Aziridines as Complex Ligands: Coordination and Ring Opening

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The photolytically induced CO substitution reactions of $CpMn(CO)_3$ with *N*-phenylaziridine and of $W(CO)_6$ with 2,2-dimethylaziridine lead to the *N*-coordinated aziridine complexes $Cp(CO)_2Mn\{N(Ph)CH_2CH_2\}$ and $(CO)_5W\{N(H)CH_2CMe_2\}$. Both are stable with respect to thermal alkene elimination. The thermal reaction of $Cp(CO)_3MoCl$ with *N*-hydroxyethylaziridine leads to the metallaheterocyclic compound $Cp(CO)_2MoNH(CH_2CH_2OH)CH_2CH_2C(O)$. It might be formed by several reaction steps including a Cl migration with nucleophilic ring opening, a CO insertion reaction forming the β-aminoacyl ligand and finally a hydrolytic process. The X-ray structure analysis of $Cp(CO)_2Mn\{N(Ph)CH_2CH_2\}$ and $(CO)_5W\{N(H)CH_2CMe_2\}$ shows three-membered-ring ligands *N*-bonded to the metal atoms with a trigonal pyramidal configuration at the nitrogen atoms. The X-ray structure analysis of $Cp(CO)_2MoNH(CH_2CH_2OH)CH_2CH_2C(O)$ reveals a five-membered heterocyclic ring system, including the molybdenum atom, a carbonyl function and an ammonium center.

Introduction

The photolytic reactions of $CpMn(CO)_3$ with thiirane, C_2H_4S, or thiirane *S*-oxide, C_2H_4SO, lead to CO substitution and elimination of ethene with formation of the intensively colored S and SO complexes, $\{CpMn(CO)_2\}_2S$ (green) and $\{CpMn(CO)_2\}_2SO$ (violet)[1][2]. Both dinuclear compounds show a central, symmetrically-bridging 3c4e-π-system. With their planar Mn_2SO_n skeleton ($n = 0, 1$), they demonstrate isolobal bis-metalorganic analogues of SO_2 and SO_3. The coordination of C_2H_4S- and C_2H_4SO ligands to transition metals via sulfur was first reported to exist in $(Ph_3P)_2Pt\{S(O)_nC_2H_4\}$ ($n = 0, 1$)[3] and $[CpRu(PPh_3)_2(S\text{-}C_2H_4)]O_3SCF_3$[4]. Ring-opening and oxidative-addition reactions of C_2H_4S and C_2H_4SO onto transition metal complexes have not yet been observed.

The isoelectronic aziridine-derivatives $N(R)CH_2CR'R''$ are expected to react in a similar fashion. Firstly, the coordination of aziridines onto transition metal centers via its nitrogen atom should also be possible. Subsequent ethene elimination might result in the formation of mono- and dinuclear nitrene complexes. This would be a new synthetic approach to nitrene complexes. A third type of reaction could be ring-opening leading to four-membered ring systems by an oxidative-addition process. However, five-membered ring systems could also form, especially with hydrido complexes of transition metals e. g., by a nucleophilic attack of the alkylidene part on the electrophilic carbon atom of a carbonyl ligand.

Beck et al. have described the reactivity of aziridines with metalcarbonyl and metalcarbonylhydrido complexes[5]. They observed two types of reactions of aziridines: simple coordination as *N*-coordinate ligands, as well as ring-opening to give metallacycles. Both types of complexes were characterized mainly by their IR spectra[5][6][7][8]. Two examples of the five-membered metallacycles have been characterized by X-ray structure analysis[9][10][11][12]. Angelici et al. reported the reaction of aziridine with platinum(II)-nitrile complexes to give aziridino-amidines, 2-imidazolines and to *trans*-$[PtCl_2\{N(H){=}C(Ph)NC_2H_4\}_2]$ complexes[13]. Coordination of the aziridine to the Pt-atom was not observed. In a recent paper, Beck et al.[14] described the reaction of a *N*-functionalized L-aziridine-2-carboxylate (ac) with some chloro-bridged transition-metal complexes to give e.g. $(OC)_2Rh(ac)$, $(\eta^5\text{-}C_5Me_5)(Cl)Ir(ac)$, $(\eta^3\text{-}C_3H_5)\text{-}Pd(ac)$, $Me_2NCH_2C_6H_4Pd(ac)$, $(R_3P)(Cl)Pd(ac)$ (R = Et, Bu, Ph), $(Ph_3P)(Cl)Pt(ac)$ and $[(Ph_3P)_2Pt(ac)]BF_4$. All these complexes are formed by HCl-elimination and by ring formation. They are the first structurally characterized N-aziridine complexes which possess an additional carboxylato-*O* bond to the transition metal (bidentate-*N,O*). Recently, the monodentate and *N*-coordinate benzylaziridine complex $Cp(CO)_2Mn\{N(Bz)CH_2CH_2\}$ was sucessfully synthesized and characterized[15].

