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Spectroscopic and structural characterization of cationic *N*-(2-aminoethyl)aziridine-*N*,*N*′ chelate complexes of the d^6-metals Rh(III) and Ir(III)

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Dedicated to Professor Dr. Gerard van Koten on the occasion of his 65th birthday.

Abstract

The syntheses of the compounds $[M(Cp^*)(aeaz)(az)](OTf)_2$ (**4**, **5**) (M = Rh(III), Ir(III); aeaz = $C_2H_4NC_2H_4NH_2$, az = C_2H_4NH (**3**)) containing cationic *N*-(2-aminoethyl)aziridine-*N*,*N*′ chelate complexes are described. The bis-aziridine complexes $[MCl(Cp^*)(az)_2]Cl$ (M = Rh (**1**), M = Ir (**2**)) react with an excess of the aziridine (az) in the presence of AgO_3SCF_3 (=AgOTf) via AgCl precipitation and az addition followed by a metal-mediated coupling reaction, to give the compounds $[M(Cp^*)(aeaz)(az)](OTf)_2$ (**4**, **5**). The new aeaz ligand is formally the dimerisation product of az. Using the same reaction conditions with the analogous, but weaker Lewis acidic ruthenium(II) complex $[RuCl(C_6Me_6)(az)_2]Cl$ (**6**) an anion exchange reaction yielding $[RuCl(C_6Me_6)(az)_2]OTf$ (**8**) is observed. After purification, all compounds are fully characterized using IR, FAB-MS, ^1H and ^{13}C NMR spectroscopy. The single crystal X-ray structure analysis reveals a distorted octahedral geometry for all complexes.

Keywords: Aziridine; Chelating ligands; Crystal structures; Iridium; Rhodium; Ruthenium

1. Introduction

Interest in the coordination chemistry of aziridines dates back to 1956, when Jones et al. reported on an unstable uranium–aziridine complex [1]. Two years later, Hieber et al. synthesized and spectroscopically characterized the first transition metal aziridine complex $[Co(az)_6]^{2+}$ $[Co(CO)_4^-]_2$ [2]. In the following years the research group of *Edwards* prepared various azridine transition metal halogenido complexes [3–6], and published the first X-ray structure analysis of an aziridine rhodium complex in 1969 [7]. A series of publications on the coordination chemistry of aziridine [8–22], including a recent report on main group metal aziridine complexes by Gal et al. subsequently followed [23].

Although aziridines are isolobal to oxiranes and thiiranes (C_2H_4X; X = NH, O, S), the ligand reactivity of the former differs considerably. Oxiranes and thiiranes act as oxidising agents towards organometallic compounds resulting in oxo or thio complexes via ethylene elimination. Though aziridines usually remain intact as three-membered rings and coordinate via nitrogen as would be expected for secondary amines, transition metal-mediated ring opening reactions are possible. Thus β-aminoacyl complexes have been synthesized and characterized which result from the nucleophilic attack of an aziridine at a metal carbonyl ligand by Beck et al. and our group [24–30]. Hillhouse and co-workers reported the oxidative addition of *N*-tosylated aziridines with nickel(0) complexes forming an azametallacyclobutane complex, which was elucidated using X-ray diffraction [31]. In addition, cyclic carbene

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ligands were synthesized using metal carbonyls and aziridine by Singh and Angelici [32,33] and also in our group [34] whereas isocyanide complexes were employed by Michelin and co-workers [35]. Beck and co-workers observed the metal-mediated dimerisation of two aziridine ligands forming the chelate *N*-(2-aminoethyl)aziridine ligand [8], and in 1997, Kojima et al. reported the first X-ray structure of a *N*-(2-amino-2-methylethyl)-2-methylaziridine cobalt(III) complex [36].

The tendency towards ring opening of aziridine is mainly a result of Baeyer and Pitzer ring strain [37], especially after NH protonation has occurred and can easily lead to nucleophilic attack. The versatility of the aziridine motif has resulted in widespread interest in this heterocycle [38–40]. Particularly in organic chemistry, aziridine compounds have a variety of synthetic applications, for example, as catalysts in asymmetric synthesis [41–44], synthones in natural product synthesis [45–48], monomers in macromolecular chemistry, [49,50] or target molecules in organic synthesis [51–53]. Another important reason for the increased interest in aziridine chemistry is its biological role, whereby *in vivo* effects of aziridine derivatives are mostly the result of ring opening and alkylation reactions. This results in the carcinogenic activity of natural and synthetic aziridine compounds [54–57]. In this context, the promising cytotoxic and anticancerogenic activities of chelating amine ligands in the coordination sphere of the platinum group metals is also worth mentioning [58]. Biological studies concerning this issue are currently being undertaken, and will be reported in future work. In this communication, the transition metal lewis acid mediated ring opening reaction of aziridine yielding the chelating ligand *N*-(2-aminoethyl)aziridine-*N*,*N*′ is reported.

