Synthesis and Structural Characterization of Bis(aziridine) Cobalt(II), Zinc(II) and Palladium(II) Complexes

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Dedicated to Prof. Dr. Herbert Mayr on the occasion of his 60 th birthday

The reactions of anhydrous metal chlorides MCl_2 [M = Co(II), Zn(II), Pd(II)] with aziridines (az) in CH_2Cl_2 at r. t. in a 1 : 5 molar ratio afforded the bis(aziridine)dichloro complexes $M(az)_2Cl_2$. After purification, all complexes were fully characterized. The solid state structures were determined using single crystal X-ray diffraction, and showed tetrahedral coordination geometries for the Co(II) and Zn(II) centers and *trans*-configurated square planar geometries for Pd(II).

Key words: Cobalt, Zinc, Palladium, Aziridine, X-Ray Crystallography

Introduction

Research into the chemistry of aziridine dates back to the year 1888, when Gabriel first reported the synthesis of aziridine as vinylamine [1] and, shortly thereafter, Marckwald proposed that aziridine adopts a three membered ring structure [2]. Following decades of subsequent research into the chemistry and medicinal properties of aziridine compounds, the versatility of the aziridine motif was established and resulted in the widespread interest in this heterocycle [3 – 6]. The reactive nature of aziridine compounds is mainly due to Baeyer [7] and Pitzer ring strain which results in ring opening reactions if protonation of the amino group or any nucleophilic attack on the ring occurs. Therefore, aziridines offer a great variety of synthetic applications in organic chemistry, for example, as synthons in natural product synthesis [8, 9], monomers in macromolecular chemistry [10, 11], or biologically important target molecules [12 – 14].

Hieber and Wiesboeck introduced aziridine ligands into organometallic chemistry [15], followed by Edwards and Fritz who focused on the synthesis and spectroscopic investigation of various aziridine complexes of transition metal halides [16]. The first solid state structure of an aziridine transition metal complex, determined by X-ray diffraction, was reported by Edwards *et al.* [17], and subsequently a series of publications on the coordination chemistry of aziridines followed [18 – 31]. The reactivity of Lewis basic aziridines towards Lewis acidic transition metal centers differs strongly from those of oxiranes and thiiranes. The latter both act as oxidizing agents towards organometallic compounds resulting in the formation of oxo- or thiocomplexes, respectively, *via* ethylene elimination [32, 33]. Aziridines, however, usually prefer metal coordination *via* the nitrogen atom without ethylene elimination. Nevertheless, transition metal mediated ring opening reactions of aziridine ligands yielding aminoethylaziridine-N,N'-complexes by dimerization [34] or β-aminoacyl complexes by reaction with metal carbonyl hydrides have been observed [19, 25]. Recently, Hillhouse *et al.* reported the synthesis and solid state structure of an azametallacyclobutane complex, formed by the oxidative addition reaction of nickel(0) complexes with *N*-tosylated aziridines [35].

Results and Discussion

Aziridine (**1a**) and 2,2-dimethylaziridine (**1b**) were prepared from β-amino-alcohols according to standard literature methods [36]. The novel bis(aziridine) dichloro transition metal complexes **5** – **7** were prepared according to Scheme 1, by suspending the anhydrous metal chlorides MCl_2 (**2**: M = Co, **3**: M = Zn, **4**:

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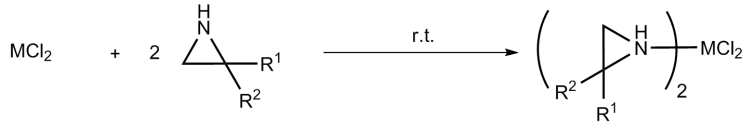

2: M = Co
3: M = Zn
4: M = Pd

1a: $R^1 = R^2 = H$
1b: $R^1 = R^2 = Me$

5b: M = Co
6a: M = Zn
6b: M = Zn
7a: M = Pd
7b: M = Pd

Scheme 1. Synthesis of the aziridine complexes **5b** – **7a**,**b** by the reaction of metal halides MCl_2 (**2** – **4**) with the aziridines **1a**,**b**.

