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Synthesis of η^2-Allene Complexes by the Reaction of a η^1-Vinylidene Tungsten Complex with Diazoalkanes

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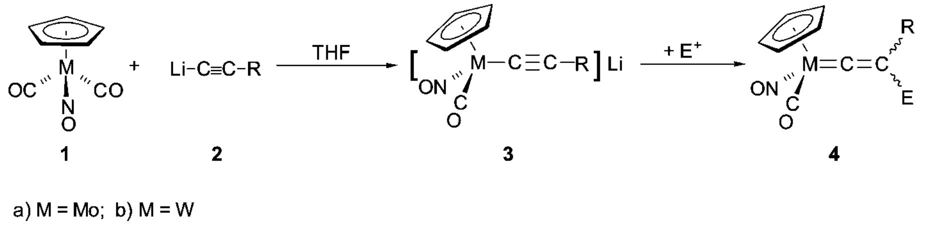
The reaction of the η^1-vinylidene complex Cp(CO)(NO)-W=C=CH$_2$ (**5**) with diazomethane, to give complex **8**, as well as with ethyl diazoacetate, to give complexes **10** and **11**, is described. The crystal structures of these complexes are reported.

Introduction

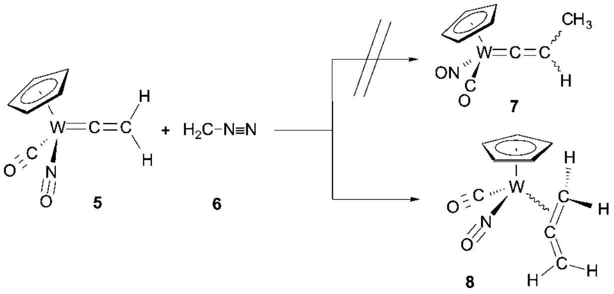
In recent years we have investigated the chemistry of tungsten and molybdenum η^1-acetylide complexes **3** and the corresponding η^1-vinylidene complexes **4**.[1] A broad range of differently substituted derivatives of **3** and **4** are prepared by the reaction of the corresponding lithium acetylide **2** with the carbonyl complex **1** in THF at –30 °C, which gives rise to the η^1-acetylide **3**, and by subsequent addition of electrophiles such as dilute acids, alkylating reagents like alkyltriflates, or iminium salts, which leads to the η^1-vinylidene complexes **4** (Scheme 1).

Because of the limited accessibility of propyne and also the low solubility of Li–C≡C–CH$_3$, the corresponding complexes **3** and **4** with R = methyl that are prepared by this procedure have low yields. In order to avoid using propyne we have also reported the preparation of **3** and **4** by the reaction of in situ prepared propynyllithium, generated by dehydrobromination of 2-bromopropene, with **1** and concomitant protonation.[2]



Scheme 1.

Owing to the high C–H acidity on the β-carbon atom of the η^1-vinylidene complexes[3] and in order to obtain complex **7** in good yield, we tested the reaction of η^1-vinylidene complex **5** with diazomethane. Contrary to the results obtained for the methylation of ruthenium η^1-vinylidene complexes with diazomethane,[4] we obtained the η^2-allene derivative **8** instead of complex **7**.[5] In this paper we describe the results of the reaction of diazomethane and ethyl diazoacetate with the η^1-vinylidene complex **5** (Scheme 2).



Scheme 2.

Results and Discussion

The reaction of diazomethane with the η^1-vinylidene complex **5** was carried out in THF/ether at –30 °C (Scheme 2). The progress of the reaction was followed by IR spectroscopy, and after the starting material had disappeared, the solvent was evaporated and the product was

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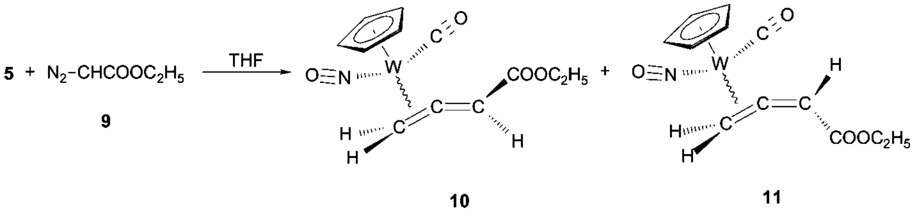

Scheme 3.