2. Results and discussion

2.1. Synthesis

Scheme 1 illustrates the reactions of the bis-aziridine complexes $[MCl(Cp^*)(az)_2]Cl$ (M = Rh: **1**, M = Ir: **2**) with first 2.2 equiv. silvertriflate and then with an excess (1:2.5) of aziridine C_2H_4HN (**3**), which leads to the formation of the *N*-(2-aminoethyl)aziridine complexes $[M(Cp^*)(aeaz)(az)](OTf)_2$ (M = Rh: **4**, M = Ir: **5**; aeaz = *N*-(2-aminoethyl)aziridine). Monitoring the first step of this reaction using IR spectroscopy shows that a triflato-*O* ligand is weakly coordinated to the metal centres forming the $[M(Cp^*)(OTf)(az)_2]$ intermediate. For related complexes, we have succeeded in the isolation and structural characterization of triflato-*O* complexes [59].

The same reaction as that described above with the analogous complex $[RuCl(C_6Me_6)(az)_2]Cl$ (**6**) and aziridine **3** did not result in the formation of the analogous complex $[Ru(C_6Me_6)(aeaz)(az)](OTf)_2$ (**7**). Obviously under the reaction conditions applied, **6** appears to be not electrophilic enough to induce the desired ring opening reaction and therefore, an anion exchange reaction occurs yielding the $[RuCl(C_6Me_6)(az)_2]OTf$ (**8**) complex. Nevertheless, even although the preparation of the desired Ru complex was unsuccessful using the mild reaction conditions applied in this work, the synthesis of this complex should be possible.

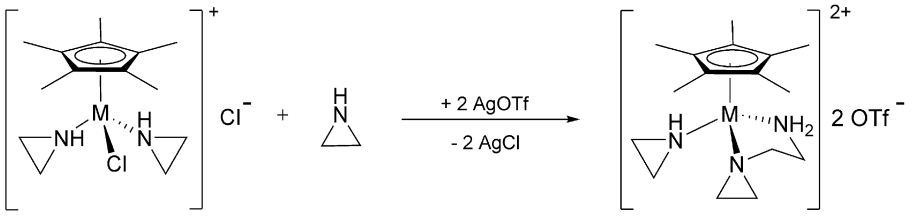
All products were obtained as colourless (**4**) or yellow (**5**, **8**) powders in acceptable yields (60–74%) and are soluble in polar solvents such as acetone, but insoluble in non-polar solvents such as *n*-pentane. Compounds **4**, **5** and **8** can be stored infinitely under an atmosphere of argon.

2.2. X-ray crystal structure analysis

The molecular structures of compounds **4**, **5** and **8** were determined using single crystal X-ray diffraction. Isothermic diffusion of *n*-pentane into solutions of **4** and **5** in acetone or of **8** in dichloromethane resulted in the formation of X-ray quality single crystals. Details of the relevant data collection and refinement are summarised in Table 1. The molecular structures of **4**, **5** and **8** are illustrated in Figs. 1–3. Bond lengths and angles within the coordination sphere of Rh(III), Ir(III) and Ru(II) are listed in Figs. 1–3, respectively.

All three complexes show similar structures with a distorted octahedral geometry as is expected for Rh(III), Ir(III) or Ru(II) transition metal centres. The aromatic ligand L (C_6Me_6 or C_5Me_5) constitutes one octahedral face, while the other three coordinating atoms (Cl or N) form the opposite one.

All of M–N bond lengths (213–218 pm) observed for **4** and **5** lie within a small range and are only slightly elongated in comparison to the M–N bond lengths of the analogous bis-aziridine complexes **1** and **2** [60]. It is worthwhile



1: M = Rh
2: M = Ir

3

4: M = Rh
5: M = Ir

Scheme 1. Synthesis of the cationic *N*-(2-aminoethyl)aziridine complexes **4** and **5**.