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Neutral *Mono*- and Cationic *Bis*-Aziridine d^6-Metal Complexes of the Type $[(\pi\text{-arene})M(Az)Cl_2]$ and $[(\pi\text{-arene})M(Az)_2Cl]Cl$ (π-arene/M = η^6-C_6Me_6/Ru; η^5-C_5Me_5/Rh, Ir)

Roman Bobka, J. Nicolas Roedel, Bernd Neumann, Christoph Krinninger, Peter Mayer, Stefan Wunderlich, Alexander Penger, and Ingo-Peter Lorenz*

München, Ludwig Maximilians University, Department of Chemistry and Biochemistry

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Abstract. The synthesis of neutral *mono*- and cationic *bis*-aziridine complexes of ruthenium(II), rhodium(III) and iridium(III) are described. The dimeric complexes $[MCl_2L]_2$ (M = Ru^{II}, L = C_6Me_6; M = Rh^{III}/Ir^{III}, L = C_5Me_5) (**1-3**) react with a series of aziridines (Az = C_2H_4NH, C_2H_3MeNH, $C_2H_2Me_2NH$, C_2H_3EtNH, C_2H_3PhNH) (**a-e**) in a 1:2 or 1:5 molar ratio to give the neutral *mono*-aziridine complexes $[MCl_2L(Az)]$ (**4e-6e**) or cationic *bis*-aziridine complexes $[MClL(Az)_2]Cl$ (**7a-9d**), respectively. After purification, all of the complexes were fully characterized and the IR, MS, ^1H and ^{13}C NMR spectra are reported and discussed. The single crystal structure analysis revealed a distorted octahedral structure for all complexes.

Keywords: Aziridine; Coordination chemistry; Crystal structures; Iridium; Rhodium; Ruthenium

Introduction

Research into the coordination chemistry of the aziridine ligand dates back to 1958, when *Hieber* et al. first introduced aziridine as a ligand [1]. In the following years, *Edwards* et al. and *Fritz* et al. characterized various aziridine transition metal halogenido complexes using elemental analysis and IR spectroscopy [2−5]. *Edwards* et al. subsequently reported the first X-ray structure analysis of an aziridine rhodium complex in 1969 [6], and a series of publications on the coordination chemistry of aziridine from various research groups followed, including the recent reports on main group metal aziridine complexes by *Gal* et al. [7−19].

Although aziridines are isolobal to oxiranes and thiiranes (C_2H_4X; X = NH, O, S), the complex formation of aziridines differs strongly from the latter two. Oxiranes and thiiranes are both suitable oxidising agents for organometallic compounds, whereby oxo or thio complexes result via ethylene elimination [20, 21]. The aziridines, however, usually remain intact as three-membered rings and coordinate via nitrogen atom. However, transition metal mediated ring opening reactions, resulting in the formation of β-aminoacyl complexes have been observed by *Beck* et al. and our research group [22−24]. In addition *Hillhouse* et al. reported the oxidative addition of *N*-tosylated aziridine to nickel(0) complexes forming the corresponding azametallacyclobutane complex, which was structurally investigated using X-ray diffraction [25].

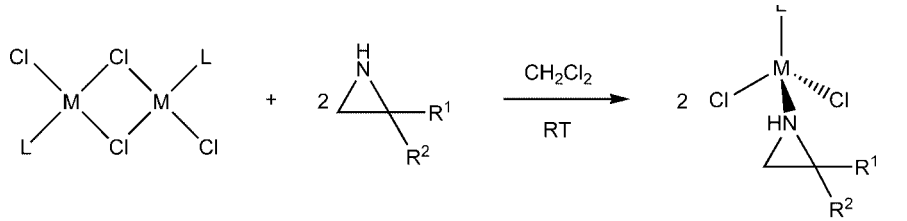
The opening of the aziridine ring, which occurs after protonation of the amino group and nucleophilic attack, is mainly due to *Baeyer* [26] and *Pitzer* ring strain. The versatility of the aziridine motif has resulted in widespread interest in this heterocycle [27−30]. In addition to being important tools in organic chemistry, aziridine compounds have a variety of synthetic applications, for example, as synthones in natural synthesis [31, 32], monomers in macromolecular chemistry [33, 34], or target molecules in organic synthesis [35−37]. Another important factor is the biological efficiency of aziridines, whereby as expected, *in vivo* effects of aziridine derivatives are mostly the result of ring opening reactions. This results in the possible carcinogenic activity of aziridine compounds. However, there are several aziridine containing classes of compounds such as the mitosanes (e.g. the well known anti tumor agent Mitomycin C), that combine both selectivity and potency as alkylation agents [28, 30, 38, 39].

* Prof. Dr. I.-P. Lorenz
Department Chemie und Biochemie
Ludwig-Maximilians-Universität München
Butenandtstraße 5?13 (Haus D)
D-81377 München, Germany
Fax: +49-(0)89-2180-77867
E-mail: ipl@cup.uni-muenchen.de

Results and Discussion

Synthesis

The ligands aziridine (**a**), 2-methylaziridine (**b**), 2,2-dimethylaziridine (**c**), 2-ethylaziridine (**d**) and 2-phenylaziridine (**e**)

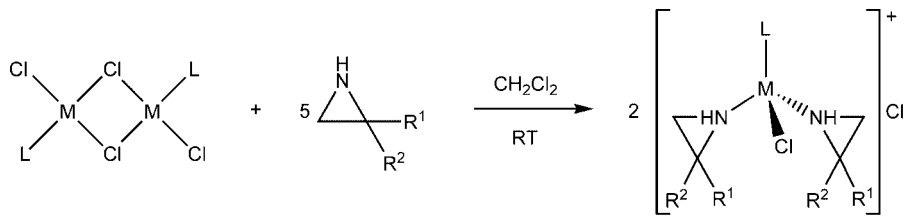


1: M = Ru, L = C_6Me_6
2: M = Rh, L = Cp*
3: M = Ir, L = Cp*

a: $R^1 = R^2 = H$
b: $R^1 = H$, $R^2 = Me$
c: $R^1 = R^2 = Me$
d: $R^1 = H$, $R^2 = Et$
e: $R^1 = H$, $R^2 = Ph$

4e: M = Ru, L = C_6Me_6
5b: M = Rh, L = Cp*
6a, b, c, e: M = Ir, L = Cp*

Scheme 1 Synthesis of the neutral *mono*-aziridine complexes **4e-6e** by the reaction of $[MCl_2L]_2$ (**1-3**) with 2 equivalents of the aziridines **a-e**.



1: M = Ru, L = C_6Me_6
2: M = Rh, L = Cp*
3: M = Ir, L = Cp*

a: $R^1 = R^2 = H$
b: $R^1 = H$, $R^2 = Me$
c: $R^1 = R^2 = Me$
d: $R^1 = H$, $R^2 = Et$
e: $R^1 = H$, $R^2 = Ph$

7a, c, d, e: M = Ru, L = C_6Me_6
8a, c, e: M = Rh, L = Cp*
9a, c, d: M = Ir, L = Cp*

Scheme 2 Synthesis of the cationic *bis*-aziridine complexes **7a-9d** by the reaction of $[MCl_2L]_2$ (**1-3**) with 5 equivalents of the aziridines **a-e**.

were prepared from β-amino-alcohols according to standard literature methods [40, 41].

Scheme 1 shows the reactions of the dimeric complexes $[MCl_2L]_2$ (**1-3**) with stoichiometric amounts (1:2) of the aziridines (**a-e**) in dichloromethane to give the corresponding neutral *mono*-aziridine complexes $[MCl_2L(Az)]$ (**4e**, **5b**, **6a**, **b**, **c**, **e**).

The cationic *bis*-aziridine complexes $[MClL(Az)_2]Cl$ (**7a**, **c**, **d**, **e**, **8a**, **c**, **e**, **9a**, **c**, **d**) were prepared by adding an excess (1:5) of the aziridines (**a-e**) to a solution of $[MCl_2L]_2$ (**1-3**) in dichloromethane (Scheme 2).

All products **4e-9d** were obtained in good yields (77−99 %) and are soluble in polar solvents such as acetone or dichloromethane, but insoluble in non-polar solvents such as *n*-pentane.

Crystal Structure Analysis

The molecular structures of compounds **4e-9d** were determined using single crystal X-ray diffraction. Single crystals were obtained by the isothermic diffusion of *n*-pentane into acetone solutions of **9a** and **9c**, and by slow evaporation of dichloromethane solutions of **4e-8e** and **9d**. Details of the relevant data collection and refinement are summarized in Tables 1-3. For each type of compound one molecular structure (**4e**, **5b**, **6a**, **7c**, **8a**, **9d**) is shown in Figures 1-6. Selected bond lengths and angles of compounds (**4e-8e**, **9d**) are summarized in Tables 4-6.

