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2*H*-Azirines as ligands: Synthesis and structural characterization of (2*H*-3-arene-azirine)$Re^I(CO)_3Br$ complexes

J. Nicolas Roedel, Xaver Wurzenberger, Ingo-Peter Lorenz *

Department of Chemistry and Biochemistry, Ludwig-Maximilians-University, Butenandtstraße 5–13 (Building D), 81377 Munich, Germany

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ABSTRACT

The synthesis and structural characterization of four 2*H*-azirine rhenium(I) complexes are described. Stabilization of the highly reactive and strained 3-arene-2*H*-azirine ligand through *N*-coordination to the transition metal is observed. The reaction of $[Re(CO)_3(THF)_2Br]$ with 3-arene-2*H*-azirine ligands (az) in THF at −20 °C in a 1:2 molar ratio afforded the neutral bis-azirine complexes $[Re(CO)_3(az)_2Br]$ (az = $NCH_2CC_6H_4R$; R = –H, –Me, –Cl, –Br). After purification, all complexes have been fully characterized. The molecular structures of the novel rhenium(I) complexes exhibit slightly distorted octahedral coordination geometries around the metal centers with *cis*-bonded az ligands.

2*H*-Azirines have attracted considerable interest from the synthetic, mechanistic and theoretical point of view, especially because of their versatile reactivity [1–3]. The reason for the increased reactivity of 2*H*-azirines is mainly due to high ring strain energy. Following von Baeyer [4] the forced deformation of bond angles in this unsaturated three membered ring system is the main reason for the ring strain. 2*H*-Azirines as reactive and versatile starting materials in organic synthesis can react as nucleophiles, electrophiles and dienophiles or dipolarophiles in cyclo addition reactions [5–7]. Interestingly, all three bonds of the azirine ring can be cleaved depending on the experimental conditions used [1,2]. Moreover, this highly strained imines are suitable precursors in the synthesis of an impressive number of heterocycles [5–10]. In this context transition metal catalyzed ring expansion or rearrangement reactions of azirines have been reported recently, for example the rearrangement of 2*H*- and 3*H*-azirines to indoles catalyzed by $[Rh(CO)_2Cl]_2$ and $[Rh_2(OCOCF_3)_4]$ [6,11–18].

Nevertheless little is known about the coordination chemistry of azirines. To the best of our knowledge only two X-ray structure analyses of $ZnBr_2$ and $PdCl_2$ azirine complexes have been reported [1,19–21]. Inspired by our recent studies on the coordination chemistry of saturated three membered aziridines [22–25], we chose to study the coordination chemistry of 2*H*-azirines as a barely investigated class of highly strained ligands. In this communication we report the synthesis and structural characterization of four 2*H*-azirine rhenium(I) complexes and the stabilization of the highly reactive 2*H*-azirine ligands in the coordination sphere of the $Re^I(CO)_3Br$ fragment.

2*H*-Azirines **3a–d** (az) and $[Re(CO)_5Br]$ (**1**) were prepared according to literature methods and stored in dry argon atmosphere [26,27]. Additionally the az ligands **3a–d** were cooled to −32 °C due to the thermic instability at r.t. (caution: 2*H*-3-phenyl-azirine and 2*H*-3-(4-methyl-phenyl)-azirine are highly irritant). The novel azirine transition metal complexes **4a–d** have been prepared as follows and illustrated in Scheme 1. Complex **2** was synthesized by solving one equivalent of **1** in dry THF and refluxing the colourless solution for 20 h. The conversion of complexes **1–2** is monitored by liquid phase IR spectroscopy in THF. Complex **2** can be assigned to the point group C_s and shows the absorption of three CO valence vibrations deduced to the symmetry race $2A' + A''$ at 2030, 1915 and 1894 cm^{-1}. The vigorously stirred solution of **2** was cooled at −20 °C and **3a–d** was added rapidly. The mixture was stirred at −20 °C for 45 min and then warmed up to room temperature and stirred for 30 min. After removal of half of the solvent in vacuo and subsequent addition of 30–40 mL of dry *n*-heptane the complexes **4a–d** precipitate as off-white (**4a**,**b**) to yellow (**4c**,**d**) solids. After filtration the solids were washed two times with 8 mL of dry *n*-heptane and dried in vacuo. All isolated complexes **4a–d** are soluble in polar solvents like chloroform and dichlormethane and stable in the solid state. All complexes

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* Corresponding author. Tel.: +49 89 2180 77486; fax: +49 89 2180 77867.
E-mail address: ipl@cup.uni-muenchen.de (I.-P. Lorenz).