M = Pd) in dichloromethane (M = Zn, Pd) or acetonitrile (M = Co) and adding two (M = Pd) or five (M = Co, Zn) equivalents of the aziridine **1a** or **1b**. After 12 h of stirring at r. t., the remaining MCl_2 was easily removed by filtration. Complex **5a** was synthesized analogously, however a pure compound was not obtained. All of the synthesized compounds are air stable and with the exception of **7a**,**b** hygroscopic. All complexes are soluble in polar solvents such as dichloromethane or acetone and insoluble in nonpolar solvents such as *n*-hexane.

Infrared and UV/vis spectra

The IR spectra of complexes **5b** – **7a**,**b** show values for the vibrational modes of the transition metal coordinated aziridine ligands similar to those reported by Fritz *et al.* for related aziridine complexes [35]. Compounds **5b** –**7a**,**b** show sharp absorption bands for the aziridine N–H stretching vibration in the range 3294 to 3202 cm^{-1} as a result of coordination to the transition metal. In addition, typical σ and δ ring vibrations in the fingerprint region of coordinated aziridines from 1659 cm^{-1} (**7a**) to 1451 cm^{-1} (**6b**) were observed [35]. As expected, the ν(C−H) absorptions were observed between 3113 and 2870 cm^{-1}. The UV/vis spectroscopic investigation of **5b** revealed three absorption bands with a maximum at 632 nm and a molar extinction coefficient $\log \varepsilon$ of 374 cm^2/mmol. Two further single electronic transitions were detected at 614 nm ($\log \varepsilon$ = 350 cm^2/mmol) and 578 nm ($\log \varepsilon$ = 236 cm^2/mmol). The three absorption bands can be classified as *d*–*d* single electronic transitions of the $^3A_2$ state into the excited states $^3T_1$ and $^3T_2$.

NMR Spectroscopy and mass spectrometry

The ^1H and ^{13}C NMR spectra of **6a**,**b** and **7a**,**b** quite generally show the aziridine signals shifted to lower field. Thus, the ^1H signals of **6a**,**b** and **7a**,**b** are all shifted to lower field (with one exception) in comparison with the signals observed for **1a**,**b** due to deshielding caused by transition metal coordination. For example, the CH_2 proton signals are observed at 2.11 ppm (**6a**), 2.09 ppm (**7a**) and 1.45 ppm (**1a**), respectively. The ^{13}C signal for the CH_2 fragment is shifted from 17.7 ppm for the non-coordinated aziridine **1a** to 21.1 ppm (**6a**) and 23.3 ppm (**7a**). Similar shifts are observed for the C_q and CH_2 signals of **6b** and **7b** as listed in the Experimental Section. For the two methyl groups in **6b** and **7b**, two singlets are observed which appear slightly shifted to higher field (**6b**: 22.8 ppm, **7b**: 23.9 ppm) and lower field (**6b**: 25.0 ppm, **7b**: 24.9 ppm) compared to the non-coordinated 2,2-dimethylaziridine (**1b**: 24.4 ppm) [37]. The ^1H and ^{13}C NMR spectra of complex **5b** do not provide any useful structural information, since complex **5b** is paramagnetic which causes a shift and broadening of the ligand signals.

Mass spectrometry was also used to investigate the complexes using either the direct EI mode or the FAB^+ mode in a 4-nitrobenzylalcohol (NBA) matrix. The Co(II) complex **5b** does not show any assignable peak in either the DEI or FAB^+ mode. However, the mass spectra obtained for the corresponding Zn(II) complexes **6a**,**b** show the $[M–Cl]^+$ peaks using the FAB^+ mode. Interestingly, the Pd(II) complexes **7a**,**b** show an assignable fragmentation pattern in the DEI mode with peaks corresponding to the successive loss of the two aziridine and chloride ligands.

