herbst-Irmer, A. de Meijere, Organometallics 12 (1993) 2556. (g) M. Duetsch, S. Vidoni, F. Stein, F. Funke, M. Noltemeyer, A. de Meijere, J. Chem. Soc. Chem. Commun. (1994) 1679. (h) R. Pipoh, R. van Eldik, G. Henkel, Organometallics 12 (1993) 2236. (i) R. Pipoh, R. van Eldik, Organometallics 12 (1993) 2668. (j) A. Rahm, W.D. Wulff, A.L. Rheingold, Organometallics 12 (1993) 597. (k) R. Aumann, P. Hinterding, Chem. Ber. 126 (1993) 421. (l) R. Aumann, Chem. Ber. 126 (1993) 1867. (m) R. Aumann, Chem. Ber. 126 (1993) 2325. (n) R. Aumann, P. Hinterding, C. Krüger, R. Goddard, J. Organomet. Chem. 456 (1993) 145. (o) R. Aumann, Chem. Ber. 127 (1994) 725. (p) R. Aumann, B. Jasper, R. Goddard, C. Krüger, Chem. Ber. 127 (1994) 717. (q) R. Aumann, B. Jasper, R. Fröhlich, Organometallics 14 (1995) 3173.

[3] For recent reviews see: (a) A. de Meijere, Pure and Appl. Chem. 68 (1996) 61. (b) R. Aumann, H. Nienaber, Adv. Organomet. Chem. 41 (1997) 163.

[4] For a recent review see: U. Kucklaender, in: Z. Rappoport (Ed.), The Chemistry of Enamines 1, John Wiley and Sons, Chichester, 1994, pp. 532–636.

[5] Reactions of (4-amino)alkenyl carbene complexes with alkynes: (a) A. de Meijere, L. Wessjohann, Synlett (1990) 20. (b) F. Stein, M. Duetsch, R. Lackmann, M. Noltemeyer, A. de Meijere, Angew. Chem. 103 (1991) 1669. F. Stein, M. Duetsch, R. Lackmann, M. Noltemeyer, A. de Meijere, Angew. Chem. Int. Ed. Engl. 30 (1991) 1658. (c) R. Aumann, P. Hinterding, Chem. Ber. 125 (1992) 2765. (d) M. Duetsch, F. Stein, F. Funke, E. Pohl, R. Herbst-Irmer, A. de Meijere, Chem. Ber. 126 (1993) 2535. (e) M. Deutsch, F. Stein, A. de Meijere, Tetrahedron Lett. 34 (1993) 5875. (f) B.L. Flynn, C.C. Silveira, A. de Meijere, Synlett (1995) 812. (g) B.L. Flynn, C.C. Silveira, A. de Meijere, Synlett (1995) 1007. (h) B.L. Flynn, F.J. Funke, M. Noltemeyer, A. de Meijere, Tetrahedron 51 (1995) 11141.

[6] (a) M. Duetsch, F. Stein, F. Funke, E. Pohl, R. Herbst-Irmer, A. de Meijere, Chem. Ber. 126 (1993) 2535. (b) R. Aumann, P. Hinterding, Chem. Ber. 125 (1992) 2765.

[7] R. Aumann, P. Hinterding, Chem. Ber. 123 (1990) 611.

[8] H. Zhang, K.C. Chan, Synthetic Commun. (1995) 3329.

[9] R. Aumann, R. Fröhlich, S. Kotila, Organometallics 15 (1996) 4842.