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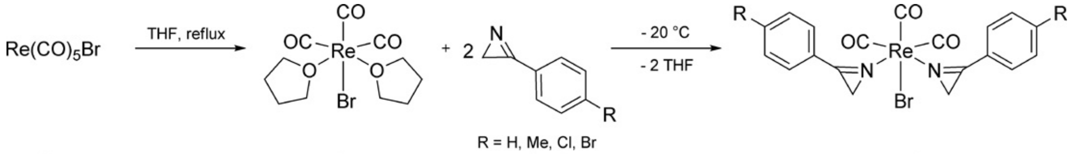

1 2 3a-d 4a-d

Scheme 1. Reaction of [Re(CO)$_5$Br] (**1**) with THF and 2*H*-3-arene-azirines (az) (**3a**–**d**) yielding [*fac*-Re(CO)$_3$(az)$_2$Br] (**4a**–**d**).

4a–**d** as well as the corresponding ligands **3a**–**d** are sensitive to protic solvents.

The connectivity within complexes **4a**–**d** was deduced by single crystal X-ray crystallography, NMR and IR spectroscopy and MS spectrometry. Single crystals of **4a**–**d** suitable for structural determination by X-ray diffraction were obtained by isothermic diffusion of *n*-pentane into dichlormethane solutions of **4a**–**d**. The ^{1}H NMR spectra of **4a**–**d** show the expected azirine signals shifted to lower field due to deshielding caused by transition metal coordination. A good indication for the *N*-coordination of the az ligands **3a**–**d** to Re(I) is the chemical shift of the CH$_2$ ring signals. The ^{13}C signals of **4a**–**d** are slightly shifted to lower field in comparison to the signals observed for **3a**–**d**. For example, the CH$_2$ ring carbon signals are observed at 22.1 ppm (**4a**) and 21.9 ppm (**4b**), respectively, compared to 19.5 ppm (**3a**) and 18.8 ppm (**3b**). Likewise in the ^{1}H NMR spectra the tendency of signal shift to lower field, compared to the corresponding signals of the free azirine, is observed [28].

Mass spectrometric investigations in the FAB$^+$ mode of the complexes **4a**–**d** exhibit similar fragmentation patterns. For example compound **4a** shows a fragmentation pattern with *m*/*z* peaks at 584, 556 and 528, 505, 500, 477 and 421 corresponding to [M]$^+$, [M−Br]$^+$, [M−nCO]$^+$ (n = 1, 2, 3) and [M−nCO−Br]$^+$ (n = 1, 3), respectively. The fragmentation pattern for the complexes **4a**–**d** is characterized by the successive loss of CO and Br or both kinds of ligands.

The IR spectra of the complexes **4a**–**d** show sharp absorption bands for the azirine C=N stretching vibrations in the range of 1760 cm^{-1} (**4b**)–1777 cm^{-1} (**4d**). The tendency of a shift to higher wavenumbers as a result of transition metal coordination with a shift of 22 cm^{-1} (**4a**) compared to ν(C=N) = 1740 cm^{-1} of az (**3a**) is detected [20]. Like complex **2** the complexes **4a**–**d** can be assigned to the point group C_s and show three CO valence vibrations of the symmetry race $2A' + A''$ at for example 2025 cm^{-1}, 1928 and 1898 cm^{-1} (**4b**) in CH$_2$Cl$_2$. As expected, the ν(C−H) absorptions of **4a**–**d** were observed in the range of 3000 cm^{-1}.

The X-ray structure analysis of **4a**–**d** revealed the formation of distorted octahedral coordination geometries. The Re(I) centers are coordinated besides the three CO ligands in *facial* positions by the nitrogen atoms of two az and one bromido ligand in complexes **4a**–**d** presenting a distorted octahedral geometry (Fig. 1). The Re−ligand bond lengths in **4a**–**d** lie within the expected ranges. Re–C$_{CO}$ and Re–Br bond lengths are comparable to those in similar Re^I(CO)$_3$L$_2$Br complexes [29]. The average value for the Re(1)–Br(1) bonds is 2.599(1) Å and those for the Re(1)–C$_{CO}$ bonds lie within the range of 1.92(1) Å and 2.01(1) Å. In all cases the Re–C$_{CO}$ bond lengths *trans* to the Re–N$_{az}$ positions are significantly shorter (average 1.92(1) Å) than those *trans* to Re–Br positions (average 2.01(1) Å). Obviously the azirine ligands act as σ-donor–π-donor ligands and favour the double bond of the π-acceptor CO in *trans* position. The Re–N$_{sp2}$ bond lengths are shortened with 2.150 Å for Re(1)−N(1) and 2.145 Å for Re(1)−N(2) (**4a**) compared to analogous aziridine complexes with Re–N$_{sp3}$ 2.199 Å and 2.202 Å [29]. Further bond lengths and angles of **4a**–**d** are listed in Table 1. The C=N, C−N, C−C bond lengths in the az ligands are comparable to bond lengths observed in uncoordinated 2*H*-azirines using single crystal X-ray diffraction methods [30]. The deviation between the mean planes of the azirine rings (defined by N(1), C(1), C(2) and N(2), C(9), C(10)) towards the equatorial coordination plane of Re(1) (defined by N(1), N(2), C(17) and C(18)) lies between 9.61° (**4a**) and 45.99° (**4d**). The azirine ring plane and the phenyl ring plane of the az ligands in the complexes **4a**–**d** are slightly bent out of a coplanar arrangement and exhibit angles between both ring planes of 4.27° and 10.10° (**4a**), 9.73° and 15.90° (**4b**), 0.94° and 8.31° (**4c**), 11.27° and 17.28° (**4d**) due to steric requirements of the az ligands. In addition in compound **4d** an *inter*molecular plane to plane π-stacking between the phenyl moieties of two az ligands is observed. The distance between the centroids of both aromatic moieties is 3.740 Å and a parallel arrangement between the planes of the two phenyl rings is formed.