Structure determinations

The molecular structures of compounds **5b** – **7a**,**b** were determined using single crystal X-ray diffraction. Single crystals were obtained by allowing *n*-pentane to slowly diffuse into dichloromethane or acetone solutions of **5b** – **7a**,**b**. The X-ray structure determination revealed tetrahedral and square planar geometries. The cobalt(II) and zinc(II) centers in **5b** and **6a**,**b** are coor-

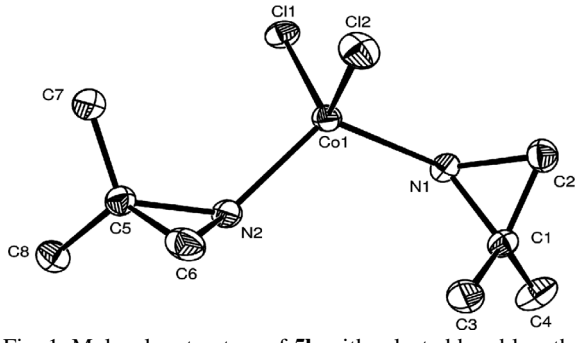

Fig. 1. Molecular structure of **5b** with selected bond lengths (Å) and angles (deg). Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity. Co(1)–N(1) 2.022(3), Co(1)–N(2) 2.026(2), Co(1)–Cl(1) 2.272(9), Co(1)–Cl(2) 2.246(10), N(1)–C(1) 1.493(4), C(1)–C(2) 1.475(5), N(1)–C(2) 1.492(4), C(1)–C(3) 1.496(5), C(1)–C(4) 1.495(5); N(1)–Co(1)–N(2) 110.73(10), N(1)–Co(1)–Cl(1) 101.68(8), N(1)–Co(1)–Cl(2) 109.94(8), N(2)–Co(1)–Cl(2) 107.00(8), N(2)–Co(1)–Cl(1) 110.10(8), Cl(1)–Co(1)–Cl(2) 117.33(4), C(2)–N(1)–Co(1) 121.49(5), C(1)–N(1)–Co(1) 128.05(2), C(2)–N(1)–C(1) 59.23(2), C(1)–C(2)–N(1) 60.41(2), C(2)–C(1)–N(1) 60.35(2), C(2)–C(1)–C(3) 119.60(3).

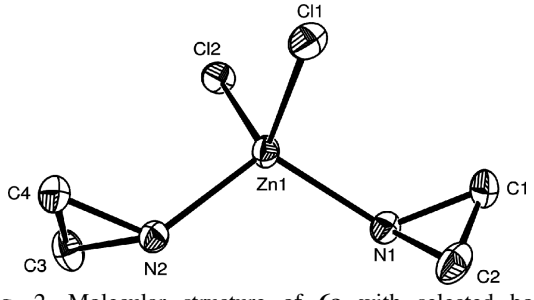

Fig. 2. Molecular structure of **6a** with selected bond lengths (Å) and angles (deg). Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity. Zn(1)–N(1) 2.001(16), Zn(1)–N(2) 2.007(15), Zn(1)–Cl(2) 2.242(6), Zn(1)–Cl(1) 2.275(6), N(1)–C(2) 1.470(3), N(1)–C(1) 1.471(3), C(1)–C(2) 1.443(3); N(1)–Zn(1)–N(2) 110.79(7), N(1)–Zn(1)–Cl(2) 114.56(5), N(1)–Zn(1)–Cl(1) 104.09(5), N(2)–Zn(1)–Cl(2) 108.48(5), N(2) –Zn(1)–Cl(1) 107.82(5), Cl(2)–Zn(1)–Cl(1) 110.88(2), C(2)–N(1)–Zn(1) 122.06(13), C(1)–N(1)–Zn(1) 122.69(13), C(2)–N(1)–C(1) 58.75(16), C(2)–C(1)–N(1) 60.57(14), C(1)–C(2)–N(1) 60.67(15).

dinated by the nitrogen atoms of two aziridine and two chloride ligands resulting in a slightly distorted tetrahedral geometry. Selected bond lengths and angles of the complexes together with the molecular structures are given in Figs. 1 – 3. Endocyclic C–C and C–N bond lengths and angles differ slightly from those of free aziridine in the solid state [38], and only marginally from those found for other 3*d* transition metal coordinated aziridines [26 – 28]. Both Co–N bond lengths of approximately 2.025 Å observed for **5b** are in good agreement with the Co–N bond lengths described for cobalt(II)-*sec*-amine compounds, and the Zn–N bond length of 2.005 (**6a**) and 2.018 Å (**6b**) are also in good agreement with the values observed for zinc(II)-*sec*-amine compounds [39, 40]. The Cl–M–Cl angles [117.33 (**5b**) and 116.87° (**6b**)] are larger than the N–M–N angles [110.73 (**5b**) and 110.70° (**6b**)]. In **6a** this effect was not observed, due to the reduced steric hindrance of the aziridine **1a**, which lacks the bulkier methyl groups of **1b**. The C–N–M angles in the range 121.14 – 128.05° for **5b**, 120.93 – 123.04° for **6a** and 120.79 – 127.68° for **7b** show a distorted tetrahedral configuration for the nitrogen atoms of the aziridines.