In this paper the photolytic reactions of $CpMn(CO)_3$ and $W(CO)_6$ with different N- and C-substituted aziridines are reported. These lead to new *N*-coordinate mono-aziridine complexes. In addition, the thermal reaction of $Cp(CO)_3MoCl$ with *N*-hydroxyethylaziridine, which results in the formation of an interesting five-membered transition-metallacycle, is described.

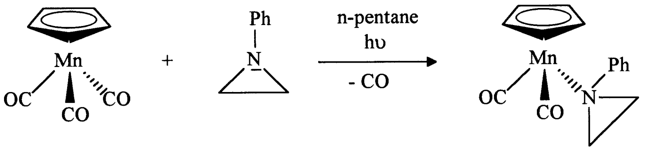
Results and Discussion

$CpMn(CO)_3$ and *N*-phenylaziridine $N(C_6H_5)C_2H_4$ (**1a**) are photolysed for 3.5 h in *n*-pentane at −35°C. The clear

1434−1948/98/0505−0645 $ 17.50+.50/0

yellow solution turns orange after warming to r. t. Crystallisation provided monoclinic orange colored crystals of **2** (Scheme 1). **2** is neither light- nor air-sensitive. The formation of **2** results from a simple substitution reaction of one CO ligand for the nucleophilic nitrogen atom of the aziridine ligand (2e donor). **2** is also obtained by photolysing first $CpMn(CO)_3$ in thf to give the labile complex $CpMn(CO)_2thf$, which then is allowed to react with the aziridine ligand within 4 h to give **2**. The yield of **2** is higher for the "direct" synthesis in *n*-pentane (76%) than for the "indirect" in thf (56%).

Scheme 1

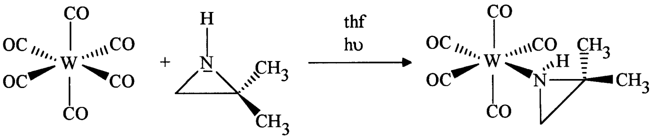


1a **2**

In accordance with the utilisation of *N*-substituted aziridines described later, the analagous reaction products of *C*-substituted N(H)-aziridines and further metal complexes are also of interest. By using such *C*-substituted aziridines the question as to whether the alkene elimination takes place by activation, therefore obtaining nitrene complexes by a new method, can be answered. In the case where alkene elimination is not observed, the N−H bond cleavage should be attempted by the nucleophilic attack of strong bases to obtain a new nucleophilic center at the N of the aziridine ligand. This would then be attempted to react with other electrophilic compounds. With 16e-fragments like $[CpMn(CO)_2]$, or 17e-fragments like $CpFe(CO)_2$ anionic or neutral μ_2-N bridged dimetallo complexes should be built up.

Thus, $W(CO)_6$ is first photolysed in thf for 2 h at r. t., followed by addition of one equivalent of 2,2-dimethylaziridine $N(H)CH_2CMe_2$ (**1b**). After evaporating the solution to dryness and removal of some $W(CO)_6$ by sublimation, the residue is dissolved in thf. Careful layering of n-pentane at −22°C yields yellow crystals of **3** (Scheme 2.). These are neither air, nor light sensitive and they are soluble in acetone, CH_2Cl_2 and thf. No $H_2C{=}CMe_2$ elimination was observed on heating.

Scheme 2



1b **3**

In contrast to both 16e complex fragments, where neutral addition products were obtained with aziridines, aziridines were reacted with 17e complex fragments in the hope of obtaining cationic addition products. Therefore, $CpMo(CO)_3Cl$ was reacted with *N*-hydroxyethylaziridine, $N(CH_2CH_2OH)C_2H_4$ (**1c**), in acetone at 60°C. After cooling to r. t., a dark red solution was obtained from which yellow-orange crystals of **4** separated on evaporation.

However, instead of the expected cationic complex $[Cp(CO)_2MoN(CH_2CH_2OH)CH_2CH_2)]Cl$, the new neutral metallacycle $Cp(CO)_2MoNH(CH_2CH_2OH)CH_2CH_2C(O)$ (**4**) was surprisingly obtained. Its formation requires several steps and the presence of traces of water. Firstly, a migration of the Cl onto the N atom giving the corresponding metallate and aziridinium ion. They undergo a nucleophilic ring opening process to give the β-aminoethyl ligand which as nucleophile attacks the electrophilic C atom of one of the CO ligands to give the β-aminoacyl ligand. The reaction is finished by the coordination of the amine to the metal to form the five-membered metallacycle. We believe that the replacement of the Cl substituent for H takes place during the long crystallization process. The presence of water could be derived from the hydroxyethyl substituent by condensation. Beck et al. have described a similar complex[5][10][11][14], the hydrido complex $CpMo(CO)_3H$ was used as a starting material. Therefore there was no hydrolytic process necessary.