purified by chromatography on a short silica column. Complex **8** was isolated in high yields as bright yellow air-stable crystals, which are soluble in most organic solvents. On the basis of the NMR spectroscopic data, it was found that the compound consists of two rotamers in a ratio of 2:1. The structure of **8** was fully characterized by spectroscopic methods (see Exp. Sect.)[6] and by single-crystal X-ray analysis of one of the rotamers. The variable-temperature measurement NMR spectroscopic studies ([D$_6$]DMSO) show that both rotamers of **8** interconvert to one another. The singlet for the Cp protons at δ = 6.0 and 5.9 ppm broadens at higher temperatures and finally collapses because of the fast equilibration of both rotamers. The free activation energy for this process, calculated from the coalescence temperature (77 kJ·mol^{-1}), is higher than the reported energies for allene complexes such as dicarbonyl η^5-cyclopentadienyl(η^2-tetramethylallene)iron.[7]

Similarly, treatment of the η^1-vinylidene complex **5** at 40 °C in THF with excess ethyl diazoacetate (**9**) resulted in the formation of the stereoisomers **10** and **11** in 87% yield (Scheme 3). According to the ^{1}H NMR spectrum, the crude product consists of a mixture of **10** and **11** in a ratio of 1:5. Complex **10** consists of two rotamers in a ratio of 3:5 depending on the relative orientation of the NO and CO ligands. Complexes **10** (mixture of rotamers) and **11** were isolated by HPLC and characterized by means of elemental analysis, spectroscopic methods (see Experimental Section), and single-crystal X-ray analysis. The significant difference between the structures of **10** and **11** is the relative orientation of the ester group toward the tungsten center (*E* or *Z*). While in the minor component **10** the orientation of the ester group and the tungsten atom is *Z* relative to each other, the orientation of these groups in complex **11** is *E*.

Molecular Structure of Complexes 8, 10, and 11

Suitable crystals for a single-crystal X-ray diffraction analysis of complexes **8** and **10** were grown from pentane and crystals of **11** from an ether solution at 4 °C. The molecular structures are shown in Figure 1, Figure 2, and Figure 3, respectively, and relevant crystal data are included in Table 1. The crystal structures of these complexes consist of a well-spaced array of molecular units, and the intermolecular contacts correspond to normal van der Waals distances and the angles are as expected. Complexes **8**, **10**, and **11** all display a piano-stool coordination geometry about the metal atom. The allene ligand is bent in a manner that is generally found in η^2-allene complexes: the C1–C2–C3

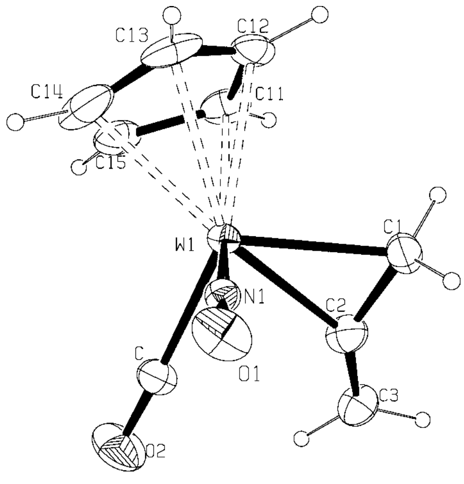

Figure 1. Molecular structure and atom-numbering scheme for complex **8**. Thermal ellipsoids are shown at the 20% probability level. Selected bond lengths [Å] and angles [°] (with standard deviations): W1–N1 1.767(10), W1–C 2.027(14), W1–C2 2.185(14), W1–C1 2.188(14), C1–C2 1.46(2), C2–C3 1.31(2), O1–N1 1.234(13), C–O2 1.096(18), N1–W1–C 91.3(5), N1–W1–C2 103.8(5), C–W1–C2 70.6(6), N1–W1–C1 93.1(5), C–W1–C1 108.1(6), C2–W1–C1 38.9(6), C2–C1–W1 70.4(8), C3–C2–C1 144.9(15), C3–C2–W1 144.3(14), C1–C2–W1 70.7(8), O1–N1–W1 176.1(9), O2–C–W1 177.5(16).