The X-ray structure analysis showed a distorted octahedral structure for all obtained compounds (**4e-9d**). The aromatic ligand L (C_6Me_6 or C_5Me_5) represents one octahedral face, while the other three coordinating atoms (Cl or N) form the opposite one. All M−N (209−215 pm) and M−Cl (239−244 pm) bond lengths are within a small range and appear to vary only slightly with different metals. In addition, the M−N and M−Cl bond lengths are comparable with those in similar complexes [42−49].

In the *mono*-aziridine complexes **4e-6e**, the aziridine ligand is always bent towards one chloride ligand, which results in larger N−M−Cl angles (87.5°−90.7°) in comparison to the other N−M−Cl angles (82.0°−86.7°). The difference between the two N−M−Cl angles is dependent on the substituent(s) in 2-position of the aziridine ring, and therefore the biggest discrepancy (8.7°) is found in the 2,2-dimethylaziridine complex **6c**. All Cl−M−Cl angles are in the range of 87.1° to 92.3° and differ only marginally from those in related complexes [42−45].

The N−M−N angles (77.4°−87.2°) of the *bis*-aziridine complexes **7a-9d** are smaller than the N−M−Cl angles (86.8°−92.6°), because in the former, both aziridines are bent towards the chloride ligand. However, this effect depends on the steric demands of the aziridine ring, whereby

Table 1 Crystal data and details of structural refinement for compounds **4e-6e**

Compound	**4e**	**5b**	**6a**	**6b**	**6c**	**6e**
Formula	$C_{20}H_{27}Cl_2NRu$	$C_{13}H_{22}Cl_2NRh$	$C_{12}H_{20}Cl_2IrN$	$C_{13}H_{22}Cl_2IrN$	$C_{14}H_{24}Cl_2IrN$	$C_{18}H_{24}Cl_2IrN$
FW	453.41	366.13	441.39	455.44	469.44	517.48
Temperature /K	200	200	200	200	200	200
Wavelength /Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Cc*	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a /Å	13.326(3)	8.4918(17)	8.5290(17)	15.7176(2)	13.502(3)	7.6823(2)
b /Å	21.549(4)	11.734(2)	11.745(2)	8.5865(5)	8.1135(2)	12.193(2)
c /Å	8.2392(16)	15.726(3)	14.142(3)	11.6753(1)	14.712(3)	19.736(4)
β /°	106.02(3)	90	90	90	93.34	98.59(3)
V /Å^3	2274.1(8)	1566.9(5)	1416.7(5)	1575.7(2)	1609.0(6)	1827.9(6)
Z	4	4	4	4	4	4
$\rho_{calc.}$ /g cm^{-1}	1.5746	1.5521	2.070	1.9199	1.938	1.880
μ /mm^{-1}	1.166	1.411	9.777	8.793	8.614	7.593
F(000)	1097	744	840	872	904	1000
Crystal size /mm	0.20 x 0.06 x 0.02	0.20 x 0.15 x 0.11	0.12 x 0.10 x 0.07	0.32 x0.11 x 0.07	0.30 x 0.22 x 0.20	0.18 x 0.15 x 0.07
θ range /°	3.18 to 26.30	3.23 to 27.48	3.13 to 27.49	2.17 to 27.98	2.11 to 27.91	1.97 to 25.88
Index Range	$-16 \le h \le 16$, $-26 \le k \le 26$, $-10 \le l \le 10$	$-8 \le h \le 11$, $-13 \le k \le 15$, $-20 \le l \le 20$	$-10 \le h \le 10$, $-15 \le k \le 13$, $-18 \le l \le 18$	$-20 \le h \le 20$, $-10 \le k \le 11$, $-14 \le l \le 15$	$-17 \le h \le 17$, $-10 \le k \le 10$, $-19 \le l \le 19$	$-9 \le h \le 9$, $-14 \le k \le 14$, $-24 \le l \le 24$
Reflns collected	8490	14148	12475	13620	13401	12659
Independent reflns	4490	3544	3235	3766	3838	3507
R_{int}	0.0292	0.0755	0.0485	0.0811	0.0794	0.0587
Completeness to θ	99.6 %	99.2 %	99.5 %	99.3 %	99.6 %	98.7 %
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data / restraints / parameters	4490 / 2 / 244	3544 / 0 / 182	3235 / 0/ 151	3766 / 0 / 152	3838 / 0 / 171	3507 / 0 / 205
S on F^2	1.030	1.069	1.082	1.024	0.990	1.034
Final R indices [I>2 σ (I)]	$R_1 = 0.0247$, $wR_2 = 0.0521$	$R_1 = 0.0338$, $wR_2 = 0.0751$	$R_1 = 0.0281$, $wR_2 = 0.0626$	$R_1 = 0.0297$, $wR_2 = 0.0674$	$R_1 = 0.0361$, $wR_2 = 0.0870$	$R_1 = 0.0585$, $wR_2 = 0.1473$
Largest difference peak/hole	0.497 and −0.234 e.Å^{-3}	0.362 and −0.653 e.Å^{-3}	1.898 and −2.245 e.Å^{-3}	1.158 and −1.272 e.Å^{-3}	3.923 and −3.408 e.Å^{-3}	10.399 and −3.038 e.Å^{-3}
CCDC number	652371	652745	652372	652375	652373	652374

Table 2 Crystal data and details of structural refinement for compounds **7a-7e**

Compound	**7a**	**7c**	**7d**	**7e**
Formula	$C_{17}H_{30}Cl_4N_2Ru$	$C_{20}H_{36}Cl_2N_2Ru$	$C_{20}H_{36}Cl_2N_2Ru$	$C_{28}H_{36}Cl_2N_2Ru$
FW	505.31	476.49	476.49	572.57
Temperature /K	200	200	200	200
Wavelength /Å	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a /Å	8.7804(18)	10.958(2)	9.985(2)	18.741(4)
b /Å	10.028(2)	15.339(3)	12.347(3)	14.852(3)
c /Å	13.090(3)	13.224(3)	12.683(3)	9.4956(19)
α /°	73.42(3)		101.67(3)	
β /°	85.05(3)	96.12(3)	90.07(3)	94.07
γ /°	79.31(3)		108.94(3)	
V /Å^3	1084.8(4)	2210.2(8)	1444.6(5)	2636.4(9)
Z	2	4	2	4
$\rho_{calc.}$ /g cm^{-1}	1.5470	1.4320	1.0954	1.4426
μ /mm^{-1}	0.965	0.957	0.732	0.816
F(000)	516	992	496	1184
Crystal size /mm	0.16 x 0.09 x 0.06	0.24 x 0.20 x 0.14	0.24 x 0.17 x 0.10	0.18 x 0.13 x 0.10
θ range /°	3.25 to 27.51	3.25 to 27.47	4.10 to 26.06	3.27 − 25.04
Index Range	$-11 \le h \le 11$, $-12 \le k \le 13$, $-16 \le l \le 16$	$-14 \le h \le 14$, $-19 \le k \le 19$, $-17 \le l \le 17$	$-12 \le h \le 11$, $-15 \le k \le 13$, $-13 \le l \le 15$	$-22 \le h \le 22$, $-17 \le k \le 17$, $-11 \le l \le 11$
Reflns collected	8929	9770	7608	8977
Independent reflns	4826	5044	5667	4648
R_{int}	0.0219	0.0126	0.1067	0.0204
Completeness to θ	96.9 %	99.7 %	99.1 %	99.7 %
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data / restraints / parameters	4826 / 0 / 217	5044 / 0 / 226	5667 / 0 / 281	4648 / 0 / 298
S on F^2	1.065	1.054	1.069	1.136
Final R indices [I>2 σ (I)]	$R_1 = 0.0293$, $wR_2 = 0.0683$	$R_1 = 0.0269$, $wR_2 = 0.0694$	$R_1 = 0.0781$, $wR_2 = 0.1968$	$R_1 = 0.0360$, $wR_2 = 0.0809$
Largest difference peak/hole	0.655 and −0.676 e.Å^{-3}	0.496 and −0.644 e.Å^{-3}	1.427 and −1.504 e.Å^{-3}	0.485 and −0.696 e.Å^{-3}
CCDC number	652367	652368	652369	652370

Table 3 Crystal data and details of structural refinement for compounds **8a-9d**