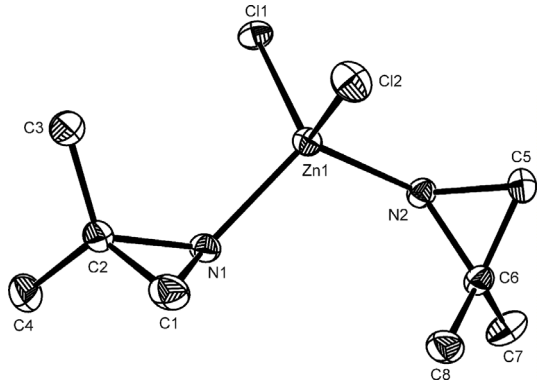

Fig. 3. Molecular structure of **6b** with selected bond lengths (Å) and angles (deg). Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity. Zn(1)–N(1) 2.018(2), Zn(1)–N(2) 2.019(2), Zn(1)–Cl(1) 2.275(7), Zn(1)–Cl(2) 2.236(8), C(1)–C(2) 1.473(4), C(1)–N(1) 1.498(3), C(2)–N(1) 1.495(3), C(2)–C(4) 1.493(4), C(2)–C(3) 1.506(4); N(1)–Zn(1)–N(2) 110.70(9), N(1)–Zn(1)–Cl(2) 107.49(7), N(1)–Zn(1)–Cl(1) 109.46(6), N(2)–Zn(1)–Cl(2) 110.39(7), N(2)–Zn(1)–Cl(1) 101.85(7), Cl(2)–Zn(1)–Cl(1) 116.87(3), C(2)–N(1)–C(1) 58.96(16), C(2)–N(1)–Zn(1) 126.21(15), C(1)–N(1)–Zn(1) 120.79(17), C(2)–C(1)–N(1) 60.43(16), C(1)–C(2)–C(4) 119.45(2), C(1)–C(2)–N(1) 60.62(16), C(1)–C(2)–C(3) 118.59(2).

The palladium(II) centers in **7a,b** are coordinated by two aziridine and two chloride ligands, and as expected for a $4d^8$ configuration, a square planar geometry is observed with aziridine and chloride ligands in *trans* positions. Selected bond lengths and angles as well as the molecular structures of **7a**,**b** are given in Figs. 4 and 5. Again, the C–C and C–N bond lengths and angles of the ligands differ only slightly from those observed for free aziridine in the solid state [38]. The Pd–N bond lengths of 2.02 and 2.04 Å observed in **7a** and **7b** are in

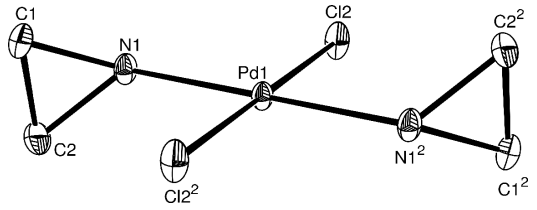

Fig. 4. Molecular structure of **7a** with selected bond lengths (Å) and angles (deg). Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity. Pd(1)–N(1) 2.019(2), Pd(1)–Cl(2) 2.300(9), N(1)–C(1) 1.482(3), N(1)–C(2) 1.476(3), C(1)–C(2) 1.464(3); N(1)–Pd(1)–Cl(2) 87.88(7), C(2)–N(1)–Pd(1) 125.28(16), C(1)–N(1)–Pd(1) 127.30(17), C(2)–N(1)–C(1) 59.32(15), C(2)–C(1)–N(1) 60.15(14), C(1)–C(2)–N(1) 60.53(15).