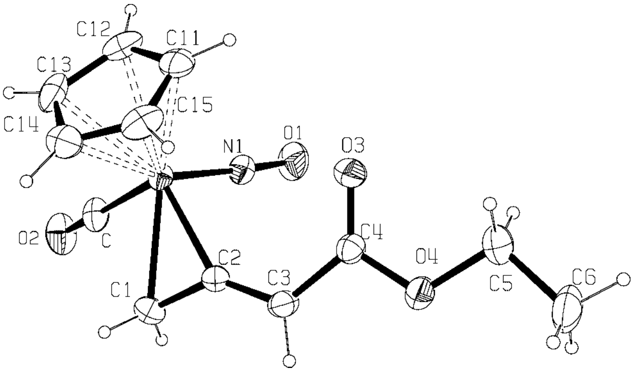

Figure 2. Molecular structure and atom-numbering scheme for complex **10**. Thermal ellipsoids are shown at the 20% probability level. Selected bond lengths [Å] and angles [°] (with standard deviations): W1–N1 1.795(5), W1–C 2.009(5), W1–C2 2.112(5), W1–C1 2.250(6), N1–O1 1.188(6), C–O2 1.121(6), C1–C2 1.402(7), C2–C3 1.330(7), C3–C4 1.454(7), C4–O3 1.203(6), N1–W1–C 90.7(2), N1–W1–C2 90.0(2), C–W1–C2 108.9(2), N1–W1–C1 102.2(2), C–W1–C1 73.6(2), C2–W1–C1 37.3(2), O1–N1–W1 176.7(5), O2–C–W1 179.4(5), C2–C1–W1 66.0(3), C3–C2–C1 139.7(5), C3–C2–W1 143.0(4), C1–C2–W1 76.7(3), C2–C3–C4 124.2(5).

angle is 144.9(15)° in complex **8**, 139.7(5)° in complex **10**, and 142.1(6)° in complex **11**.[8] The length of the coordinated double bond in **8** [C1=C2, 1.46(2) Å] is significantly longer than that of the uncoordinated bond [C2=C3, 1.330(7) Å]. However, relative to the C1–C2 bond in **8**, the coordinated double bonds in complexes **10** and **11** are slightly shorter: 1.402(7) Å in **10** and 1.393(8) Å in **11**. The length of the C4–O3 bond of the acyl function falls into the expected average value range for an α-β unsaturated ketone: 1.203(6) Å in **10** and 1.215(0) Å in **11**.[9] The distance from the metal to the central carbon atom of the allene ligand (W–C2) is slightly shorter than the distance from the metal to the terminal carbon atom (W–C1). This difference is 0.138 Å in complex **11** and 0.45 Å in **10**.[10] The overlap between a filled d orbital on the metal and both of the unoccupied orthogonal π* orbitals of the central carbon atom contribute to this difference.[11] However, this interaction seems to be unpronounced in complex **8**.

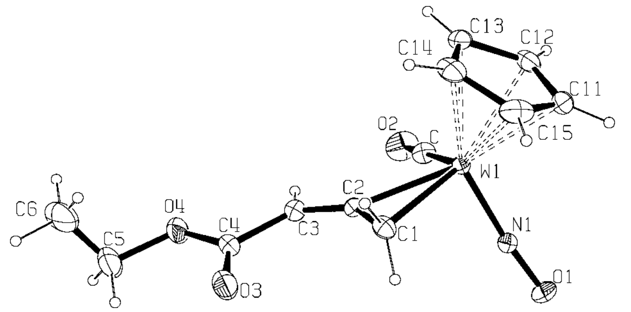

Figure 3. Molecular structure and atom-numbering scheme for complex **11**. Thermal ellipsoids are shown at the 20% probability level. Selected bond lengths [Å] and angles [°] (with standard deviations): W1–N1 1.783(5), W1–C 1.964(7), W1–C2 2.175(5), W1–C1 2.220(6), C1–C2 1.393(8), C2–C3 1.314(8), C3–C4 1.478(9), N1–O1 1.212(6), N1–W1–C 92.6(3), N1–W1–C2 99.5(2), C–W1–C2 74.9(3), N1–W1–C1 92.0(2), C–W1–C1 111.4(3), C2–W1–C1 37.0(2), C2–C1–W1 69.8(3), C3–C2–C1 142.1(6), C3–C2–W1 144.5(5), C1–C2–W1 73.3(3), C2–C3–C4 122.4(7), O1–N1–W1 173.8(4), O2–C–W1 178.1(7).

Experimental Section

General Considerations: All reactions were carried out under an argon atmosphere (99.99%, by Messer-Griesheim). Solvents were purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare $[(\eta^5C_5H_5)(CO)(NO)W{=}C{=}CH_2]$ (**5**),[12] CH_2N_2,[13] and $N_2CHCO_2CH_3$[14]. All other compounds were commercially available. NMR spectra were obtained with Bruker AM 400 and AC 200 spectrometers. Proton and

Table 1. Crystal data and structure refinements of **8**, **10**, and **11**.

