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2*H*-Azirines as Ligands: Structural Characterization of the First Neutral and Cationic (η^5-C_5Me_5)Rh(III) 2*H*-Azirine Complexes

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Dedicated to Professor H.-P. Boehm on the Occasion of his 80th Birthday

Abstract. The synthesis and structural characterization of two azirine rhodium(III) complexes are described. The stabilization, *N*-coordination and phenylgroup π-stacking of the highly reactive and strained 3-phenyl-2*H*-azirine by transition metal coordination is observed. The reaction of the dimeric complex $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ with 3-phenyl-2*H*-azirine (az) in CH_2Cl_2 at room temperature in a 1:2 molar ratio afforded the neutral mono-azirine complex $[(\eta^5\text{-}C_5Me_5)RhCl_2(az)]$. The subsequent reaction of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ with six equivalents of az and 4 equivalents of AgOTf yielded the cationic tris-azirine complex $[(\eta^5\text{-}C_5Me_5)Rh(az)_3](OTf)_2$. After purification, all complexes have been fully characterized. The molecular structures of the novel rhodium(III) complexes exhibit slightly distorted octahedral coordination geometries around the metal atoms.

Keywords: Rhodium; Azirine; π-stacking; X-ray crystallography

Introduction

2*H*-Azirines have attracted considerable interest from the synthetic, mechanistic and theoretical point of view, especially because of their versatile reactivity [1−3]. This is in contrast to 1*H*-azirines which are only known as transient intermediates representing a cyclic conjugated anti-aromatic system with four π-electrons. The reason for the increased reactivity of 2*H*-azirines is mainly due to high ring strain energy. *Sordo* et al. calculated ring strain energies of 46.7 kcal/mol at the B3LYP/6-31G* level of theory for 3,4-dihydro-1a*H*-azirine-2,3-c-pyrrol-2-one [4]. The forced deformation of bond angles in this unsatured three membered ring system is the main reason for the ring strain, which was first taken into consideration by *A. von Baeyer* in his strain theory [5].

2*H*-Azirines as versatile starting materials in organic synthesis can react as nucleophiles, electrophiles and dienophiles or dipolarophiles in cyclo addition reactions [6−8]. Interestingly, all three bonds of the azirine ring can be cleaved depending on the experimental conditions used [1]. Moreover, this highly strained imines are suitable precursors in the synthesis of an impressive number of heterocycles [6, 7, 9−11]. In this context transition metal catalyzed ring expansion or rearrangement reactions of azirines have been reported, for example the rearrangement of 2*H*- and 3*H*-azirines to indoles catalyzed by $[Rh(CO)_2Cl]_2$ and $[Rh_2(OCOCF_3)_4]$ or the reaction of two azirines to yield pyrazine or pyrrole derivatives catalyzed by $[Mo(CO)_6]$ and $[Fe_2(CO)_9]$ [7, 12−19].

Concerning 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, 20−22]. The authors discussed the surprising effect of stabilization by coordination. The azirine *N* atoms coordinate to the lewis acidic transition metal centres which results in the typical tetrahedral coordination geometry for the zinc(II) complex and a square planare geometry with a *trans* arrangement of the azirine ligands for the palladium(II) complex. Inspired by our recent results on the aziridine coordination chemistry of manganese(I), cobalt(II), nickel(II), copper(II), rhenium(I), ruthenium(II) and palladium(II) [23−26], we chose to study the coordination chemistry of 2*H*-azirines as a barely investigated class of highly strained ligands. At the beginning we chose to study the reactivity of 2*H*-azirines towards the dimeric rhodium(III) complex $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$. In this communication we report the synthesis and structural characterization of two 2*H*-azirine rhodium(III) complexes and the stabilization of the highly reactive 3-phenyl-2*H*-azirine in the coordination sphere of the (η^5-C_5Me_5)Rh(III) cation.