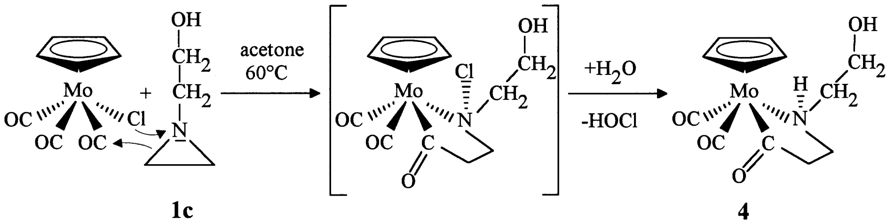
The composition and structure of **2**, **3** and **4** were confirmed by elemental analyses, MS, ^1H-, $^{13}C\{^1H\}$-NMR and IR spectra, as well as by X-ray structure analyses.

The IR spectrum of **2** shows two ν(CO) vibrations at 1917.7 and 1839.1 cm^{-1} (in CH_2Cl_2), or 1915.8 and 1844.8 cm^{-1} (in KBr), respectively. The IR spectrum in KBr also shows the ν(CH) at 3106.4 and 3011.2 cm^{-1}, as well as the $\nu(C-N_{tert.})$ vibration at 1358.6 cm^{-1}. The IR spectrum of **3** exhibits three bands at 1974.7, 1924.8 and 1888.6 cm^{-1} for terminal CO groups ($2A_1 + E$, C_{4V} local symmetry). In the IR spectrum of **4**, ν(CO) bands at 2020.7 and 1936.3 cm^{-1} are observed for the two terminal ligands. A third ν(CO)-band at 1844.9 cm^{-1} is due to the carbonyl group within the ring.

In the EI-MS spectrum of **2**, the $[M^+]$ signal appears at 295.0 u, together with signals at 239.0 u and 120.0 u for $[M^+ - 2\ CO]$ and $[M^+ - 2\ CO - N(Ph)CH_2CH_2]$. In the EI-MS spectrum of **3**, the parent ion $[M^+]$ appears at 395.0 u, together with peaks at 367.0 for $[M^+ - CO]$, 339.0 for $[M^+ - 2\ CO]$, 309.0 for $[M^+ - 3\ CO - 2\ H]$, 281.0 for $[M^+ - 4\ CO]$, 253.0 for $[M^+ - 5\ CO]$ and 71.0 for $[HNCH_2CMe_2]$. **4** does not give the $[M^+]$ signal, the mass spectrum shows only fragments.

In the ^1H-NMR spectrum of **2**, the phenyl protons are found as singlets at 7.27 (*ortho*), 7.20 (*meta*) and 7.06 (*para*) ppm. In comparison with the free *N*-phenylaziridine ligand, these are deshielded by 0.11 to 0.40 ppm. The Cp protons give rise to a singlet at δ 4.25, which in comparison with $CpMn(CO)_3$ lies 0.51 ppm upfield. The aziridine ring protons are observed at 2.38 ppm as a broad singlet in **2**, whereas in **1a** two triplets are found at δ 3.58 and 3.38. The ^1H-NMR spectrum of **3** is characterized by 2 triplets at 2.50 and 2.35 ppm for the CH_2 ring protons, a triplett at δ 4.35 for the NH proton (ABX system), and two singlets at δ 1.40 and 1.35 for the methyl groups. In the ^1H-NMR spectrum of **4**, the Cp protons are observed at δ 5.32 as a singlet, shifted 0.56 ppm upfield from the $CpMo(CO)_3Cl$ starting

Scheme 3



1c

4

material. At 5.29 ppm, the OH proton of **4** is better shielded by 0.19 ppm relative to the free *N*-hydroxyethyl aziridine ligand. The signals for the *N*-2-hydroxyethyl and for the ethene group within the ring in **4** appear as 4 triplets at 3.80 (CH_2O), 3.63 (CH_2CO), 2.99 (CH_2N) and at δ 2.82 (CH_2N).