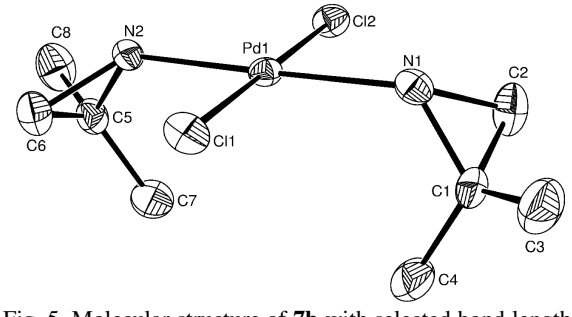

Fig. 5. Molecular structure of **7b** with selected bond lengths (Å) and angles (deg). Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity. Pd(1)–N(1) 2.042(4), Pd(1)–N(2) 2.035(4), Pd(1)–Cl(1) 2.298(12), Pd(1)–Cl(2) 2.303(12), N(1)–C(1) 1.461(6), N(1)–C(2) 1.490(6), C(1)–C(2) 1.473(7), C(1)–C(4) 1.487(7), C(1)–C(3) 1.504(7); N(2)–Pd(1)–N(1) 178.55(16), N(2)–Pd(1)–Cl(1) 91.81(12), N(2)–Pd(1)–Cl(2) 88.13(12), N(1)–Pd(1)–Cl(1) 87.96(12), N(1)–Pd(1)–Cl(2) 92.10(12), Cl(1)–Pd(1)–Cl(2) 179.90(5), C(1)–N(1)–Pd(1) 125.19(3), C(2)–N(1)–Pd(1) 127.00(3), C(6)–N(2)–Pd(1) 126.74(3), C(5)–N(2)–Pd(1) 125.66(3).

good agreement with those reported for palladium(II)-*sec*-amine compounds [41]. In addition, the M–Cl bond lengths of complexes **5b** – **7b** are within the values expected for chloride complexes [39 – 41]. The Cl–M–N angles of 92.12 and 87.88° (**7a**) and 87.96 – 92.10° (**7b**), as well as the N–M–N angles of 179.98 (**7a**) and 178.55° (**7b**) are consistent with the square planar complex geometry. Remarkably, the ligand arrangements in **7a** and **7b** are different. In complex **7a** the aziridine ring planes are aligned almost orthogonal to the plane formed by the nitrogen and chlorine atoms with an angle of 86.05°. Corresponding to the presence of an inversion center, the aziridine ligands point in opposite directions. The aziridine ligands in **7b**, however, are bent out of the plane in the same direction, with both methyl groups in anti-positions. The angles between the aziridine ring planes and the plane formed by the nitrogen and chlorine atoms are 50.29 and 51.32° in **7b**.

Experimental Section

General procedures

All manipulations were performed under a dry argon atmosphere using Schlenk line techniques. Aziridine (**1a**) and 2,2-dimethylaziridine (**1b**) were prepared according to literature methods, distilled from sodium and stored under argon [36]. Anhydrous $CoCl_2$, $ZnCl_2$ and $PdCl_2$ were used as received from Fluka without further purification. Dichloromethane was distilled from calcium hydride; *n*-pentane and *n*-hexane were distilled from sodium, and acetonitrile from P_4O_{10}; acetone was dried over 4 Å molecular sieves. All solvents were stored under dry argon atmosphere and over 3 Å or 4 Å molecular sieves. The ^1H and ^{13}C NMR spectra were recorded using Jeol Eclipse 270 and 400 instruments operating at 270 and 400 MHz (^1H) or 68 and 100 MHz (^{13}C). All chemical shifts are given in ppm relative to TMS (^1H, ^{13}C). Mass spectra were measured using a JEOL Mstation JMS 700 in the direct EI mode (DEI) or FAB^+ mode. Data given for multi-isotope containing fragments refer to the isotope with the highest abundance. UV/vis spectra were measured using a Perkin Elmer Lambda 16 UV/vis spectrometer. Infrared spectra were recorded with Nicolet 520 FT-IR and Perkin Elmer Spectrum One FT-IR spectrometers in the 4000 – 400 cm^{-1} range. Elemental analyses were provided by the Microanalytical Laboratory of the Department of Chemistry and Biochemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

X-Ray structure determinations

Single crystal X-ray diffraction data were collected on a Nonius Kappa CCD instrument using graphite-monochromated MoK_α radiation. Semi-empricial absorption corrections using equivalent reflections were applied. The structures were solved by Direct Methods using SHELXS-97 and refined by full-matrix least-squares on F^2 with SHELXL-97 using anisotropic displacement parameters [42]. The CCDC numbers in Table 1 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.