Results and Discussions

Synthesis

Scheme 1 and 2 illustrate the reaction of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ with 2 equivalents az (**2**) yielding $[(\eta^5\text{-}C_5Me_5)RhCl_2(az)]$ (**3**) and with 6 equivalents of az in the presence

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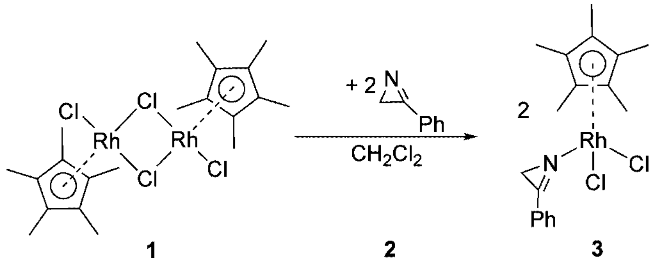
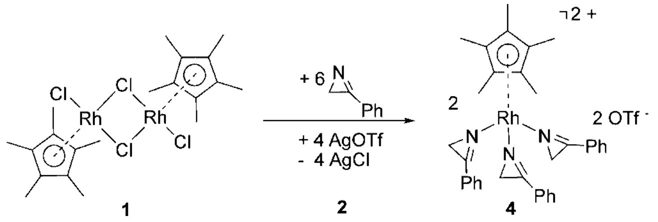
of 4 equivalents of AgOTf yielding $[(\eta^5\text{-}C_5Me_5)Rh(az)_3](OTf)_2$ (**4**), respectively. Further synthetic details are given in the experimental section. Both compounds are sensitive to moisture and protic solvents and are soluble in polar solvents such as dichloromethane and insoluble in nonpolar solvents such as *n*-hexane. The molecular structures of **3** and **4** are illustrated in Figures 2 and 3 together with selected bond lengths and angles.



Scheme 1 Reaction of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (**1**) with 3-phenyl-2*H*-azirine (**2**) yielding $[(\eta^5\text{-}C_5Me_5)RhCl_2(az)]$ (**3**).



Scheme 2 Reaction of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (**1**) with AgOTf and 3-phenyl-2*H*-azirine (**2**) yielding $[(\eta^5\text{-}C_5Me_5)Rh(az)_3](OTf)_2$ (**4**).

Spectroscopy

The ^{1}H NMR spectra of **3** and **4** 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 az to Rh^{III} is the chemical shift of the CH_2 ring signal. The ^{1}H signals of **3** and **4** are slightly shifted to lower field in comparison to the signals observed for **2**. For example, the CH_2 ring proton signals are observed at 1.88 ppm (**3**) and 2.68 and 2.41 ppm (**4**), respectively, compared to 1.75 ppm for **2**. Likewise in the ^{13}C NMR spectra the tendency of signal shift to lower field, compared to the corresponding signals of the free azirine, is observed [27]. The *intra*molecular π-stacking interaction of the phenyl groups of two az ligands of **4**, which is found later on in the solid state, can be observed in solution by ^{1}H NMR spectroscopic measurements at r. t. and 55 °C (in $CDCl_3$), respectively. At r. t. the CH_2 signals of two az ligands are observed at 2.68 ppm and that of the third at 2.41 ppm in 2:1 ratio (**A** in Fig. 1). Heating up this solution to 55 °C delivers only one corresponding broad signal for all three az ligands at 2.44 ppm (**B** in Fig. 1). Obviously, the *intra*molecular π-stacking is lost at higher temperatures. After cooling this solution to 30 °C both signals again appear, now at 2.72 and 2.43 ppm.