In the $^{13}C\{^1H\}$-NMR spectrum of **2**, the signals for the CO groups and the Cp ligand lie at δ 288.36 and 83.70, respectively. The different carbon atoms of the phenyl ring are detected between δ 129.28 and 122.70 (4 signals). Coordination of **1a** to the manganese atom in **2** leads to two signals which are very close together and shifted upfield for

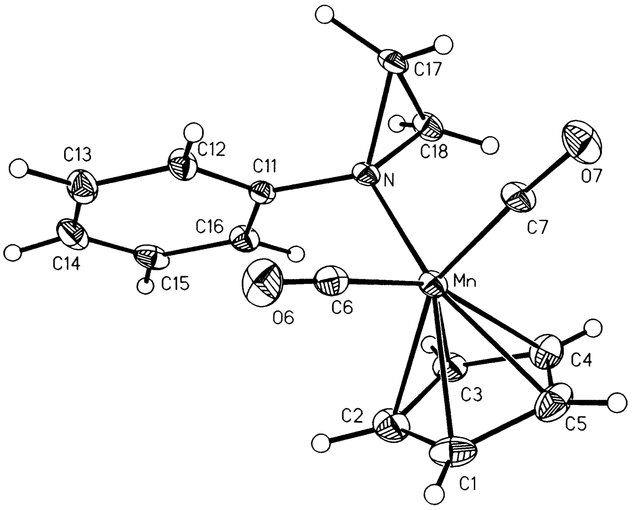
Table 1. Crystal data and data collection of **2**, **3**, and **4**

	2	**3**	**4**
Empirical formula	$C_{15}H_{14}MnNO_2$	$C_9H_9NO_5W$	$C_{12}H_{15}MoNO_4$
Formula weight [g/mol]	295.21	395.02	333.19
Crystal size [mm^3]	0.40 x 0.40 x 0.12	0.25 x 0.10 x 0.05	0.35 x 0.30 x 0.26
Crystal color and habit	orange plate	yellow needle	orange-red plates
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions [Å],	a = 10.828(3)	a = 6.584(3)	a = 16.912(3)
	b = 9.326(3)	b = 10.608(4)	b = 8.707(2)
	c = 13.864(3)	c = 17.276(6)	c = 18.668(4)
[°]	β = 106.34(2)	β = 94.669(1)	β = 107.99(3)
Volume [Å^3]	1343.5(6)	1202.6(8)	2614.5(9)
Z	4	4	8
Density (calc.) [g/cm^3]	1.460	2.182	1.693
Absorption coefficient [mm^{-1}]	0.978	9.609	1.009
F(000)	608	736	1344
Scan type	ω-Scan	Hemisphere	ω-Scan
Temperature [K]	213(2)	183(2)	293(2)
2Θ range for data collection [°]	5.34−46.00	4.52−57.64	3.90−57.90
Index ranges	$-1 \leq h \leq 11$	$-8 \leq h \leq 8$	$-21 \leq h \leq 22$
	$0 \leq k \leq 10$	$-13 \leq k \leq 13$	$-10 \leq k \leq 11$
	$-15 \leq l \leq 14$	$-16 \leq l \leq 23$	$-20 \leq l \leq 23$
Reflections collected	2129	6600	12645
Independent reflections	1847 (R_{int} = 0.1357)	2104 (R_{int} = 0.0474)	5342 [R_{int} = 0.0492]
Observed reflections	1438 [$F > 4\sigma(F)$]	1827 [$F>4\sigma(F)$]	4235 [$F > 4\sigma(F)$]
Absorption correction	not necessary	semi empirical	semi empirical
Max. and min. transmission	0.465 and 0.694	0.159 and 0.394	0.6422 and 0.8542
Experimental details:			
Scan-speed in ω	variable; 3 to 60°/min		variable; 3 to 60°/min
Scan range (ω)	1.6°		1.2°
Solution and refinement			
Structure solution program	XS (Siemens)	XS (SHELXTL-Ver.5)	XS (Siemens)
Weighting scheme	$w^{-1} = \sigma^2Fo^2+(0.0862P)^2 +2.0719P$ where $P = (Fo^2+2Fc^2)/3$	$w^{-1} = \sigma^2Fo^2+(0.0330P)^2 +11.5843P$ where $P = (Fo^2+2Fc^2)/3$	$w^{-1} = \sigma^2Fo^2+(0.0690P)^2 +6.4669P$ where $P = (Fo^2+2Fc^2)/3$
Data/restraints/parameter	1841 / 0 / 214	1951 / 0 / 151	5337 / 0 / 325
Final R indices [$F>4\sigma(F)$]	R_1 = 0.0612, wR_2 = 0.1572	R_1 = 0.0396, wR_2 = 0.0929	R_1 = 0.0475, wR_2 = 0.1326
R indices (all data)	R_1 = 0.0831, wR_2 = 0.2026	R_1 = 0.0433, wR_2 = 0.0967	R_1 = 0.0678, wR_2 = 0.1522
Goodness-of-Fit on F^2	1.151	1.249	1.158
Largest and mean Δ/σ	0.002 0.000	0.001 0.000	−0.001 0.000
Largest difference peak / hole [eÅ^{-3}]	0.78 /−0.964	1.422 /−1.744	0.613 / −1.557

the two ring carbon atoms. They lie at 41.92 and 41.85 ppm, compared with δ 45.43 and 43.18 for free **1a**. In the $^{13}C\{^1H\}$-NMR spectrum of **3**, a signal at δ 191.21 for the tertiary carbon atom, at 68.05 ppm for the CH_2N ring group and only a singlet at 25.67 ppm for the two CH_3 substituents is observed. In the $^{13}C\{^1H\}$-NMR spectrum of **4**, signals are observed at 213.43 and 205.86 ppm (CO ligand and carbonyl function), 94.45 (Cp), 64.05 (s, $C(12)H_2O$) and at 52.09 ppm (s, $C(11)H_2N$). The C atoms of the five-membered ring are found at 50.66 ppm (s, $C(10)H_2N$) and 44.14 ppm (s, $C(9)H_2CO$).