Concluding we have reported the synthesis of four 2*H*-3-(arene)-azirine complexes of Re^I. Of note, these complexes are the first fully characterized transition metal carbonyl 2*H*-azirine

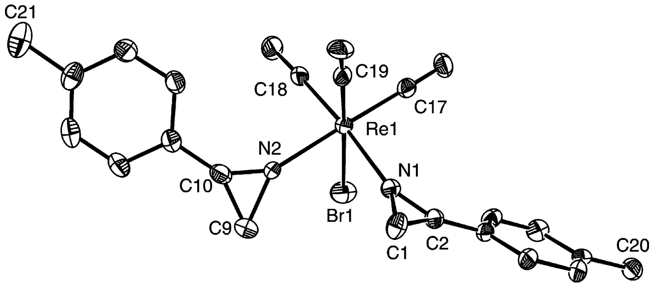

Fig. 1. Molecular structure of **4b** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) of the complexes **4a**–**d**

	4a	**4b**	**4c**	**4d**
Bond lengths (Å)				
Re(1)–N(1)	2.150(10)	2.137(5)	2.135(6)	2.142(9)
Re(1)–N(2)	2.145(10)	2.151(5)	2.148(5)	2.143(9)
Re(1)–Br(1)	2.615(2)	2.606(1)	2.585(1)	2.592(2)
Re–C(17)	1.928(14)	1.921(7)	1.915(7)	1.932(13)
Re–C(18)	1.906(14)	1.908(7)	1.933(8)	1.939(12)
Re–C(19)	1.957(14)	1.983(8)	2.047(10)	2.070(13)
N(1)–C(1)	1.535(15)	1.521(8)	1.525(10)	1.518(12)
N(1)–C(2)	1.260(16)	1.266(8)	1.262(9)	1.290(13)
C(1)–C(2)	1.456(17)	1.458(9)	1.445(10)	1.467(15)
Bond angles (°)				
N(1)–Re(1)–N(2)	84.2(4)	85.0(2)	83.5(2)	82.1(3)
N(1)–Re(1)–Br(1)	84.1(3)	84.03(13)	81.82(16)	86.7(2)
C(17)–Re(1)–N(1)	95.6(5)	94.5(3)	93.7(3)	94.7(4)
C(19)–Re(1)–Br(1)	176.7(4)	175.0(2)	175.9(2)	175.0(3)
C(2)–C(1)–N(1)	49.7(7)	50.3(4)	50.2(4)	51.2(6)
C(2)–N(1)–C(1)	61.9(8)	62.3(4)	61.6(5)	62.4(7)
N(1)–C(2)–C(1)	68.4(9)	67.4(5)	68.2(5)	66.4(8)
Δ_1[a]	9.61	36.84	22.55	34.02
Δ_2[b]	32.34	40.27	32.12	45.99

[a] Angle between the equatorial coordination plane of Re(1) (defined by N(1), N(2), C(17), C(18)) and the azirine ring plane defined by N(1), C(1), C(2) or that [b] defined by N(2), C(9), C(10).

complexes with intact three membered rings. A remarkable stabilization of the highly strained and reactive ligand is observed after coordination to the Re(CO)$_3$Br fragment. The connectivity within both complexes was deduced by single crystal X-ray crystallography, NMR and IR spectroscopy. The coordination chemistry of further 2*H*-azirine ligands to other transition metal complexes especially metal carbonyls is under investigation. This also includes C$-$N bond breaking reactions for interesting novel template reactions like in the case of saturated aziridines [31].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2008.03.035.

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