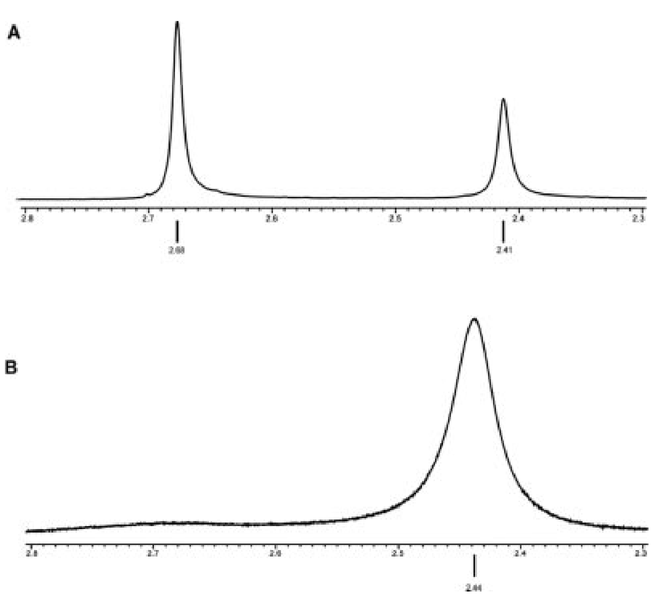


Fig. 1 ^{1}H NMR signals of the three CH_2 az groups of **4** at r. t. (**A**) and 55 °C (**B**).

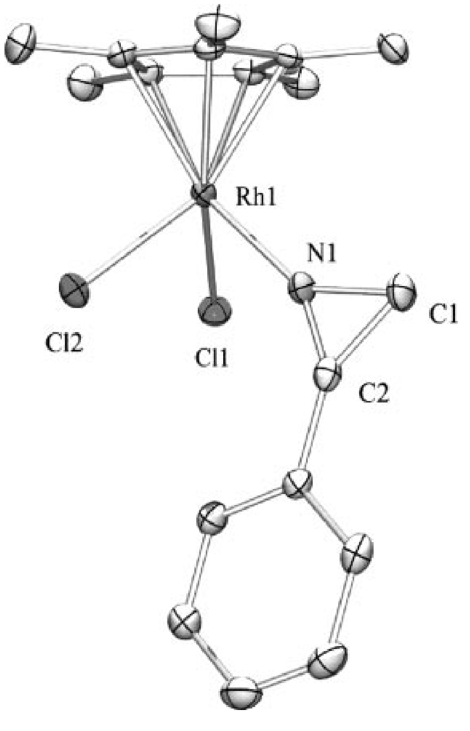


Fig. 2 Molecular structure of $[(\eta^5\text{-}C_5Me_5)RhCl_2(az)]$ (**3**). The thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity.

Selected bond lengths/Å and angles/°: Rh(1)−N(1) 2.103(3), Rh(1)−C(9) 2.145(3), Rh(1)−C(10) 2.160(3), Rh(1)−C(11) 2.129(3), Rh(1)−C(12) 2.149(3), Rh(1)−C(13) 2.156(3), Rh(1)−Cl(1) 2.421(10), Rh(1)−Cl(2) 2.390(9), N(1)−C(1) 1.526(4), N(1)−C(2) 1.255(4), C(1)−C(2) 1.456(4), N(1)−Rh(1)−Cl(1) 87.22(7), N(1)−Rh(1)−Cl(2) 87.72(7), Cl(1)−Rh(1)−Cl(2) 90.94(3), C(2)−C(1)−N(1) 49.72(18), C(2)−N(1)−C(1) 62.2(2), N(1)−C(2)−C(1) 68.0(2).

Mass spectrometric investigations in the FAB$^+$ mode of complex **3** revealed fragmentation peaks for the cleavage of the az ligand (M^+−az), and the subsequent separation of chlorido ligands (M−az−n Cl) (n = 1, 2). In the FAB^+ spectra of the *tris*-azirine complex **4** the peak for the intact cation $[(\eta^5\text{-}C_5Me_5)Rh(az)_3]^{2+}$ was not detected. The fragmentation pattern resulting from the successive cleavage of the azirine ligands and the coordination of one triflato group with peaks for (M−n az−OTf) to $[(\eta^5\text{-}C_5Me_5)Rh(az)_{3-n}]^{2+}$ (n = 1, 2, 3) or (M−n az−2 OTf) (n = 1, 2) were observed, respectively.