Single crystals suitable for X-ray diffraction analysis of **2**, **3** and **4** were obtained. The crystal structure analysis data are summarized in Table 1 and the molecular structures and the most important bond lengths and angles are given in Figures 1, 2 and 3.

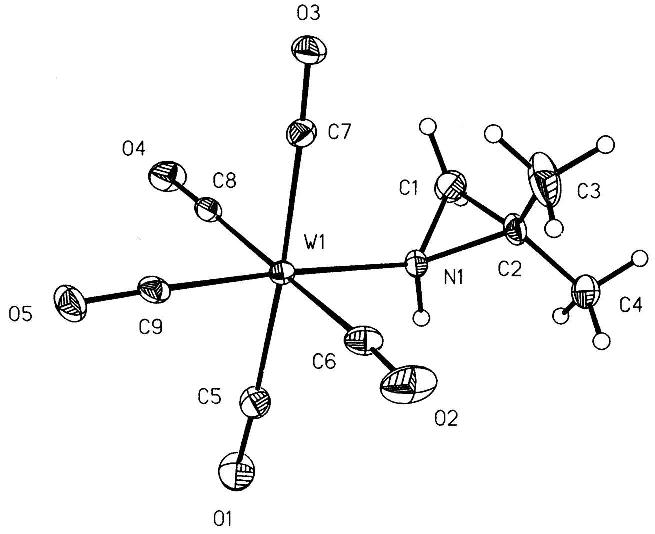
Figure 1. Molecular structure of **2**[a] in the crystal. Thermal ellipsoids are represented at a 25% probability scale



[a] Selected bond lenghts [Å] and bond angles [°]: Mn−N 2.096(5), Cp−Mn$_{average}$ 2.141(7), N−C11 1.446(7), N−C17 1.506(7), N−C18 1.491(8), C17−C18 1.480(9), C11−N−Mn 115.2(3), C17−N−Mn 121.7(4), C18−N−Mn 119.5(4), C7−Mn−C6 88.1(3), Mn−C6−O6 175.3(6), Mn−C7−O7 174.0(6), C18−N−C17 59.2(4), C17−C18−N 60.9(4), C18−C17−N 59.9(4), C11−N−C18 116.3(5), C11−N−C17 113.6(5).

The configuration at the Mn- and the N-atom of **2** is distorted tetrahedral. The Mn−N bond length of 2.096(5) Å indicates a single bond; the two bonds N−C17 (1.506(7) Å) and N−C18 (1.491(8) Å) are practically of equal length, while N−C11 (1.446(7) Å) is somewhat shorter. The bond length C17−C18 with 1.480(9) Å is a little bit shorter in comparison with typical C−C-single bonds and as found in aziridines[9]. While the C18−N−C17 angle within the ring is 59.2(4)°, the two angles C11−N−C17 and C11−N−C18 outside the ring lie between 116.3(5)° and 113.6(5)°. The angles C17−N−Mn (121.7(4)°) and C18−N−Mn (119.5(4)°), containing a manganese atom, are close to 120°. The angle C11−N−Mn (115.2(3)°), C11 being the *ipso*-carbon of the phenyl ligand, is also very large. The plane of the aziridine ligand nearly approaches orthogonality to the plane of the cyclopentadienyl ligand (71.3°).

Figure 2. Molecular structure of **3**[a] in the crystal. Thermal ellipsoids are represented at a 25% probability scale