	8	**10**	**11**
Formula	$C_9H_9NO_2W$	$C_{12}H_{13}NO_4W$	$C_{12}H_{13}NO_4W$
M_r [g·mol^{-1}]	347.02	419.08	419.08
Color and habit	yellow		
Crystal system	monoclinic		
Space group	$P2_1/n$	$P2_1/a$	$P2_1/n$
a [Å]	7.3511(7)	6.7864(5)	11.1820(13)
b [Å]	6.1294(6)	21.0383(18)	10.6952(12)
c [Å]	21.249(3)	9.2890(8)	11.6848(12)
β [°]	97.683(13)	97.671(10)	111.296(12)
V [Å^3]	948.8517	1314.36(19)	1302.0(2)
Z	2	4	4
$\rho_{calcd.}$ [g·cm^{-3}]	2.429	2.118	2.138
Linear absorption coefficient [cm^{-1}]	121.38	8.794	8.877
Diffractometer	Stoe IPDS		
Radiation	Mo-K_α (λ = 0.71069 Å)		
Monochromator	graphite		
Scan range [°]	$4.29 \le \theta \le 25.90$	$2.21 \le \theta \le 25.97$	$2.67 \le \theta \le 27.50$
	$-8 \le h \le 8$	$-8 \le h \le 8$	$-14 \le h \le 14$
	$-7 \le k \le 7$	$-25 \le k \le 25$	$-13 \le k \le 13$
	$-25 \le l \le 26$	$-11 \le l \le 11$	$-15 \le 1 \le 14$
Reflections collected	6223	9598	11083
R_{int}	0.0210	0.0524	0.0396
Independent reflections	1712	2388	2976
Applied corrections	Lorentz and polarization coefficients		
Structure determination and refinement	W positional parameters from Patterson synthesis (program SHELXS-86)[a]		
Data/restraints/parameters	1712/0/119	2388/0/163	2976/ 0/163
Goodness-of-fit on F_2	1.356	1.029	1.076
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0343	R_1 = 0.0235	R_1 = 0.0303
	wR_2 = 0.0999	wR_2 = 0.0625	wR_2 = 0.0729
R indices (all data)	R_1 = 0.0385	R_1 = 0300	R_1 = 0.0353
	wR_2 = 0.1234	wR_2 = 0.0652	wR_2 = 0.0747

[a] G. M. Sheldrick, SHELXS-86; Program for the Solution of Crystal Structures, University of Göttingen, **1986**); further atoms from F-synthesis (program SHELXL-93: G. M. Sheldrick, SHELXL-93; Program for Crystal Structure Refinement, University of Göttingen, **1993**); structure refinement by the anisotropic full-matrix least-squares procedure for all non-hydrogen atoms. Atomic scattering factors from: Int. Tables for Crystallography, vol. C (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, **1992**.

carbon chemical shifts were referenced to tetramethylsilane. MS measurements (70 eV) were performed with a Varian MAT 311-A. IR spectra were recorded with a Bruker FT-IR IFS 85. Microanalyses were done on a Carlo–Erba 1104 elemental analyzer.

Preparation of [(η^5-C_5H_5)(CO)(NO)W(η^2-$H_2C=C=CH_2$)] (8): A solution of CH_2N_2 (0.14 M, 230 mL) in diethyl ether (33.3 mmol) was slowly added to a solution of **5** (990 mg, 3.3 mmol) in THF (10 mL) at –30 °C, and the progress of the reaction was monitored by IR Spectroscopy. After 6 h, the solvent was removed under vacuum, and the crude product was purified by chromatography on silica gel with a pentane/ether mixture (1:1). The yellow compound was recrystallized from an ether/pentane solution to give 700 mg of complex **8** (61% yield), which consists of two isomers with a diasteriomeric ratio of 2:1, determined from ^{1}H NMR spectroscopic data. $C_9H_9O_2NW$ (347.01): calcd. C 31.15, H 2.61, N 4.04; found: C 31.52, H 2.28, N 3.89. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91 and 6.86 (t, $^4J_{H,H}$ = 3.5 Hz for both rotamers, 1 H, C3) and 6.09 and 5.81 (t, $^4J_{H,H}$ = 3.5 Hz for both rotamers, 1 H, C3), 5.71 and 5.66 (Cp), 1.86 and 2.19 and 1.77 (the major component: t, $^4J_{H,H}$ = 3.5 Hz; the minor component: two dt, $^2J_{H,H}$ = 11 Hz, $^4J_{H,H}$ = 3.5 Hz, 2 H, C1) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.7 and 215.0 (CO), 161.3 and 160.2 (C2), 110.3 and 107.1 (C3), 95.9 and 95.5 (Cp), 7.2 and –4.1 (C1) ppm. IR (KBr): $\tilde{\nu}$ = 1988 ($C\equiv O$), 1599 ($N\equiv O$) cm^{-1}.