The IR spectra of the complexes **3** and **4** show sharp absorption bands for the azirine C=N stretching vibrations at 1769 cm^{-1} (**3**) and 1765 cm^{-1} (**4**). A shift of 29 cm^{-1} (**3**) and 25 cm^{-1} (**4**) to higher wavenumbers compared to ν(C=N) = 1740 cm^{-1} of az is detected [21]. In addition, the typical σ- and δ-ring vibrations of az, the C_5Me_5 ligand and OTf anions in the fingerprint region were observed. The stretching and deformation vibrations of the CF_3 and SO_3 groups in compound **4** are dectected at 1031 cm^{-1} (σ), 637 cm^{-1} (δ) (SO_3) and 1266 cm^{-1} (σ), 769 cm^{-1} (δ) (CF_3) [28, 29]. As expected, the ν(C-H) absorptions of **3** and **4** were observed between 2907 cm^{-1} and 3086 cm^{-1}.

Crystal Structure Analysis

The molecular structures of the compounds **3** and **4** have been determined by single crystal X-ray diffraction analysis. Single crystals were obtained by isothermic diffusion of *n*-pentane into the dichloromethane solutions of **3** or **4**, respectively. The X-ray structure analysis of **3** and **4** revealed the formation of octahedral coordination. The Rh^{III} centres are coordinated besides the η^5-C_5Me_5 ligand by the nitrogen atom of one az and two chlorido ligands in complex **3** and by the *N* atoms of three az ligands in **4**, both presenting a slightly distorted octahedral coordination.

All of the Rh−ligand bond lengths in **3** lie within the expected ranges and are comparable to those in similar complexes [20], for example 2.103 Å for Rh(1)−N(1). The C=N, C−N, C−C bond lengths in the az ligand are slightly enlarged compared to bond distances observed in uncoordinated 2*H*-azirines using single crystal X-ray diffraction. The az ligand is almost coplanar and exhibits an angle between the azirine ring plane and the phenyl ring plane of 4.86°. Moreover in compound **3** an *inter*molecular plane to plane π-stacking between the η^5-C_5Me_5 ligand and the phenyl ring of the az ligand is observed. The distance between the centroids of both aromatic systems is measured at 4.039 Å and a distortion angle of 7.92° between the planes of the η^5-C_5Me_5 ligand and the phenyl ring is formed [30].

The structure of compound **4** shows that the Rh^{3+} ion is bonded to the η^5-C_5Me_5 ligand and to the three az ligands and is best described as a slightly distorted octahedron. The solid state structure of compound **4** also shows two triflato anions for each twofold cationic $[(\eta^5\text{-}C_5Me_5)Rh(az)_3]^{2+}$ fragment. All of the Rh−C bond distances in **4** are within the expected range [26]. It is noteworthy that the Rh−N bond lengths in **4** differ slightly. Rh(1)−N(1) and Rh(1)−N(3) with 2.108 Å and 2.107 Å are almost equal to the corresponding Rh(1)−N(1) bond in complex **3**. Rh(1)−N(2) with 2.089 Å, however, is a little bit shortened. The C=N, C−N, C−C bond lengths in all three az ligands are almost equal to each other and slightly enlarged compared to bond distances observed in the free 2*H*-azirine [31]. The angles between the planes of the azirines and the phenyl rings of **4** show the values 5.26°, 11.57° to 22.51°. For one az ligand in compound **4** an almost coplanar ring arrangement of 4.86° is observed, whereas the other two az ligands exhibit much larger distortion angles of 11.57° and 22.51° due to steric reasons. In addition in compound **4** the *intra*molecular plane to plane π-stacking between the phenyl moieties of two az ligands is observed as it has been already demonstrated by ^1H NMR spectra. The distance between the centroids of both aromatic moieties is 4.023 Å and an angle of 7.92° between the planes of the the two phenyl rings is formed.