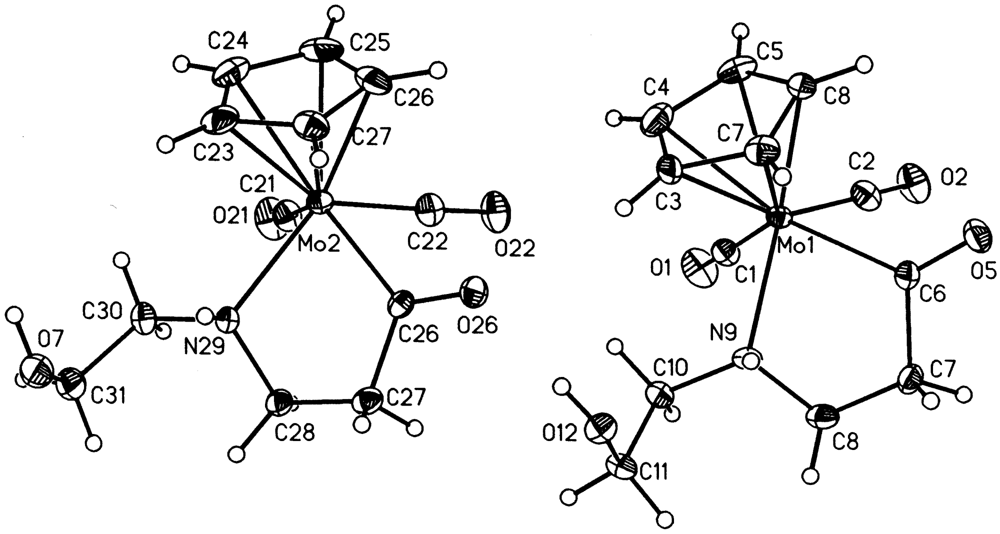


[a] Selected bond lenghts [Å] and bond angles [°]: W1−N1 2.307(8), N1−C1 1.488(14), N1−C2 1.500(13), C1−C2 1.48(2), C2−C3 1.49(2), C2−C4 1.504(14), C9−W1−C6 89.3(4), C6−W1−C8 177.9(3), C6−W1−C7 90.4(4), C7−W1−C5 176.2(4), C2−C1−N1 60.7(7), C1−C2−N1 59.9(7), C1−N1−C2 59.4(7), C1−N1−W1 128.8(6), C2−N1−W1 132.9(6), C8−W1−N1 91.0(4), C5−W1−N1 88.6(4), C3−C2−N1 116.8(9), C1−C2−C3 120.6(11), C3−C2−C4 115.0(10), N1−C2−C4 114.5(8).

The coordination sphere around the tungsten atom in **3** can be described as a distorted octahedron with maximum deviations of 4.8° for C7−W1−N1 and 3.5° for C9−W1−N1 from 90° and 180°, respectively. The W1−N1 bond length of 2.307(8) Å lies in the expected region for a single bond. The distance C1−C2 of 1.48(2) Å is again slightly shorter than that found for C−C single bonds and comparable to C17−C18 of **2**[9]. However, both bonds C2−C3 and C2−C4 are found to be somewhat longer (1.49(2) Å and 1.504(14) Å). The bond lengths N1−C1 and N1−C2 are to be considered to be of equal length (1.49(1) Å and 1.50(1) Å). Because of the C2 substituents both angles C1−N1−W1 and C2−N1−W1 are different (128.8(6)° and 132.9(6)°). The ring-angle C1−N1−C2 is again the smallest (59.4(7)°).

In **4**, the molybdenum atom possesses a distorted tetragonal pyramidal configuration with the Cp ligand in apical position. It is also part of the five-membered heterocyclic ring system, which is formed by the β-aminoacyl ligand[6][8][10][11]. Whereas the Mo1−N10 bond of 2.267(4) Å is very long, that of Mo1−C8 is remarkably shorter at 2.180(5) Å. The bonds N10−C10 and N10−C11 are almost equal (1.473(6) Å and 1.484(6) Å) and their length is typical for N−C single bonds. Of both C−C bonds within the ring, that of C8−C9 (1.536(7) Å) is significantly larger than that of C9−C10 (1.497(7) Å). While the atom distance O9−C8 of the carbonyl group is 1.233(6) Å, the bond length O12−C12, where O12 belongs to an OH group, corresponds with a single bond (1.432(6) Å). Within the five-membered ring with envelope conformation, the angle C8−Mo1−N10 of 73.4(2)° is the most acute and the angle

Figure 3. Molecular structure of **4**[a] in the crystal. Thermal ellipsoids are represented at a 25% probability scale



[a] Selected bond lenghts [Å] and bond angles[°]: Cp−$Mo1_{average}$ 2.348(5), Mo1−N10 2.267(4), Mo2−N31 2.280(4), Mo1−C8 2.180(5), Mo2−C28 2.162(4), Mo1−C6 1.929(6), O9−C8 1.233(6), O28−C28 1.239(5), C8−C9 1.536(7); C9−C10 1.497(7), N10−C10 1.473(6), N10−C11 1.484(6), C11−C12 1.523(6), C12−O12 1.432(6), C6−Mo1−C7 75.4(2), C7−Mo1−C8 121.3(2), C7−Mo1−N10 82.6(2), C8−Mo1−N10 73.4(2), Mo1−C6−O6 178.5(5), Mo1−C7−O7 175.5(4), N10−Mo1−C8 73.4(2), Mo1−C8−C9 127.5(4), C8−C9−C10 111.8(4), C9−C10−N10 108.7(4), C10−N10−Mo1 109.8(3).