Compound	**8a**	**8c**	**8e**	**9a**	**9c**	**9d**
Formula	$C_{14}H_{25}Cl_2N_2Rh$	$C_{18}H_{33}Cl_2N_2Rh$	$C_{26}H_{33}Cl_2N_2Rh$	$C_{14}H_{25}Cl_2IrN_2$	$C_{18}H_{33}Cl_2IrN_2$	$C_{18}H_{33}Cl_2IrN_2$
FW	395.17	451.27	547.37	484.48	540.59	540.59
Temperature /K	200	200	200	200	200	200
Wavelength /Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	*C2/m*	*Pbca*	$P2_1/c$	*Pna*21	*Pbca*	$P2_1/c$
a /Å	14.652(3)	14.948(3)	18.062(4)	19.2782(6)	15.002(3)	11.814(2)
b /Å	12.260(3)	13.185(3)	15.146(3)	13.7418(5)	13.161(3)	10.483(2)
c /Å	11.516(2)	21.506(4)	9.1475(2)	13.2466(3)	21.523(4)	18.184(4)
β /°	100.64(3)		92.96(3)			108.24(3)
V /Å^3	2032.9(7)	4238.5(2)	2499.2(9)	3509.25(2)	4249.6(2)	2138.9(7)
Z	4	8	4	8	8	4
$\rho_{calc.}$ /g cm^{-1}	1.5687	1.4152	1.4548	1.834	1.6899	1.6788
μ /mm^{-1}	1.364	1.059	0.913	7.904	6.537	6.494
F(000)	976	1872	1128	1872	2128	1064
Crystal size /mm	0.45 x 0.38 x 0.30	0.20 x 0.14 x 0.08	0.14 x 0.13 x 0.03	0.04 x 0.12 x 0.17	0.11 x 0.08 x 0.05	0.12 x 0.06 x 0.03
θ range /°	2.18 to 27.87	3.27 to 27.48	3.37 to 27.52	3.13 to 27.49	3.24 to 27.46	3.13 to 27.46
Index Range	$-19 \le h \le 19$, $-15 \le k \le 16$, $-15 \le l \le 14$	$-19 \le h \le 19$, $-17 \le k \le 17$, $-27 \le l \le 27$	$-23 \le h \le 23$, $-19 \le k \le 19$, $-11 \le l \le 11$	$-25 \le h \le 22$, $-17 \le k \le 17$, $-14 \le l \le 16$	$-19 \le h \le 19$, $-17 \le k \le 17$, $-27 \le l \le 27$	$-15 \le h \le 15$, $-13 \le k \le 13$, $-23 \le l \le 23$
Reflns collected	8729	9158	11092	32268	9187	9149
Independent reflns	2522	4841	5714	7505	4846	4843
R_{int}	0.1022	0.0230	0.0371	0.089	0.0218	0.0360
Completeness to θ	99.3 %	99.8 %	99.5 %	97.7 %	99.8 %	99.0 %
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data / restraints / parameters	2522 / 0 / 111	4841 / 0 / 208	5714 / 0 / 280	7505 / 0 / 343	4846 / 0 / 212	4843 / 0 / 216
S on F^2	1.063	1.052	1.026	1.00	1.067	1.026
Final R indices [I>2 σ (I)]	$R_1 = 0.0439$, $wR_2 = 0.1117$	$R_1 = 0.0349$, $wR_2 = 0.0832$	$R_1 = 0.0342$, $wR_2 = 0.0739$	$R_1 = 0.0418$, $wR_2 = 0.0792$	$R_1 = 0.0265$, $wR_2 = 0.0554$	$R_1 = 0.0414$, $wR_2 = 0.0987$
Largest difference peak/hole	1.299 and −1.937 e.Å^{-3}	0.947 and −0.806 e.Å^{-3}	0.561 and −0.680 e.Å^{-3}	0.95 and −1.49 e.Å^{-3}	1.168 and −1.381 e.Å^{-3}	1.616 and −1.737 e.Å^{-3}
CCDC number	652376	652381	652379	652359	652378	652377

Table 4 Selected bond lengths /Å and angles /° of compounds **4e**, **5b**, **6a-c**, **6e**

Compound	**4e**	**5b**	**6a**	**6b**	**6c**	**6e**
M−N	2.137(2)	2.120(4)	2.123(4)	2.116(5)	2.123(4)	2.146(1)
M−Cl	2.4112(9) / 2.4391(9)	2.409(1) / 2.430(1)	2.401(1) / 2.436(1)	2.404(2) / 2.418(2)	2.412(1) / 2.429(1)	2.398(3) / 2.436(3)
N−M−Cl	83.68(7) / 87.45(7)	86.7(1) / 89.9(1)	85.4(1) / 88.0(1)	84.8(2) / 88.7(2)	82.0(1) / 90.7(1)	84.3(3) / 88.2(3)
Cl−M−Cl	88.29(4)	92.34(4)	89.40(5)	89.69(7)	87.14(6)	90.4(1)

Table 5 Selected bond lengths /Å and angles /° of compounds **7a**, **c-e**

Compound	**7a**	**7c**	**7d**	**7e**
M−N	2.121(2) / 2.127(2)	2.138(2) / 2.153(2)	2.116(5) / 2.127(6)	2.121(3) / 2.134(3)
M−Cl	2.4181(8)	2.4188(7)	2.414(2)	2.413(1)
N−M−Cl	86.80(6) / 87.42(7)	89.41(5) / 90.37(6)	88.6(2) / 89.4(2)	88.55(8) / 89.03(8)
N−M−N	83.74(8)	77.35(6)	79.3(2)	79.0(1)

Table 6 Selected bond lengths /Å and angles /° of compounds **8a**, **c**, **e**, **9a**, **c-d**

Compound	**8a**	**8c**	**8e**	**9a**	**9c**	**9d**
M−N	2.101(2)	2.126(2) / 2.140(2)	2.122(2) / 2.127(2)	2.119(8) / 2.125(9)	2.130(3) / 2.141(3)	2.094(5) / 2.102(5)
M−Cl	2.396(1)	2.3998(9)	2.3895(8)	2.405(3)	2.405(1)	2.419(2)
N−M−Cl	90.05(9)	91.44(7) / 92.59(7)	89.84(7) / 90.54(7)	88.2(2) / 88.5(2)	89.7(1) / 91.06(9)	88.2(2) / 89.5(2)
N−M−N	87.2(1)	78.76(9)	80.87(9)	86.4(3)	77.9(1)	86.6(2)

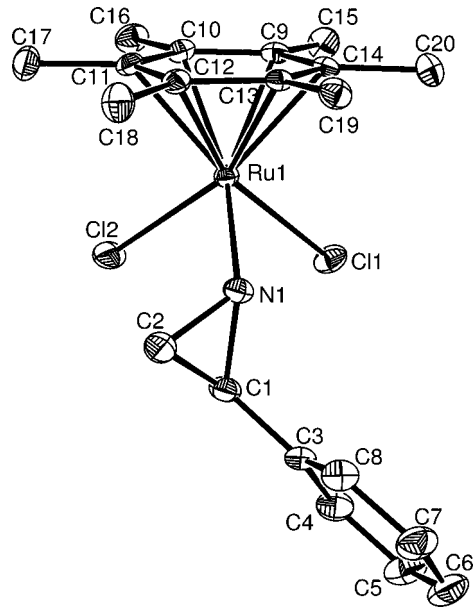


Figure 1 Molecular structure of **4e**. The thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms and one dichloromethane molecule are omitted for clarity.

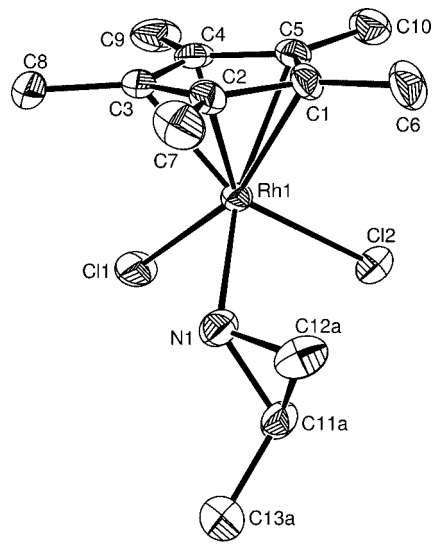


Figure 2 Molecular structure of **5b**. The thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms and disordered aziridine atoms are omitted for clarity.

with more or larger substituents at the aziridine ring, the N−M−N angle decreases and the N−M−Cl angles increase.