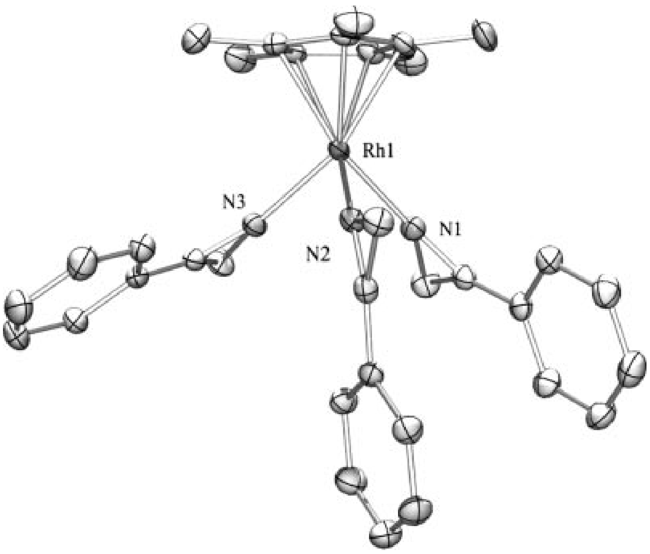


Fig. 3 Molecular structure of $[(\eta^5\text{-}C_5Me_5)Rh(az)_3](OTf)_2$ (**4**). The thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms, one dichloromethane molecule and two triflate anions are omitted for clarity.

Selected bond lengths/Å and angles/°: Rh(1)−N(1) 2.108(3), Rh(1)−N(2) 2.089(3), Rh(1)−N(3) 2.107(3), Rh(1)−C(25) 2.146(4), Rh(1)−C(26) 2.157(3), Rh(1)−C(27) 2.161(3), Rh(1)−C(28) 2.145(3), Rh(1)−C(29) 2.175(4), N(1)−C(1) 1.535(5), N(1)−C(2) 1.258(5), C(1)−C(2) 1.465(5), N(2)−Rh(1)−N(1) 84.25(11), N(2)−Rh(1)−N(3) 89.00(11), N(3)−Rh(1)−N(1) 87.17(11), C(2)−N(1)−C(1) 62.3(3), C(2)−C(1)−N(1) 49.5(2), N(1)−C(2)−C(1) 68.1(3).

Experimental Part

General Methods and Materials:

All manipulations were performed under a dry argon atmosphere using Schlenk line techniques. Dichlormethane was distilled from CaH_2, *n*-pentane and *n*-hexane were distilled from sodium. All solvents were stored under dry argon atmospheres and over 3 Å molecular sieves (dichlormethane) respectively or sodium pieces (*n*-pentane, *n*-hexane). The ^1H, ^{13}C and ^{19}F NMR spectra were recorded using a Jeol Eclipse 270 and a Jeol Eclipse 400 instrument

Table 1 Crystal data and details of the structure refinement for compounds **3** and **4**.

Compound	**3**	**4**
Formula	$C_{18}H_{22}Cl_2NRh$	$C_{37}H_{38}Cl_2F_6N_3O_6RhS_2$
FW	426.19	972.65
Temperature /K	200(2)	200(2)
Wavelength /Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a /Å	8.5382(17)	12.116(2)
b /Å	14.524(3)	17.612(4)
c /Å	14.574(3)	20.178(4)
β /°	104.86(3)	103.34(3)
V /Å^3	1746.9(6)	4189.8(14)
Z	4	4
$\rho_{calc.}$ /g cm^{-1}	1.6205(6)	1.5420(5)
μ /mm^{-1}	1.279	0.709
F(000)	864	1976
Crystal size /mm	0.15 x 0.08 x 0.01	0.20 x 0.16 x 0.04
θ range /°	3.16 to 27.48	3.20 to 26.00
Index Range	$-11 \leq h \leq 11$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$	$-14 \leq h \leq 14$, $-21 \leq k \leq 21$, $-24 \leq l \leq 24$
Reflns collected	7611	15979
Independent reflns	3997	8197
R_{int}	0.0343	0.0254
Completeness to θ	99.8 %	99.7 %
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data / restraints / parameters	3997 / 0 / 196	8197 / 0 / 520
S on F^2	1.061	1.040
Final R indices [I>2 σ (I)]	$R_1 = 0.0331$, $wR_2 = 0.0693$	$R_1 = 0.0443$, $wR_2 = 0.1154$
R indices (all data)	$R_1 = 0.0540$, $wR2 = 0.0770$	$R_1 = 0.0612$, $wR_2 = 0.1268$
Largest difference peak/hole	0.675 and −0.530 e.Å^{-3}	1.258 and −0.975 e.Å^{-3}
CCDC number	677717	677718