C9−C8−Mo1 of 115.7(3)° the most open, because of the sp^2-hybridized C8 atom. The other three angles C8−C9−C10 (111.8(4)°), C9−C10−N10 (108.7(4)°) and C10−N10−Mo1 (109.8(3)°) are approximately equal. The ring shows envelope conformation, where N10 is placed −0.75 Å out of the plane Mo1−C8−C9−C10, with an interplanar angle to the Mo1−N10−C10 plane of 47.2° (respective data for N31 is −0.75 Å and for Mo2−C28−C29−C30 the interplanar angle to the Mo2−N31−C30 plane is 46.3°). The isolated crystals contain only one of the possible isomers with the relative configuration *RS*/*SR*.

Conclusion and Scopes

The results demonstrate that aziridine ligands coordinate much more effectively to transition metals than thiiranes. The latter prefer an ethene elimination and formation of sulfur complexes. The first aziridine complex has only recently been published[15]. **2** and **3** are two further examples. **3** is the first aziridine complex with a chiral N atom. We are continuing investigations in this field with more electrophilic, metalorganic-complex fragments to induce ethene elimination as a new synthetic approach to nitrene complexes. Moreover, aziridines can react, after coordination, with carbonyl ligands via ring-opening and by a redox reaction to produce the new metallaheterocycle **4**. We hope to elucidate the mechanism of its formation.

These complexes may find use in the therapeutic use of aziridines, which has been known since the fifties. Currently, there are detailed investigations on the cytostatic, cytotoxic and mutagenic activity of aziridine components[16][17][18][19][20][21][22]. In recent years organometallic transition complexes have gained a wide interest in cancer diagnostics[23]. It is planned to test such aziridine and aziridine-based complexes for such applications.

Experimental Section

To remove oxygen, all operations were carried out under an argon atmosphere in dry and argon-saturated solvents[24] . $CpMn(CO)_3$[25], $W(CO)_6$[25], $CpMo(CO)_3Cl$[25], *N*-phenylaziridine[26] and 2,2-dimethylaziridine[27] were prepared in accordance with literature procedures. *N*-hydroxyethylaziridine was used as purchased from Aldrich. The photolytic reactions were carried out by using a mercury-high-pressure lamp TQ 150 Hanau (as an inside dipping lamp) in a modified glass apparatus with an overflow tube, which allows a sufficient vertical mixing of the reaction solution. − IR: Perkin-Elmer 598 and Nicolet FT-IR. − NMR: Jeol EX-400 (^1H: 399.784 MHz and ^{13}C: 100.540 MHz) and Jeol GSX-270 (^1H: 240.0 MHz and ^{13}C: 61.0 MHz), both with [D_6]acetone and $CDCl_3$ as solvents and TMS as internal standard. − MS: Finnigan MAT 900 (20 kV), Varian MAT CH7 (70 eV).

N-Phenylaziridine-dicarbonyl-η^5-cyclopentadienyl-manganese(I) (**2**): 0.81 g (6.8 mmol) $CpMn(CO)_3$ and 2.73 g (13.4 mmol) of **1a** were photolysed at −35°C in 400 ml *n*-pentane for 3.5 h with strong stirring. The elimination of 1 mol of CO was controlled by IR spectroscopy. Thereafter, the clear orange solution was allowed to attain r. t. during 4 h and then the solvent was partially evaporated. After 24 h, orange crystals of **2** had formed; yield 1.54 g (76.6%); m.p. 149°C. − IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 1917.7vs, 1839.1 vs (CO); IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3106.4 s, 3011.2 s (CH); 1915.8 vs, 1844.8 vs (CO); 1358.6 s (C-$N_{tert.}$). − ^1H-NMR ([D_6]acetone): δ = 7.27 (s, o-Ph, 2 H), 7.20 (s, m-Ph, 2 H), 7.06 (s, *p*-Ph, 1 H), 4.25 (s, Cp, 5 H), 2.38 (s, $(CH_2)_2$, 4 H). − $^{13}C\{^1H\}$-NMR ([D_6]acetone): δ = 288.36 (s, CO), 129.28 (s, Ph, C_{ipso}), 129.25 (s, Ph, C_{ortho}), 123.06 (s, Ph, C_{meta}), 122.70 (s, Ph, C_{para}), 83.70 (s, Cp), 41.92 (s, CH_2), 41.85 (s, CH_2). − MS-EI (70 eV): 296.0 [M^+ + H], 295.0 [M^+], 239.0 [M^+ − 2 CO], 211.0 [M^+ − 2 CO − C_2H_4], 176.0 [M^+

– $N(Ph)C_2H_4$], 148.0 [M^+ – CO – $N(Ph)C_2H_4$], 120.0 [M^+ – 2 CO – $N(Ph)C_2H_4$]. – $C_{15}H_{14}MnNO_2$ (295.22): calcd. C 61.05, H 4.74, N 4.74; found. C 60.55, H 5.02, N 4.84.