The endocyclic C−C and C−N bond lengths of the coordinated aziridine ligands in all complexes investigated in this work differ only slightly from those of the free aziridine [50], and the endocyclic C−C−N and C−N−C angles are found to be approximately 60°.

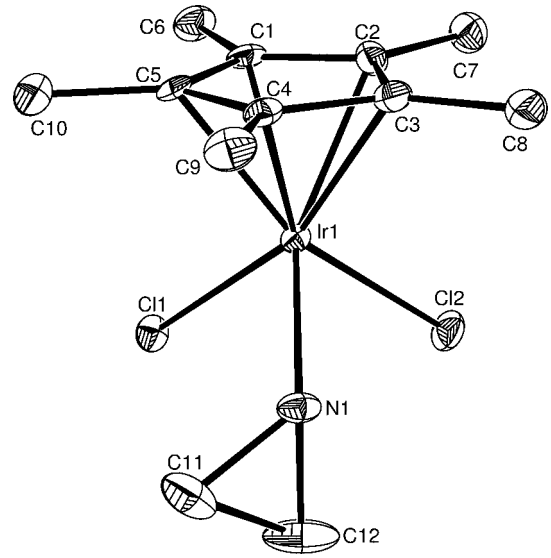


Figure 3 Molecular structure of **6a**. The thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity.

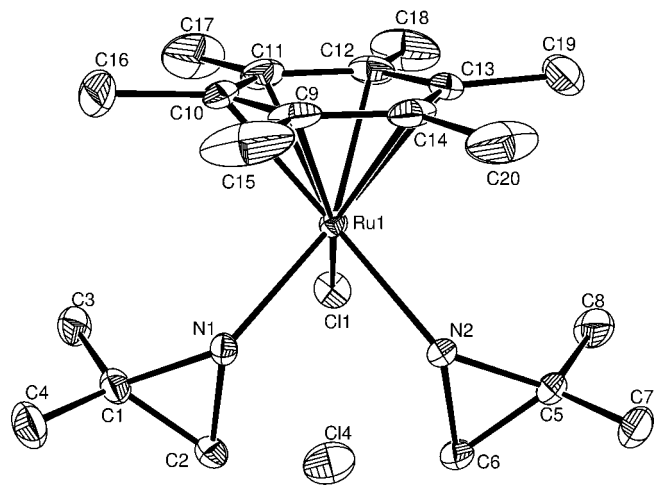


Figure 4 Molecular structure of **7c**. The thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms and one dichloromethane molecule are omitted for clarity.

Spectroscopy

The IR, ^{1}H, ^{13}C NMR and mass spectra of compounds **4e-9d** were obtained.

The IR spectra of compounds **4e-9d** show absorptions for the N−H stretching vibrations in the expected range of 3282 to 3004 cm^{-1}, as well as the characteristic bands for the deformation vibrations of the aziridine ring (891−763 cm^{-1}) [5]. As expected, the C−H absorptions of the alkyl moieties of the aziridine ligands are observed in the range of 3091 to 2875 cm^{-1}.

In the mass spectra of the *mono*-aziridine complexes **4e-6e**, the parent signals for the intact molecules were measured at *m*/*z* = 453 (**4e**), 365 (**5b**), 441 (**6a**), 455 (**6b**), 469

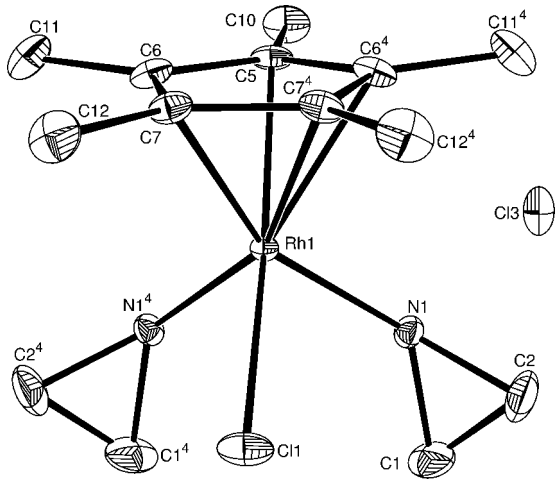


Figure 5 Molecular structure of **8a**. The thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms and two dichloromethane molecules are omitted for clarity.

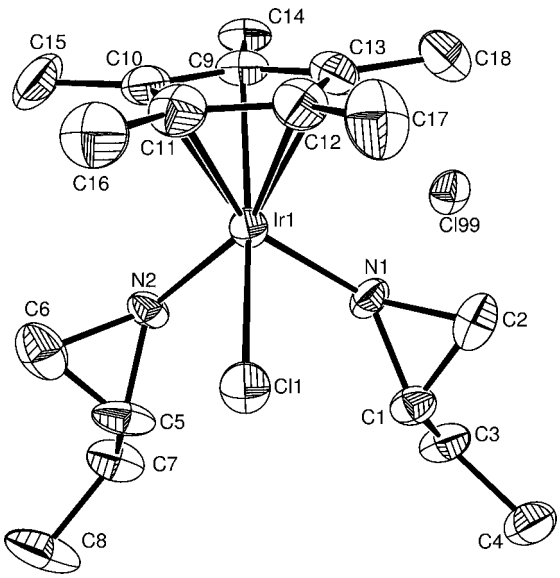


Figure 6 Molecular structure of **9d**. The thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity.

(**6c**) and 517 (**6e**). In all cases, fragmentation signals for the cleavage of the aziridine ligand ($M^+ - Az$), and the subsequent separation of the chlorido ligand ($M^+ - Az - Cl$) were detected. In the FAB^+ spectra of the *bis*-aziridine complexes **7a-9d** the signals for the intact cations were obtained: *m/z* = 385 (**7a**), 441 (**7c**), 441 (**7d**), 537 (**7e**), 359 (**8a**), 415 (**8c**), 511 (**8e**), 449 (**9a**), 505 (**9c**), 506 (**9d**). The fragmentation pattern resulting from the cleavage of one and two aziridines ($M^+ - n\ Az$) (n = 1, 2) were also observed for these compounds.

In the ^1H and ^{13}C NMR spectra signals of isomers for the complexes **6c**, **7c-e**, **8c**, **8e** and **9d** were observed. On coordination to the transition metal the nitrogen inversion is hindered, generating a new chirality at the nitrogen atom (*N*-chirality), if substituted aziridines (**b-e**) are used [14, 51, 52]. This and the use of racemic mixtures of the aziridines **d** and **e** could lead to isomers. Therefore, up to four different signals for each group were obtained. Just one *mono*-aziridine complex (**6c**) forms an isomer with signals of minor intensity. In particular for the *bis*-aziridine complexes **7d**, **7e**, **8e** and **9d** where the aziridine ligands are *mono* substituted in 2-position, many signals for the possible isomers were detected.

In the ^1H NMR spectra all of the signals corresponding to the aziridine protons were more or less shifted to lower field in comparison with the signals of the free aziridines **a-e** [53−55]. The N*H* (1.60−5.59 ppm), ring protons Az-CH_2 (1.30−2.78 ppm) and Az-C*H* (2.22−3.73 ppm) signals were observed in the expected ranges and showed a larger low-field shift than the signals of the exocyclic hydrogen atoms Et-CH_2 (1.21−2.16 ppm), CH_3 (0.94−1.58 ppm) and Ph-C*H* (7.23−7.66 ppm). Only in complexes **5b** and **6b** the signals of the N*H* proton could not be localized, because they are hidden by the signals of the ring protons. Due to the *N*-coordination to the transition metal atom, not only ^3J couplings between the ring protons of the alkyl moieties were observed, but also between N*H* and Az-CH_2 and Az-C*H*. The values of the couplings range from 5.1 and 8.7 Hz. An additional ^2J coupling of 1.0 Hz for the Az-CH_2 group was detected in the spectrum of **4e**.

In general, in the ^{13}C NMR spectra of all compounds the signals of the ring carbon atoms Az−*C*H_2 (19.04−33.34 ppm), Az−*C*H (31.80−41.35 ppm) and Az−C_q (39.39−41.63 ppm) were shifted to lower-field, compared to the corresponding signals of the free aziridines **a-e** [53−55]. The signals for the methyl (19.26, 19.40 ppm) and ethyl groups (10.14−11.40 ppm; 23.82−26.34 ppm) of the 2-methylaziridine and 2-ethylaziridine complexes differ only slightly from those of the free azirdines **b** and **d**. For the 2-phenylaziridine complexes **4e**, **6e**, **7e** and **8e**, the aromatic C_q signals (135.12−137.54 ppm) are shifted to higher field, whereas the aromatic *C*H signals (126.22−129.13 ppm) are shifted to lower field. Due to the coordination of the 2,2-dimethylaziridine **c** in complexes **6c-9c**, the signals of the methyl groups are now not equivalent. In comparison with the free aziridine **c**, the signals of the methyl groups, which are turned away from the metal atom, (20.15−21.44 ppm) were detected at higher field, and the others (25.90−27.46 ppm) at lower field.