Syntheses

Anhydrous MCl_2 was suspended in 20 mL of dry CH_2Cl_2 [M = Zn(II), Pd(II)] or dissolved in 20 mL of dry CH_3CN [M = Co(II)]. The aziridine was added, and the solution was

Table 1. Crystal data and details of the structure refinement for compounds **5b** – **7a,b**.

Compound	**5b**	**6a**	**6b**	**7a**	**7b**
Formula	$C_8H_{18}Cl_2CoN_2$	$C_4H_{10}Cl_2N_2Zn$	$C_8H_{18}Cl_2N_2Zn$	$C_4H_{10}Cl_2N_2Pd$	$C_8H_{18}Cl_2N_2Pd$
M_r	272.08	222.43	278.54	263.46	319.57
Crystal color	blue	colorless	colorless	yellow	yellow
Crystal size, mm^3	$0.12 \times 0.02 \times 0.02$	$0.13 \times 0.10 \times 0.08$	$0.25 \times 0.08 \times 0.06$	$0.18 \times 0.12 \times 0.10$	$0.25 \times 0.09 \times 0.06$
Temperature, K	200	200	200	200	200
Wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	$Pbca$	$P2_1/c$	$P\bar{1}$	$Pbca$
a, Å	10.152(2)	12.386(3)	10.136(2)	4.9474(10)	9.0863(18)
b, Å	6.1464(12)	9.815(2)	6.1420(12)	6.3903(13)	15.710(3)
c, Å	20.754(4)	14.086(3)	20.730(4)	6.7743(14)	17.957(4)
α, deg	90	90	90	82.09(3)	90
β, deg	102.00(3)	90	101.97(3)	82.48(3)	90
γ, deg	90	90	90	73.81(3)	90
V, Å^3	1266.7(4)	1712.3(6)	1262.6(4)	202.76(8)	2563.3(9)
Z	4	8	4	1	8
$D_{calc.}$, g cm^{-1}	1.4267(5)	1.7257(6)	1.4653(5)	2.1577(7)	1.6562(6)
μ, mm^{-1}	1.739	3.414	2.331	2.864	1.828
$F(000)$	564	896	576	128	1280
θ range, deg	3.15 – 27.47	3.29 – 27.48	3.47 – 27.55	3.34 – 27.48	3.19 – 26.00
hkl range	$-13 \le h \le 13$, $-7 \le k \le 7$, $-26 \le l \le 26$	$-16 \le h \le 16$, $-12 \le k \le 12$, $-18 \le l \le 18$	$-13 \le h \le 13$, $-7 \le k \le 7$, $-26 \le l \le 26$	$-6 \le h \le 5$, $-8 \le k \le 8$, $-8 \le l \le 8$	$-11 \le h \le 11$, $-9 \le k \le 19$, $-22 \le l \le 22$
Refl. collected	5497	3660	5460	1692	4689
Independent refl.	2895	1969	2897	925	2514
R_{int}	0.0543	0.0152	0.0186	0.0313	0.0137
Completeness to θ	0.998	0.999	0.995	0.994	0.998
Data/parameters	2895/118	1969/82	2897/126	925/47	2514/126
GoF (F^2)	1.011	1.061	1.088	1.120	1.061
Final R indices					
$[I \ge 2\sigma(I)]$	$R1 = 0.041$, $wR2 = 0.091$	$R1 = 0.027$, $wR2 = 0.062$	$R1 = 0.031$, $wR2 = 0.075$	$R1 = 0.018$, $wR2 = 0.043$	$R1 = 0.039$, $wR2 = 0.105$
R indices (all data)	$R1 = 0.089$, $wR2 = 0.105$	$R1 = 0.035$, $wR2 = 0.066$	$R1 = 0.037$, $wR2 = 0.078$	$R1 = 0.018$, $wR2 = 0.043$	$R1 = 0.055$, $wR2 = 0.116$
$\Delta\rho_{fin}$ (max/min), eÅ^{-3}	0.43/−0.42	0.38/−0.47	0.45/−0.44	0.42/−0.91	1.88/0.94
CCDC numbers	638751	638753	638750	638754	638752