operating at 270 MHz (^{1}H), 400 MHz (^{1}H), 68 MHz (^{13}C), 100 MHz (^{13}C) and 376 MHz (^{19}F). All chemical shifts are given in ppm relative to TMS (^{1}H, ^{13}C). Mass spectra were measured using a JEOL Mstation JMS 700 in the FAB$^+$ mode (NBA matrix). Multi-isotope containing fragments refer to the isotope with the highest abundance. Infrared spectra were recorded with a Nicolet 520 FT-IR and Perkin Elmer Spectrum One FT-IR spectrometer in the 4000 − 400 cm^{-1} range. Single crystal X-ray diffraction data were collected on a Nonius Kappa CCD using graphite-monochromated Mo-K$_\alpha$ radiation. Single crystal X-ray structure analyses were performed using direct methods using the SHELXS software and refined by full-matrix least-squares with SHELXL-97 [32]. Table 1 contains the crystallographic data and details of the structural refinement of **3** and **4**. The CCDC numbers of compounds **3** and **4** contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via **www.ccdc.cam.ac.uk/data_request/cif**. Elemental analysis were performed by the Microanalytical Laboratory of the Department of Chemistry and Biochemistry, LMU Munich using a Heraeus Elementar Vario El. Uncorrected melting points were obtained using a Büchi Melting Point B-540 device.

General method for the synthesis of [(η^5-C$_5$Me$_5$)RhCl$_2$(az)] (3) *and* [(η^5-C$_5$Me$_5$)Rh(az)$_3$](OTf)$_2$ (4)

3-phenyl-2*H*-azirine (az) (**2**) and [η^5-(C$_5$Me$_5$)RhCl$_2$]$_2$ (**1**) were prepared according to literature methods and stored in dry argon atmosphere [33, 34]. Additionally az was cooled to −32 °C due to the thermic instability at r.t. (Caution: 3-phenyl-2*H*-azirine is highly irritant).

The novel azirine transition metal complexes **3** and **4** have been prepared as follows. Complex **3** was synthesized by solving one equivalent of **1** in dry dichloromethane and the direct addition of two equivalents of az (**2**). The reaction mixture was stirred at r.t. for 45 min. After removal of the solvent in vacuo the residue was purified by washing the solid with dry *n*-hexane (20 mL). The orange solid was dried in vacuo. The red crystalline product was obtained after recrystallization from a dichloromethane / *n*-pentane solution.

Complex **4** was synthesized by reacting [η^5-(C$_5$Me$_5$)RhCl$_2$]$_2$ (**1**) with four equivalents of silver(I)triflate. After 3 hours of stirring at ambient temperature the precipitated AgCl was removed by centrifugation and decantation of the solution. Subsequently 6 equivalents of 3-phenyl-2*H*-azirine (**2**) were added and again the solution was stirred for 15 min at r.t. resulting in the formation of the tris-azirine complex **4**. After removal of the solvent in vacuo the brownish residue was purified by stirring in dry *n*-hexane (10 mL) for 12 hours at ambient temperature. The *n*-hexane phase was then removed by decantation and the brownish red solid was dried in vacuo.

[(η^5-C$_5$Me$_5$)RhCl$_2$(az)] (3):

Reagents: 129 mg (0.194 mmol) **1**, 114 mg (0.971 mmol) **2**. Yield 37 % (31 mg, 0.072 mmol); red crystals; decomposition > 170 °C; $C_{18}H_{22}Cl_2NRh$ (426.19); C 51.28 (calc. 50.73); H 5.05 (5.20); N, 3.67 (3.29) %.