Experimental Part

General Procedures: All experiments were performed under a dry argon atmosphere using Schlenk line techniques. Aziridine, 2-monomethylaziridine, 2,2-dimethylaziridine, 2-Ethylaziridine, 2-Phenylaziridine, $[RhCl_2Cp^*]_2$, $[IrCl_2Cp^*]_2$, and $[RuCl_2(C_6Me_6)]$ were prepared according to the literature methods [40, 41, 56, 57]. Dichloromethane was distilled from calcium hydride, and *n*-pentane and *n*-hexane were distilled from sodium. All solvents were stored under a dry argon atmosphere with 3 Å molecular sieve. ^1H and ^{13}C NMR spectra were measured on a Jeol Eclipse 270, Jeol Eclipse

400 and Jeol EX400 spectrometer. ^{1}H and ^{13}C chemical shifts were determined relative to TMS as external standard. IR spectra (KBr) were recorded using a Nicolet 520 FT-IR and Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectra were obtained by a Finnigan MAT 90, Joel MStation JMS 700, electron energy 70 eV (EI), NBA matrix (FAB). Single crystal X-Ray diffraction data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation. Single crystal X-ray structure analyses were performed by direct methods using the SHELXS software and refined by full-matrix least-squares with SHELXL-97 [58]. Tables 1−3 contain the crystal data and details of the structural refinement of **4e-9d**. Elemental analysis were performed by the Microanalytical Laboratory of the Department of Chemistry and Biochemistry, LMU Munich using a Heraeus Elementar Vario El.

General method for the synthesis of the mono-aziridine complexes

The synthesis of the *mono*-aziridine complexes **4e-6e** was achieved by dissolving $[MCl_2L]_2$ (**1-3**) in dichloromethane (20 mL), followed by the addition of the aziridine (**a-e**) in a 1:2 molar ratio. After stirring at room temperature, the solvent was removed in vacuo. The residue was purified by stirring in dry *n*-hexane (20 mL) 12 h. The *n*-hexane phase was subsequently removed by decantation, and the powder was dried in vacuo.

$[RuCl_2(C_6Me_6)(C_2H_3PhNH)]$ (4e):

Reagents: 131 mg (0.196 mmol) **1**; 45.6 μL (0.392 mmol) **e**; reaction time: 12 h.
Yield 77 %; orange powder; decomposition > 220 °C; $C_{20}H_{27}Cl_2NRu$ (453.41); C 52.26 (calc. 52.98); H 5.86 (6.00); N 3.07 (3.09) %.

IR (KBr): 3282 w, 3026 m, 3010 m, 2921 m, 1605 m, 1501 m, 1301 w, 1235 w, 1188 w, 1137 s, 1092 w, 1072 m, 1023 m, 953 m, 887 s, 822 w, 761 vs, 554 w cm^{-1}. **MS** (FAB-pos): *m/z* = 453 (M^+, 9 %), 418 (M^+ −Cl, 100 %), 382 (M^+ −2 Cl, 10 %), 334 (M^+ −Az, 26 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.60 (br, 1 H, N*H*), 2.02 (s, 18 H, $C_6Me_6-CH_3$), 2.35 (ddd, ^2J = 1.0 Hz, ^3J = 5.1 Hz, ^3J = 8.6 Hz, 1 H, Az−*H*CH), 2.41 (ddd, ^2J = 1.0 Hz, ^3J = 6.6 Hz, ^3J = 6.6 Hz, 1 H, Az−HC*H*), 3.30 (ddd, ^3J = 5.1 Hz, ^3J = 5.8 Hz, ^3J = 6.1 Hz, 1 H, Az−C*H*), 7.29-7.47 (m, 5 H, Ph−CH). **^{13}C NMR** (CD_2Cl_2) δ = 15.58 ($C_6Me_6-CH_3$), 30.91 (Az−CH_2), 38.49 (Az−*C*H), 90.26 ($C_6Me_6-C_q$), 126.60, 128.48, 129.13 (Ph−*C*H), 137.00 (Ph−C_q).

$[RhCl_2(Cp^*)(C_2H_3MeNH)]$ (5b):

Reagents: 252 mg (0.408 mmol) **2**, 58.3 μL (0.816 mmol) **b**; reaction time: 10 min.
Yield 84 %; deep orange powder; decomposition > 185 °C; $C_{13}H_{22}Cl_2NRh$ (366.13); C 41.15 (calc. 42.65); H 6.05 (6.06); N 2.65 (3.83) %.

IR (KBr): 3190 vs, 3068 w, 3043 w, 2962 m, 2914 m, 1452 s, 1400 m, 1372 m, 1361 m, 1311 w, 1241 m, 1214 w, 1161 w, 1148 w, 1111 w, 1067 m, 1028 s, 962 m, 892 w, 845 s, 800 w, 766 w, 730 w, 696 w, 620 w, 587 w, 540 w, 503 w, 541 w, 442 w cm^{-1}. **MS** (EI): *m/z* = 365 (M^+, 9 %), 308 (M^+ −Az, 59 %), 273 (M^+ −Az −Cl, 71 %), 236 (M^+ −Az −2 Cl, 100 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.37 (d, ^3J = 5.8 Hz, 3 H, Az−CH_3), 1.63 (s, 15 H, Cp*−CH_3), 1.79 (dd, ^3J = 5.0 Hz, ^3J = 8.2 Hz, 1 H, Az−*H*CH), 2.12 (dd, ^3J = 6.1 Hz, ^3J = 6.1 Hz, 1 H, Az−HC*H*), 2.43 (m, 1 H, Az−C*H*). **^{13}C NMR** (CD_2Cl_2) δ = 8.90 (Cp*−CH_3), 19.26 (Az−CH_3), 29.71 (Az−CH_2), 31.80 (Az−*C*H), 93.26 (d, ^1J (C, Rh) = 10.8 Hz, Cp*−C_q).

$[IrCl_2(Cp^*)(C_2H_4NH)]$ (6a):

Reagents: 184 mg (0.231 mmol) **3**, 24.9 μL (0.462 mmol) **a**; reaction time: 16 h.
Yield 93 %; deep yellow powder; decomposition > 211 °C; $C_{12}H_{20}Cl_2IrN$ (441.42); C 33.28 (calc. 32.65); H 4.58 (4.57); 2.85 (3.17) %.

IR (KBr): 3200 s, 3091 m, 3020 w, 3002 m, 2985 m, 2968 m, 2918 m, 2700 w, 2445 w, 1490 m, 1452 m, 1438 m, 1405 w, 1383 m, 1376 m, 1369 m 1358 w, 1228 m, 1158 w, 1136 w, 1123 w, 1108 m, 1091 w, 1081 w, 1032 m, 1023 m, 940 w, 887 s, 825 w, 794 w, 734 w, 616 w, 583 w, 535 w, 467 w, 452 w, 411 w cm^{-1}. **MS** (FAB-pos): *m/z* = 441 (M^+, 15 %), 406 (M^+ −Cl, 83 %), 398 (M^+ −Az, 25 %), 363 (M^+ −Cl −Az, 100 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.62 (s, 15 H, Cp*−C*H*$_3$), 2.18 (br, 4 H, Az−C*H*$_2$), 4.37 (br, 1 H, N*H*). **^{13}C NMR** (CD_2Cl_2) δ = 8.68 (Cp*−*C*H$_3$), 23.47 (Az−*C*H$_2$), 84.87 (Cp*−C_q).

$[IrCl_2(Cp^*)(C_2H_3MeNH)]$ (6b):

Reagents: 239 mg (0.300 mmol) **3**, 42.8 μL (0.600 mmol) **b**; reaction time: 30 min.
Yield 90 %; deep yellow powder; decomposition > 208 °C; $C_{13}H_{22}Cl_2IrN$ (455.44); C 34.98 (calc. 34.28); H 4.71 (4.87); 3.01 (3.08) %.