Preparation of (*E*/*Z*)-{(η^5-C_5H_5)(CO)(NO)W[η^2(2,3)-$H_2C=C=CH$-$C(O)OCH_2CH_3$]} (10 and 11): A solution of ethyl diazoacetate (464 mg, 4 mmol) in THF (10 mL) was added to a solution of the vinylidene complex **5** (1 mmol, 333 mg) in THF (10 mL) at a rate of 1 ml per hour at 45 °C. The reaction mixture was monitored by IR Spectroscopy, and the reaction reached completion after 12 h. The solvent was removed under vacuum. The crude product was redissolved in pentane and purified by chromatography on a silica column. The yellow band was eluted with CH_2Cl_2/pentane (1:2), which resulted in 182 mg of a mixture of two stereoisomers **11** and **10** (87% yield), in a ratio of 5:1. The isomers were separated by HPLC, with TBME/hexane as the eluent mixture on a Diol-Phase. $C_{12}H_{13}O_4NW$ (405.07): calcd. C 34.39, H 3.13, N 3.34; found C 34.34, H 3.15, N 3.31.

(*Z*)-{(η^5-C_5H_5)(CO)(NO)W[η^2(2,3)-$H_2C=C=CHC(O)OCH_2CH_3$]} (10): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (t, X part of an ABX spin system, 1 H, C3), 5.80 (s, 5 H, Cp), 4.24 (m, 2 H, C5); 2.07 (dd, $^2J_{H,H}$ = 12.1, $^4J_{H,H}$ = 2.7 Hz, B part of the ABX system, 1 H, C1), 1.77 (dd, $^2J_{H,H}$ = 12.1 Hz, $^4J_{H,H}$ = 3.2 Hz, A part of the ABX system, 1 H, C1), 1.33 (t, 3 H, C6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.9 (*C*O), 180.0 (C4), 167.8 (C2), 117.0 (C3), 96.7 (Cp), 59.6 (C5), 14.5 (C6), 3.9 (C1) ppm. IR (KBr): $\tilde{\nu}$ = 2030 (W–$C\equiv O$), 1703 (C=O ester), 1625 and 1671 ($N\equiv O$) cm^{-1}.

(*E*)-{(η^5-C_5H_5)(CO)(NO)W[η^2(2,3)-$H_2C=C=CHC(O)OCH_2CH_3$]} (11): The major component was recrystallized from an ether/pentane solution and consisted of two rotamers in a ratio of 3:5. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.67 and 6.47 (t, $^4J_{H,H}$ = 3.0 Hz, $^4J_{H,H}$ = 3.6 Hz, C3, X part of ABX spin-system, 1 H), 5.72 and 5.70 (s, 5 H, Cp), 4.24 (m, 2 H, C4); 2.58 and 2.29, (dd, AB part, $^2J_{H,H}$ = 12.8 Hz, $^4J_{H,H}$ = 3.0 Hz, 1 H, C1 with the first order approximation), 2.24 and 2.17 (dd, $^2J_{H,H}$ = 12.8 Hz, $^4J_{H,H}$ = 3.0 Hz, 1 H, C1 with the first order approximation), 1.31 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, C6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.0 and 210.8 (C*O*), 179.1 and 176.4 (C4), 165.9 and 164.9 (C2), 118.9 and 115.7 (C3), 96.0 and 95.6 (Cp), 60.2 and 60.6 (C5), 14.4 and 14.3 (C6), 10.4 and –0.2 (C1) ppm. IR (KBr): $\tilde{\nu}$ = 2006 (W–$C\equiv O$), 1717 (C=O ester), 1681 and 1598 ($N\equiv O$) cm^{-1}.

CCDC-288085 to -288087 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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