2,2-Dimethylaziridine-pentacarbonyl-tungsten(0) (**3**): A solution of 1.0 g (2.8 mmol) of $W(CO)_6$ was photolysed while stirring in 400 ml thf at r. t. for 2 h. The elimination of 1 mole CO was observed by IR-spectroscopy. Then 0.20 g (2.8 mmol) of **1b** were added. The yellow solution turned orange within 1 h. After evaporating the solvent and sublimation of unreacted $W(CO)_6$ from the residue in vacuum at 60°C, the remaining material was dissolved in 50 ml of thf and covered with a layer of *n*-pentane (10 ml). After 48 h at –22°C yellow crystals of **3** had formed; yield 0.53 g (47%); m.p. 98°C. – IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 1974.7 m, 1924.8 vs, 1888.6 m (CO). – ^1H-NMR ($CDCl_3$): δ = 1.85 (m, CH_2, 2 H), 1.40 (s, CH_3, 3 H), 1.35 (s, CH_3, 3 H). – $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ = 191.21 (CMe_2), 68.05 (CH_2N), 25.67 (CH_3). – EI-MS (70 eV); *m/z* (%): 395.0 [M^+], 367.0 [M^+ – CO], 339.0 [M^+ – 2 CO], 309.0 [M^+ – 3 CO – 2 H], 281.0 [M^+ – 4 CO], 253.0 [M^+ – 5 CO], 71.0 [$HNCH_2CMe_2$]. – $C_9H_9NO_5W$ (395.02): calcd. C 27.36, H 2.30, N 3.54; found. C 27.00, H 2.03, N 2.68.

1,1-Dicarbonyl(η^5-cyclopentadienyl)-2-hydroxyethylmolybda(1)-aza(2)-cyclopentan(5)-one (**4**): To the red solution of 0.38 g (1.4 mmol) of $CpMo(CO)_3Cl$ in 125 ml acetone, were added two mol-equivalents of **1c** (0.22 ml, 2.7 mmol) while stirring. The solution was then heated to 60°C for 1 h, during which the color of the solution became darker. After cooling to r. t. and partially evaporating the solvent in a vacuum, yellow-orange crystals of **4** formed; yield 0.23 g (60%); m.p. 113°C. – IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2020.7 m, 1936.3 vs $(CO)_{terminal}$, 1844.9 s $(CO)_{carbonyl}$. – ^1H-NMR ([D_6]acetone): δ = 5.32 (s, Cp, 5 H), 5.29 (s, OH, 1 H), 3.80 (t, CH_2O, 2 H), 3.63 (t, $C(11)H_2$, 2 H), 2.99 (t, $C(10)H_2$, 2 H), 2.82 (t, $C(9)H_2$, 2 H). – $^{13}C\{^1H\}$-NMR ([D_6]acetone): δ = 213.43 $(CO)_{terminal}$, 205.86 $(CO)_{carbonyl}$, 94.45 (Cp), 64.05 (CH_2OH), 52.09 ($C(11)H_2$), 50.66 ($C(10)H_2$), 44.14 ($C(9)H_2$). – $C_{12}H_{15}MoNO_4$ (333.20): calcd. C 43.26, H 4.54, N 4.20; found. C 43.12, H 4.67, N 4.77.

X-Ray Structure Determinations of **2**, 3 and **4**[28]: The crystal structure, experimental specifications and refinement data are given in Table 1. Selected single crystals were mounted on in a glass fiber or a capillary with perfluoroether oil, and aligned on a Siemens P4 diffractometer in a N_2 cold stream equipped with a scintillation counter (**2**) or a CCD area detector (**3**, **4**). Data collection for the determination of the unit cell as well as for the structure determination was performed at –80°C (**2**), using MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator. Data reduction was performed with programs XSCANX Ver. 2.2 or SAINT Ver. 4 (Siemens Analytical Instruments), and structure solution with direct (**2**, **4**) or heavy atom methods (**3**). The SHELXL and SHELX93 programs were used for structure refinement (on F^2) and documentation. Non hydrogen atoms are presented in anisotropic description. Hydrogen atoms were placed in calculated positions and refined with fixed isotropic U using the riding model (**3**) or freely unfined (**2**, **4**). In case of compound **3** the atom H1 was found in the difference Fourier synthesis and was freely refined isotropically.

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[28] Crystallographic data (excluding structure factors) for the structures **2**, **3** and **4** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 100778. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: int. code + 44(1223) 336–033, E-mail: deposit@ccdc.cam.ac.uk).

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