IR (KBr): 3199 s, 3051 w, 2962 m, 2918 m, 2870 w, 1454 m, 1402 w, 1383 m, 1362 w, 1333 w, 1242 w, 1213 w, 1159 w, 1148 w, 1113 w, 1070 m, 1035 m, 962 w, 894 w, 844 m, 763 w, 617 w, 584 w, 540 w, 514 w, 464 w, 440 w, 407 w cm^{-1}. **MS** (EI): *m/z* = 455 (M^+, 15 %), 398 (M^+ −Az, 35 %), 363 (M^+ −Cl −Az, 100 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.43 (d, ^3J = 5.8 Hz, 3 H, Az−C*H*$_3$), 1.60 (s, 15 H, Cp*−C*H*$_3$), 1.94 (dd, ^3J = 5.2 Hz, ^3J = 8.0 Hz, 1 H, Az−*H*CH), 2.32 (dd, ^3J = 6.1 Hz, ^3J = 6.1 Hz, 1 H, Az−HC*H*), 2.54-2.62 (m, 1 H, Az−C*H*). **^{13}C NMR** (CD_2Cl_2) δ = 9.00 (Cp*−*C*H$_3$), 19.40 (Az−*C*H$_3$), 31.12 (Az−*C*H$_2$), 33.36 (Az−*C*H), 85.06 (Cp*−C_q).

$[IrCl_2(Cp^*)(C_2H_2Me_2NH)]$ (6c):

Reagents: 251 mg (0.315 mmol) **3**, 56.9 μL (0.630 mmol); reaction time: 1 h.
Yield 98 %; deep yellow powder; decomposition > 235 °C; $C_{14}H_{24}Cl_2IrN$ (469.47); C 35.83 (calc. 35.82); H 5.17 (5.15); N 2.99 (2.98) %.

IR (KBr): 3184 s, 3009 w, 2988 w, 2960 m, 2916 m, 2872 w, 1480 w, 1448 m, 1384 m, 1363 w, 1349 w, 1331 w, 1287 w, 1160 w, 1145 w, 1119 m, 1110 w, 1081 w, 1034 m, 978 w, 922 w, 812 m, 682 w, 615 w, 585 w, 530 w, 523 w, 462 w, 453 w, 436 w cm^{-1}. **MS** (FAB-pos): *m/z* = 469 (M^+, 12 %), 434 (M^+ −Cl, 100 %), 398 (M^+ −Az, 18 %), 363 (M^+ −Cl, −Az, 70 %).**^{1}H NMR** (CD_2Cl_2) δ = 1.28, 1.35 (s, 3 H, Az−C*H*$_3$), 1.47, 1.56 (s, 3 H, Az−C*H*$_3$), 1.62, 1.74 (s, 15 H, Cp*−C*H*$_3$), 1.76, 1.87 (d, ^3J = 8.6 Hz, 1 H, Az−*H*CH), 2.15 (br, 1 H, N*H*), 2.17, 2.44 (d, ^3J = 6.1 Hz, 1 H, Az−HC*H*). **^{13}C NMR** (CD_2Cl_2) δ = 9.16, 9.85 (Cp*−*C*H$_3$), 21.11, 21.24 (Az−*C*H$_3$), 25.98, 26.94 (Az−*C*H$_3$), 31.96, 33.36 (Az−*C*H$_2$), 40.65, 41.66 (Az−C_q), 85.05, 86.55 (Cp*−C_q).

$[IrCl_2(Cp^*)(C_2H_3PhNH)]$ (6e):

Reagents: 275 mg (0.345 mmol) **3**, 80.3 μL (0.690 mmol) **e**; reaction time: 30 min.
Yield 99 %; deep yellow powder; decomposition > 190 °C; $C_{18}H_{24}Cl_2IrN$ (517.51); C 41.92 (calc. 41.78); H 4.50 (4.67); N 2.67 (2.71) %.

IR (KBr): 3226 m, 3062 m, 3034 m, 3011 m, 2983 m, 2965 m, 2919 m, 1603 w, 1498 m, 1457 s, 1406 w, 1383 m, 1356 w, 1300 w, 1240 w, 1183 w, 1148 m, 1141 m, 1079 w, 1032 m, 955 w, 927 w, 884 w, 852 w, 827 w, 770 vs, 745 w, 705 s, 618 w, 584 w, 574 w, 548 w, 464 w, 440 w, 407 w cm^{-1}. **MS** (FAB-pos): *m/z* = 517 (M^+, 14 %), 482 (M^+ −Cl, 100 %), 398 (M^+ −Az, 15 %), 363 (M^+ −Cl −Az, 92 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.59 (s, 15 H, Cp* −C*H*$_3$), 2.08 (br, 1 H, N*H*), 2.63 (dd, ^3J = 5.3 Hz, ^3J = 8.2 Hz, 1 H, Az−*H*CH), 2.78 (dd, ^3J = 6.5 Hz, ^3J = 6.5 Hz, 1 H, Az−HC*H*), 3.68-3.73

(m, 1 H, Az−C*H*), 7.34-7.40 (m, 5 H, Ph−C*H*). **^{13}C NMR** (CD_2Cl_2) δ = 8.78 (Cp*−CH_3), 30.62 (Az−CH_2), 39.03 (Az−*C*H), 85.01 (Cp*−C_q), 127.14, 128.76, 129.10 (Ph−*C*H), 135.85 (Ph−C_q).

General method for the synthesis of the bis-aziridine complexes

The synthesis of the *bis*-aziridine complexes **7a-9d** was achieved by dissolving $[MCl_2L]_2$ (**1-3**) in dichloromethane (20 mL), followed by the addition of the aziridine (**a-e**) in a 1:5 molar ratio. After stirring for 5 min to 2 h at room temperature, the solvent was removed in vacuo. The residue was purified by stirring in dry *n*-hexane (20 mL) overnight. The *n*-hexane phase was subsequently removed by decantation, and the powder was dried in vacuo.

$[RuCl(C_6Me_6)(C_2H_4NH)_2]Cl$ (7a):

Reagents: 113 mg (0.169 mmol) **1**, 45.5 μL (0.845 mmol) **a**; reaction time: 12 h.
Yield 80 %; yellow powder; decomposition > 215 °C; $C_{16}H_{28}Cl_2N_2Ru$ (420.38); C 45.09 (calc. 45.71); H 6.43 (6.71); N 5.80 (6.66) %.

IR (KBr): 3226 s, 3083 m, 3031 s, 3012 s, 2997 s, 2923 m, 2724 w, 1445 m, 1432 m, 1386 s, 1344 w, 1258 w, 1226 m, 1141 w, 1096 m, 1089 m, 1070 m, 1024 w, 936 w, 884 vs, 818 w, 799 w, 515 w, 463 w cm^{-1}. **MS** (FAB-pos): *m/z* = 385 (M^+, 36 %), 342 (M^+ −Az, 100 %), 299 (M^+ −2 Az, 50 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.50 (ddd, ^3J = 5.9 Hz, ^3J = 6.3 Hz, ^3J = 6.6 Hz, 1 H, Az−*H*CH), 1.63 (ddd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, ^3J = 5.8 Hz, 1 H, Az−HC*H*), 1.86-1.97 (m, 4 H, Az−CH_2), 2.05, 2.12 (s, 18 H, C_6Me_6−CH_3), 2.15-2.19 (m, 1 H, Az−*H*CH), 2.40 (ddd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^3J = 5.2 Hz, 1 H, Az−HC*H*), 4.36 (br, 2 H, NH). **^{13}C NMR** (CD_2Cl_2) δ = 15.46 (C_6Me_6−*C*H$_3$), 19.04, 22.82, 23.66 (Az−*C*H$_2$), 90.15, 91.96 (C_6Me_6−C_q).

$[RuCl(C_6Me_6)(C_2H_2Me_2NH)_2]Cl$ (7c):

Reagents: 77 mg (0.115 mmol) **1**, 51.9 μL (0.576 mmol) **c**; reaction time: 12 h.
Yield 74 %; yellow powder; decomposition > 235 °C; $C_{20}H_{36}Cl_2N_2Ru$ (476.49); C 48.19 (calc. 50.41); H 7.10 (7.62); N 5.58 (5.88) %.