stirred overnight at ambient temperature (21 °C). If necessary, the residual MCl_2 was filtered off and the solvent was removed *in vacuo*. The residue was purified by stirring in dry *n*-hexane (20 mL) overnight at ambient temperature. The *n*-hexane phase was then removed by decantation and the solid was dried *in vacuo*.

*(C$_4$H$_9$N)$_2$CoCl$_2$ (**5b**)*

Reagents: Anhydrous $CoCl_2$ (138 mg, 1.06 mmol), 2,2-dimethylaziridine (**1b**) (378 mg, 480 μL, 5.0 equiv., 5.32 mmol). – Blue powder, yield: 248 mg (86 %). Blue single crystals were obtained by slow isothermic diffusion of *n*-pentane into a dichloromethane solution of **5b**. – IR (KBr, cm^{-1}): ν = 3253 (vs), 3109 (w), 3012 (w), 2970 (m), 2930 (w), 2876 (w), 1596 (w), 1450 (m), 1390 (m), 1382 (m), 1351 (w), 1337 (m), 1269 (w), 1248 (w), 1198 (w), 1137 (m), 1125 (m), 1103 (m), 1053 (w), 1031 (w), 1002 (w), 968 (w), 901 (m), 809 (m), 672 (w), 505 (w), 433 (w). – UV/vis ($CHCl_3$): $\lambda_{max}(\log\varepsilon_{max})$ = 578 nm (236), 614 nm (350), 632 nm (374). – $(C_4H_9N)_2CoCl_2$ (272.08): calcd. C 35.32, H 6.67, N 10.30; found C 37.44, H 6.95, N 10.96.

*(C$_2$H$_5$N)$_2$ZnCl$_2$ (**6a**)*

Reagents: Anhydrous $ZnCl_2$ (150 mg, 1.10 mmol), aziridine (**1a**) (237 mg, 296 μL, 5.0 equiv., 5.50 mmol). – Colorless powder, yield: 240 mg (98 %). Colorless crystals were obtained by slow isothermic diffusion of *n*-pentane into an acetone solution of **6a**. – IR (KBr, cm^{-1}): ν = 3294 (s), 3249 (m), 3017 (w), 1588 (w), 1440 (w), 1292 (m), 1231 (m), 1147 (w), 1127 (w), 1103 (w), 1056 (w), 1005 (w), 929 (w), 879 (vs), 809 (w), 795 (w). – ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.11 (s, br, CH_2, 4H). – $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 21.1 (CH_2). – MS (FAB/NBA): *m/z* (%) = 187.0 (100) $[M–Cl]^+$. – $(C_4H_9N)_2ZnCl_2$ (222.45): calcd. C 21.60, H 4.53, N 12.59; found C 21.90, H 4.54, N 12.54.

*$(C_4H_9N)_2ZnCl_2$ (**6b**)*

Reagents: Anhydrous $ZnCl_2$ (82 mg, 0.60 mmol), 2,2-dimethylaziridine (**1b**) (214 mg, 272 μL, 5.0 equiv., 3.01 mmol). – Colorless powder, yield: 163 mg (97 %). Colorless crystals were obtained by slow isothermic diffusion of *n*-pentane into a dichloromethane solution of **6b**. – IR (KBr, cm^{-1}): ν = 3259 (vs), 3012 (w), 2983 (w), 2964 (w), 2934 (w), 1451 (m), 1391 (m), 1383 (w), 1355 (w), 1338 (w), 1268 (w), 1140 (w), 1126 (w), 1104 (m), 1055 (w), 1032 (w), 969 (w), 905 (m), 863 (w), 809 (m), 675 (w), 502 (w), 434 (w). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60 (s, br, NH, 2H), 2.09 (s, CH_2, 4H), 1.46 (s, CH_3, 12H). – $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 38.5 (C_q), 35.5 (CH_2), 25.0 (CH_3), 22.8 (CH_3). – MS (FAB/NBA): *m/z* (%) = 241.4 (100) $[M–Cl]^+$. – $(C_4H_9N)_2ZnCl_2$ (278.54): calcd. C 34.50, H 6.51, N 10.06; found C 34.34, H 6.45, N 9.86.