IR (KBr, cm^{-1}): 3086 w, 3042 w, 2970 w, 2907 w, 1769 s, 1598 w, 1579 w, 1464 m, 1451 m, 1376 w, 1360 w, 1341 w, 1327 w, 1307 w, 1275 w, 1184 w, 1161 w, 1129 w, 1084 w, 1021 m, 927 w, 837 w, 796 w, 765 s, 733 w, 693 m, 686 s, 617 w, 546 w, 532 w cm^{-1}. **MS** (FAB-pos): *m*/*z* = 426 (M$^+$, 8 %), 391 (M$^+$ − Cl, 100 %), 273 (M$^+$−az−Cl, 92 %), 237 (M$^+$−az−2 Cl, 66 %). **^{1}H NMR** (270 MHz, CDCl$_3$): δ = 8.03 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 2 H, Ph-az), 7.63-7.51 (m, 3 H, Ph-az), 1.88 (s, 2 H, CH$_2$-az), 1.61 (s, br, 15 H, Me-C$_5$Me$_5$) ppm. **^{13}C {^{1}H} NMR** (68 MHz, CD$_2$Cl$_2$): δ = 165.7 (C$_q$-C=N), 133.5 (CH-az), 130.6 (C$_q$-az), 129.2 (CH-az), 94.3 (br, C$_q$-C$_5$Me$_5$), 19.5 (CH$_2$-az), 9.5 (CH$_3$-C$_5$Me$_5$) ppm.

[(η^5-C$_5$Me$_5$)Rh(az)$_3$](OTf)$_2$ (4):

Reagents: 131 mg (0.212 mmol) **1**, 150 mg (1.280 mmol) **2**, 223 mg (0.868 mmol) AgOTf. Yield 84 % (158 mg, 0.178 mmol); brownish red powder; decomposition > 113 °C; $C_{36}H_{36}F_6N_3O_6RhS_2$ (887.71): C 48.80 (calc. 48.71); H 3.95 (4.09); N 4.69 (4.73).

IR (KBr, cm^{-1}): 3067 w, 1765 m, 1596 w, 1491 w, 1452 w, 1378 w, 1266 vs, 1224 w, 1161 m, 1132 w, 1074 w, 1031 s, 1000 w, 833 w, 769 w, 689 w, 637 s, 573 w, 548 w, 518 w cm^{-1}. **MS** (FAB-pos): *m*/*z* = 621 (M$^+$−OTf−az, 18 %), 504 (M$^+$−OTf−2 az, 100 %), 472 (M$^+$−2 OTf−az, 34 %), 387 (M$^+$−OTf−3 az, 89 %), 355 (M$^+$−2 OTf−2 az, 73 %). **^{1}H NMR** (400 MHz, CD$_2$Cl$_2$): δ 7.83 (d, ^3J = 7.4 Hz, 2 H, Ph-az), 7.74-7.45 (m, 13 H, Ph-az), 2.68 (s, 4 H, CH$_2$-az), 2.41 (s, 2 H, CH$_2$-az), 1.87 (s, br, 7 H, Me-C$_5$Me$_5$), 1.79 (s, br, 8 H, Me-C$_5$Me$_5$) ppm. ^{13}C {**^{1}H**} **NMR** (100 MHz, CD$_2$Cl$_2$): δ = 171.1 (C$_q$-C=N), 169.4 (C$_q$-C=N), 136.8 (CH-az), 136.3 (CH-az), 131.6 (CH-az), 130.6 (CH-az), 130.1 (CH-az), 129.7 (CH-az), 129.3 (CH-az), 129.2 (CH-az), 129.0 (CH-az), 122.2 (q, $^1J_{C,F}$ = 320 Hz, CF$_3$), 121.3 (C$_q$-az), 120.8 (C$_q$-az), 21.4 (CH$_2$-az), 21.3 (CH$_2$-az), 9.5 (CH$_3$-C$_5$Me$_5$) ppm. **^{19}F {^{13}C} NMR** (376 MHz, CD$_2$Cl$_2$): δ = −79.3 (s, CF$_3$-OTf) ppm.

Conclusion

Two 2*H*-3-phenylazirine complexes of Rh(III) have been prepared and isolated. Of note, these complexes are the first fully characterized organometallic 2*H*-azirine complexes. A remarkable stabilization of the highly strained and reactive ligand is observed by coordination. The connectivity within both complexes was deduced by single crystal X-ray crystallography and NMR spectroscopy. The coordination chemistry of further 2*H*-azirine ligands to other transition metal complexes is under investigation.

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