IR (KBr): 3084 vs, 3072 vs, 3004 m, 2993 m, 2967 m, 2929 m, 1450 m, 1395 s, 1372 w, 1336 m, 1299 w, 1290 w, 1182 w, 1153 w, 1123 m, 1117 s, 1070 w, 1046 w, 1022 w, 992 m, 976 m, 919 w, 827 w, 813 w, 690 w, 658 w, 458 w cm^{-1}. **MS** (FAB-pos): *m/z* = 441 (M^+, 13 %), 370 (M^+ −Az, 100 %), 334 (M^+ −Az −Cl, 10 %), 299 (M^+ −2 Az, 30 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.30, 1.38 (s, 6 H, Az−CH_3), 1.46, 1.58 (s, 6 H, Az−CH_3), 1.53, 1.59 (d, ^3J = 8.7 Hz, 2 H, Az−*H*CH), 1.63, 1.86 (d, ^3J = 6.1 Hz, 2 H, Az−HC*H*), 1.97, 2.07, 2.19 (s, 18 H, C_6Me_6−CH_3), 4.55 (br, 2 H, N*H*). **^{13}C NMR** (CD_2Cl_2) δ = 15.69, 15.90, 16.62 (C_6Me_6−*C*H$_3$), 20.15, 21.11 (Az−*C*H$_3$), 26.00, 27.46 (Az−*C*H$_3$), 31.55, 33.25 (Az−CH$_2$), 40.28 (Az−C_q), 89.60, 90.15, 91.85 (C_6Me_6−C_q).

$[RuCl(C_6Me_6)(C_2H_3EtNH)_2]Cl$ (7d):

Reagents: 79 mg (0.116 mmol) **1**, 51.6 μL (0.591 mmol) **d**; reaction time: 12 h.
Yield 84 %; yellow powder; decomposition > 215 °C; $C_{20}H_{36}Cl_2N_2Ru$ (476.49); C 49.04 (calc. 50.41); H 7.41 (7.62); N 5.57 (5.88) %.

IR (KBr): 3004 s, 2964 vs, 2932 s, 2875 m, 1456 s, 1390 s, 1264 w, 1232 w, 1151 w, 1104 w, 1076 s, 1021 s, 946 w, 912 m, 852 m, 806 m, 767 w, 659 w, 551 w, 486 w cm^{-1}. **MS** (FAB-pos): *m/z* = 441 (M^+, 21 %), 370 (M^+ −Az, 100 %), 334 (M^+ −Az −Cl, 11 %), 299 (M^+ −2 Az, 41 %). **^{1}H NMR** ($CDCl_3$) δ = 0.94, 1.03 (t, ^3J = 8.0 Hz, 6 H, Et−CH_3), 1.21-1.33, 1.41-1.45, 1.47-1.55 (m, 4 H, Et−CH_2), 1.58 (dd, ^3J = 6.3 Hz, ^3J = 6.3 Hz, 1 H, Az−*H*CH), 1.83-1.94, 1.96-2.06 (m, 4 H, Az−CH_2) 2.12, 2.14, 2.15 (s, 18 H, C_6Me_6−CH_3), 2.22-2.31, 2.35-2.43 (m, 2 H, Az−C*H*) 4.00, 4.41, 4.74 (br, 2 H, N*H*). **^{13}C NMR** ($CDCl_3$) δ = 10.14, 10.21, 10.44, 10.51 (Et−CH_3), 14.82, 14.86, 14.92 15.00 (C_6Me_6−*C*H$_3$), 23.82, 23.87, 24.81, 24.91 (Et−*C*H$_2$), 25.82, 26.00, 28.98, 29.45 (Az−*C*H$_2$), 32.87, 33.04, 37.90, 38.21 (Az−*C*H), 89.24, 91.00 91.04, 91.11 (C_6Me_6−C_q).

$[RuCl(C_6Me_6)(C_2H_3PhNH)_2]Cl$ (7e):

Reagents: 88 mg (0.132 mmol) **1**, 76.6 μL (0.658 mmol) **e**; reaction time: 12 h.
Yield 79 %; yellow powder; m.p. 169 °C; $C_{28}H_{36}Cl_2N_2Ru$ (572.57); C 56.50 (calc. 58.73); H 6.24 (6.34); N 4.80 (4.89) %.

IR (KBr): 3061 s, 3035 s, 2922 m, 1605 w, 1584 w, 1501 m, 1459 m, 1386 m, 1291 w, 1256 w, 1242 w, 1190 w, 1156 m, 1072 m, 1020 m, 965 w, 884 m, 763 vs, 701 vs, 594 w, 552 w, 548 w, 477 w, 458 w, 419 w cm^{-1}. **MS** (FAB-pos): *m/z* = 537 (M^+, 64 %), 418 (M^+ −Az, 100 %), 383 (M^+ −Az −Cl, 7 %), 299 (M^+ −2 Az, 28 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.30, 1.96, 2.35 (dd, ^3J = 8.4 Hz, ^3J = 5.2 Hz, 2 H, Az−*H*CH), 2.00, 2.02, 2.10 (s, 18 H, C_6Me_6−CH_3), 2.13-2.20 (m), 2.41, 2.52 (dd, ^3J = 6.2 Hz, ^3J = 6.2 Hz, 2 H, Az−HC*H*), 2.82, 2.88, 3.30, 3.59 (ddd, ^3J = 6.7 Hz, ^3J = 6.7 Hz, ^3J = 5.3 Hz, 2 H, Az−C*H*) 5.15, 5.41 (br, 2 H, N*H*), 7.23-7.40, 7.43-7.51, 7.60-7.66 (m, 10 H, Ph−C*H*). **^{13}C NMR** (CD_2Cl_2) δ = 15.64, 15.83, 15.91 (C_6Me_6−*C*H$_3$), 30.13, 30.81, 30.90, 32.87 (Az−*C*H$_2$), 35.32, 38.43, 40.91, 41.35 (Az−*C*H), 90.25, 92.21, 92.27 (C_6Me_6−C_q), 126.34, 126.58, 127.55, 127.93, 128.01, 128.28, 128.96, 129.10, (Ph−*C*H), 135.12, 137.43, 137.54 (Ph−C_q).

$[RhCl(Cp^*)(C_2H_4NH)_2]Cl$ (8a):

Reagents: 299 mg (0.484 mmol) **2**, 130 μL (2.42 mmol) **a**; reaction time: 2 h.
Yield 93 %; pale orange powder; decomposition > 167 °C; $C_{14}H_{25}Cl_2N_2Rh$ (395.18); C 42.33 (calc. 42.55); H 6.46 (6.38); N 6.92 (7.09) %.

IR (KBr): 3050 m, 3001 m, 2913 w, 2702 w, 1649 w, 1554 w, 1538 w, 1491 w, 1453 m, 1422 w, 1383 w, 1362 w, 1248 w, 1226 m, 1160 w, 1093 m, 1033 m, 955 w, 885 s, 798 w, 672 w, 652 w cm^{-1}. **MS** (FAB-pos): *m/z* = 359 (M^+, 24 %), 316 (M^+ −Az, 100 %), 273 (M^+ −2 Az, 40 %), 237 (M^+ −2 Az −Cl, 14 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.63 (ddd, ^3J = 6.2 Hz, ^3J = 6.2 Hz, ^3J = 6.2 Hz, 2 H, Az−*H*CH), 1.74 (s, 15 H, Cp*−CH_3), 1.75-1.79 (m, 2 H, Az−HC*H*), 1.99 (ddd, ^3J = 5.8 Hz, ^3J = 5.8 Hz, ^3J = 5.9 Hz, 2 H, Az−*H*CH), 2.34 (ddd, ^3J = 7.6 Hz, ^3J = 7.6 Hz, ^3J = 5.3 Hz, 2 H, Az−HC*H*), 4.81 (br, 2 H, N*H*). **^{13}C NMR** (CD_2Cl_2) δ = 8.76 (Cp*−CH_3), 19.36, 22.28 (Az−*C*H$_2$), 94.61 (d, ^1J (C, Rh) = 8.8 Hz, Cp*−C_q).

$[RhCl(Cp^*)(C_2H_2Me_2NH)_2]Cl$ (8c):

Reagents: 320 mg (0.517 mmol) **2**, 189 μL (2.10 mmol) **c**; reaction time: 2 h.
Yield 91 %; pale orange powder; decomposition > 190 °C; $C_{18}H_{33}Cl_2N_2Rh$ (451.32); C 47.24 (calc. 47.90); H 7.17 (7.39); N 5.84 (6.21) %.