*$(C_2H_5N)_2PdCl_2$ (**7a**)*

Reagents: Anhydrous $PdCl_2$ (268 mg, 1.51 mmol), aziridine (**1a**) (129 mg, 163 μL, 2.0 equiv., 3.02 mmol). – Pale yellow solid, yield: 389 mg (98 %). Yellow crystals were obtained by slow isothermic diffusion of *n*-pentane into a methanol solution of **7a**. – IR (KBr, cm^{-1}): ν = 3740 (w), 3703 (w), 3257 (vs), 3113 (w), 3025 (w), 2625 (w), 2440 (w), 2396 (w), 2220 (w), 2146 (w), 2071 (w), 1864 (w), 1659 (w), 1598 (w), 1461 (w), 1434 (m), 1317 (w), 1251 (w), 1230 (m), 1222 (m), 1198 (m), 1145 (w), 1132 (w), 1094 (w), 1083 (w), 1056 (w), 1056 (w), 1019 (w), 984 (w), 935 (w), 885 (m), 883 (w), 762 (w), 477 (w). – ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.09 (t, ^3J = 5.4 Hz, CH_2, 4H), 1.89 (t, ^3J = 7.7 Hz, CH_2, 4H). – $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 23.3 (CH_2). – MS (DEI): *m/z* (%) = 264 (100) $[M]^+$, 229 (20) $[M–Cl]^+$, 192 (18) $[M–2Cl]^+$, 149 (50) $[M–2Cl–C_2H_5N]^+$, 106 (11) $[M–2Cl–2C_2H_5N]^+$. – $(C_2H_5N)_2PdCl_2$ (263.46): calcd. C 18.24, H 3.83, N 10.63; found C 18.73, H 3.67, N 9.92.

*$(C_4H_9N)_2PdCl_2$ (**7b**)*

Reagents: Anhydrous $PdCl_2$ (236 mg, 1.33 mmol), 2,2-dimethylaziridine (**1b**) (190 mg, 240 μL, 2.0 equiv., 2.66 mmol). – Pale yellow solid, yield: 121 mg (90 %). Yellow crystals were obtained by slow isothermic diffusion of *n*-pentane into a dichloromethane solution of **7b**. – IR (KBr, cm^{-1}): ν = 3202 (vs), 3089 (w), 3008 (w), 2969 (s), 2928 (m), 2870 (w), 2757 (w), 2685 (w), 2614 (w), 2547 (w), 2482 (w), 2242 (w), 2110 (w), 1461 (m), 1446 (m), 1383 (m), 1343 (m), 1330 (m), 1272 (w), 1142 (m), 1117 (s), 1056 (w), 1033 (w), 967 (m), 928 (s), 814 (s), 557 (w), 540 (w), 449 (w). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.08 (s, br, CH_2, 2H), 1.72 (s, br, CH_2, 2H), 1.71 (s, CH_3, 3H), 1.70 (s, CH_3, 3H), 1.30 (s, CH_3, 3H), 1.29 (s, CH_3, 3H). – $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 38.9 (C_q), 36.1 (CH_2), 35.7 (CH_2), 24.9 (CH_3), 23.9 (CH_3). – MS (DEI): *m/z* (%) = 320 (43) $[M]^+$, 284 (38) $[M–Cl]^+$, 248 (54) $[M–2Cl]^+$, 177 (100) $[M–2Cl–C_4H_9N]^+$, 106 (11) $[M–2Cl–2C_4H_9N]^+$. – $(C_4H_9N)_2PdCl_2$ (319.57): calcd. C 30.07, H 5.68, N 8.77; found C 29.78, H 5.51, N 8.54.

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