IR (KBr): 3049 s, 2996 m, 2963 m, 2917 m, 1450 m, 1394 m, 1380 m, 1336 m, 1300 w, 1289 w, 1261 w, 1183 w, 1153 w, 1119 s, 1080 w, 1025 m, 994 w, 976 w, 930 w, 918 m, 825 m, 812 m, 692 w, 620 w, 586 w, 538 w, 526 w, 503 w, 430 w cm^{-1}. **MS** (FAB-pos): *m/z* = 415 (M^+, 5 %), 344 (M^+ −Az, 100 %), 273 (M^+ −2 Az, 34 %), 237 (M^+ −2 Az −Cl, 14 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.36 (s, 6 H, Az−CH_3), 1.55 (s, 6 H, Az−CH_3), 1.71 (d, ^3J = 8.4 Hz, 2 H, Az−*H*CH), 1.66, 1.77 (s, 15 H, Cp*−CH_3), 1.88 (d, ^3J = 7.7 Hz, 2 H, Az−*H*CH), 4.92 (br, 2 H, N*H*). **^{13}C NMR** (CD_2Cl_2) δ = 9.29, 9.93 (Cp* −CH_3), 21.44 (Az−*C*H$_3$), 26.17 (Az−*C*H$_3$), 32.22, 33.31 (Az−*C*H$_2$), 39.39 (Az−C_q), 95.01 (d, ^1J (C, Rh) = 8.5 Hz, Cp*−C_q).

$[RhCl(Cp^*)(C_2H_3PhNH)_2]Cl$ (8e):

Reagents: 256 mg (0.414 mmol) **2**, 193 μL (1.66 mmol) **e**; reaction time: 2 h.

Yield 93 %; pale orange powder; m.p. 187 °C; $C_{18}H_{33}Cl_2N_2Rh$ (547.12); C 55.55 (calc. 57.07); H 6.22 (6.09); N 4.87 (5.12) %.

IR (KBr): 3087 s, 3007 m, 2914 w, 1604 w, 1582 w, 1500 m, 1480 w, 1455 s, 1427 w, 1380 m, 1343 w, 1314 w, 1242 m, 1190 m, 1174 m, 1156 m, 1107 w, 1079 m, 1027 m, 963 m, 886 m, 878 m, 839 w, 776 s, 766 s, 701 s, 619 w, 585 w, 551 w, 537 w, 456 w, 439 w cm^{-1}. **MS** (FAB-pos): *m/z* = 511 (M^+, 7 %), 392 (M^+ −Az, 100 %), 273 (M^+ −2 Az, 23 %), 237 (M^+ −2 Az −Cl, 14 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.34-1.37 (m, 1 H, Az−*H*CH), 1.59, 1.62, 1.68 (s, 15 H, Cp*−C*H*$_3$), 2.11-2.19 (m, 2 H, Az−C*H*$_2$), 2.62-2.68 (m, 1 H, Az−HC*H*), 3.03-3.08 (m, 2 H, Az−C*H*), 5.59 (br, 2 H, N*H*), 7.26-7.46, 7.56-7.60 (m, 10 H, Ph−C*H*). **^{13}C NMR** (CD_2Cl_2) δ = 8.96, 9.06, 9.16 (Cp*−*C*H$_3$), 29.73, 29.98, 31.54 (Az−*C*H$_2$), 35.64, 39.45, 39.89 (Az−*C*H), 93.51, 94.99, 95.17 (d, ^1J (C, Rh) = 8.5 Hz, Cp*−C_q), 126.22, 127.22, 128.16, 128.50, 129.98, 129.11 (Ph−*C*H), 137.13, 137.30 (Ph−C_q).

[IrCl(Cp*)($C_2H_4NH)_2$]Cl (9a):

Reagents: 109 mg (0.137 mmol) **3**, 36.9 μL (0.684 mmol) **a**; reaction time: 2 h.

Yield 99 %; pale yellow powder; m.p. 160 °C; $C_{14}H_{25}Cl_2IrN_2$ (484.49); C 34.64 (calc. 34.71); H 5.07 (5.20); N 5.78 (5.62) %.

IR (KBr): 3011 s, 2985 s, 2919 m, 2740 m, 2480 w, 2417 w, 2201 w, 1488 w, 1455 m, 1426 w, 1395 m, 1388 m, 1227 m, 1159 w, 1114 m, 1100 m, 1039 m, 956 w, 891 m, 615 w, 573 w, 539 w, 451 w cm^{-1}. **MS** (FAB-pos): *m/z* = 449 (M^+, 22 %), 406 (M^+ −Az, 100 %), 363 (M^+ −2 Az, 46 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.69 (s, 15 H, Cp*−C*H*$_3$), 1.69-1.81 (m, 4 H, Az−C*H*$_2$), 2.29 (ddd, ^3J = 5.5 Hz, ^3J = 5.5 Hz ^3J = 6.8 Hz, 2 H, Az−*H*CH), 2.45 (ddd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, ^3J = 5.3 Hz, 2 H, Az−HC*H*), 5.27 (br, 2 H, N*H*). **^{13}C NMR** (CD_2Cl_2) δ = 8.55 (Cp*−*C*H$_3$), 19.37, 23.94 (Az−*C*H$_2$), 86.07 (Cp*−C_q).

[IrCl(Cp*)($C_2H_2Me_2NH)_2$]Cl (9c):

Reagents: 97 mg (0.122 mmol) **3**, 44.1 μL (0.609 mmol) **c**; reaction time: 2 h.

Yield 99 %; pale yellow powder; m.p. 168 °C; $C_{18}H_{33}Cl_2IrN_2$ (540.59); C 39.46 (calc. 39.99); H 5.90 (6.15); N 4.94 (5.18) %.

IR (KBr): 3081 s, 3005 s, 2974 m, 2962 m, 2920 m, 2755 w, 2655 w, 2586 w, 1454 m, 1396 m, 1381 m, 1335 m, 1304 w, 1294 w, 1261 w, 1188 w, 1160 m, 1119 s, 1082 w, 1034 m, 997 m, 978 m, 916 m, 826 m, 812 m, 687 w, 621 w, 599 w, 537 w, 516 w, 456 w, 421 w cm^{-1}. **MS** (FAB-pos): *m/z* = 505 (M^+, 13 %), 434 (M^+ −Az, 100 %), 363 (M^+ −2 Az, 37 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.28 (s, 6 H, Az−C*H*$_3$), 1.55 (s, 6 H, Az−C*H*$_3$), 1.75 (s, 15 H, Cp*−C*H*$_3$), 1.76 (d, ^3J = 5.2 Hz, 2 H, Az−*H*CH), 2.17 (d, ^3J = 5.9 Hz, 2 H, Az−*H*CH), 5.41 (br, 2 H, N*H*). **^{13}C NMR** (CD_2Cl_2) δ = 9.83 (Cp*−*C*H$_3$), 21.04 (Az−*C*H$_3$), 25.90 (Az−*C*H$_3$), 31.87 (Az−*C*H$_2$), 40.52 (Az−C_q), 86.52 (Cp*−C_q).

[IrCl(Cp*)($C_2H_3EtNH)_2$]Cl (9d):

Reagents: 253 mg (0.467 mmol) **3**, 134 μL (1.87 mmol) **d**; reaction time: 2 h.

Yield 89 %; pale yellow powder; m.p. 206 °C; $C_{18}H_{33}Cl_2IrN_2$ (540.59); C 39.30 (calc. 39.99); H 6.13 (6.15); N 5.07 (5.18) %.

IR (KBr): 3018 s, 2963 s, 2933 m, 2876 m, 2757 w, 2718 m, 1455 m, 1402 w, 1384 m, 1316 w, 1277 w, 1231 w, 1216 w, 1154 w, 1129 w, 1099 w, 1080 m, 1036 m, 1002 w, 949 w, 912 m, 852 m, 806 w, 768 w, 621 w, 582 w, 461 w, 431 w cm^{-1}. **MS** (FAB-pos): *m/z* = 506 (M^+, 19 %), 435 (M^+ −Az, 100 %), 363 (M^+ −2 Az, 44 %). **^{1}H NMR** (CD_2Cl_2) δ = 1.01-1.08 (m, 6 H, Et−C*H*$_3$), 1.64-1.72 (m, 15 H, Cp*−C*H*$_3$), 2.05-2.16 (m, 4 H, Et−C*H*$_2$), 2.24-2.31 (m, 2 H, Az−*H*CH), 2.45-2.55 (m, 2 H, Az−HC*H*), 2.73-2.83 (m, 2 H, Az−C*H*), 4.80, 5.06 (br, 2 H, N*H*). **^{13}C NMR** (CD_2Cl_2) δ = 8.48, 8.65, 8.82, (Cp*−*C*H$_3$), 10.74, 10.79, 11.16, 11.40 (Et−*C*H$_3$), 24.74, 24.79, 26.34 (Et−*C*H$_2$), 25.33, 25.44, 30.36, 30.69 (Az−*C*H$_2$), 34.06, 34.30, 39.40, 39.79 (Az−*C*H), 85.93, 85.95 (Cp*−C_q).

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