Axial Chirality in Square-Planar Metal Complexes

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Metal complexes with a square-planar arrangement of ligands are frequently found for the late Transition Metals. The incorporation of C1-symmetrical planar ligands (e.g. nucleophilic carbene) in an orientation perpendicular to the square-plane of the complex leads to various isomers which are characterized by means of an axis of chirality employing the well established Cahn-Ingold-Prelog R/S-nomenclature.

Introduction

Square-planar coordination spheres are common for complexes of the late Transition Metals Rh, Ir, Ni, Pd, and Pt. Many of these complexes contain ligands bearing stereochemical information [1]. In contrast to tetrahedral structures, which may additionally contain a stereogenic center at the metal atom, or to octahedral complexes with helical chirality [2], square-planar complexes containing a chirality information additional to that within the ligand sphere are rare. An exception are complexes bearing planar ligands with C1 symmetry in an orientation perpendicular to the reference plane of the complex. Examples of such ligands are guanosines [3], tetrazoles [4], and some nucleophilic carbene [5]. The existence of different diastereomers has been described for these complexes, but only an insufficient proposal for a nomenclature expanding the complex to a virtual octahedron and describing the helicity of two skew lines has been developed [2,3]. As this ΔΔ nomenclature can only be applied to one pair of enantiomers omitting all other isomers, we now want to report a comprehensive concept of classification based on axial chirality. The axis is represented by the metal-ligand bond, and the two perpendicular planes are the reference plane of the complex and the plane of the ligand, respectively [6,7].

Discussion

Square-planar metal complexes incorporating between one and four carbene ligands perpendicular to the reference plane of the complex are already known [8]. We reported on the preparation of chiral (triazolylmethylene)Rh(COD) complexes I, which were obtained with diastereomeric excesses of up to de = 97% [7]. The absolute configuration of these compounds could be determined by X-ray structure analysis and NMR spectroscopic investigations. For the definition of the configuration, the chlorine atom and the olefin are the substituents of the first plane, the two nitrogen atoms neighbouring the carbene carbon are the substituents of the second plane. The priorities can be assigned according to the CIP rules looking along the metal-carbene bond, and termed as Rα and Sα, respectively (Fig. 1) [9].

Other examples of complexes bearing one planar C1-symmetrical ligand may be envisaged depending on the character of the different ligands a, b, and c (the priority of these achiral ligands is defined as a>b>c>carbene, and ball (o) higher priority than stick (l)) (Fig. 2).

Complexes of type A and trans-B containing a mirror plane are achiral. A trans-(amino)carbene)diiodopalladium(II) complex as an example for type trans-B has already been prepared in this laboratory [6]. Complexes such as cis-B (see compound 1) and C with one axis of chirality have to be described by the configuration of this axis and by the arrangement of the different ligands. According to IUPAC rules, the numeral (complex
type C) indicates the priority of the ligand opposite to ligand a with the highest priority in order to describe the sequence of the different ligands [2].

We have also reported on the preparation of palladium complexes incorporating two identical chiral carbene ligands [6]. A mixture of different cis- and trans-isomers was obtained, the cis- and trans-isomers were separated chromatographically, and the two trans-isomers by crystallisation. NMR spectroscopic investigations and X-ray structure analysis revealed the individual orientation of the ligands (Fig. 3).

Three different cis-complexes 2 were obtained. With identical achiral ligands one meso-form and two enantiomers are possible. The ligands may have the same orientation (meso-form \( R_a,S_a-D \), indicated as syn) or different orientations (two enantiomers \( R_a,R_a-D \) and \( S_a,S_a-D \), indicated as anti) (Fig. 4).

With two different ligands a and b two diastereomeric pairs of enantiomers are possible. The configuration of the carbene ligand opposite to ligand a (with highest priority) is mentioned first for complexes of type E.

In the case of the dicarbenediiodopalladium(II) complexes 2, two trans-isomers were obtained with the ligands possessing the same orientation (syn) or opposite orientations (anti) (Fig. 5) [6]. For two different ligands a and b, one meso-form (syn-E) and two enantiomers (anti-E) are possible as in the case of the cis-syn-complexes with achiral ligands (Fig. 6).

As far as we know, complexes bearing three \( C_1 \)-symmetrical carbene ligands have not yet been prepared. However, a cationic (imidazolinylidene)palladium complex 3 has already been described [10]. Four oxazolidin-2-ylidenes or tetrazole rings are the ligands of the homoleptic Pd(II) [11] and Au(III) [4] complexes 4 and 5 which have different structures caused by the orientation of the ligands (Fig. 7).
Fig. 7. Ionic Pd(II) (3,4) and Au(III) (5) complexes.

An examination of the different possible isomers for complexes of type F with three \(C_1\)-symmetrical ligands shows two \(meso\)-forms and one pair of enantiomers (Fig. 8). The two \(meso\)-forms are differentiated by the position of the carbene ligand opposite to a. They can be described by a pseudo-axis of chirality (\(s_a\) or \(r_a\)) \([12]\) due to the same orientation of the carbene ligands \(cis\) to a with the descriptors \(R_a\) and \(S_a\) (\(R_a\) higher priority than \(S_a\)). The two enantiomers \(R_a,R_a\)-F and \(S_a,S_a\)-F contain only two axes of chirality. The ligand opposite to a could have either orientation without causing a new diastereomer due to the two identical carbene ligands with the same configuration as substituents of the first plane of the axis.

The incorporation of four ligands leads to achiral complexes G, and different isomers are possible depending on the \(syn\)-\(anti\) orientation of the ligands (Fig. 9). An efficient differentiation of the compounds can be achieved employing point groups as there is no stereogenic unit within the molecules.

In order to have a unified nomenclature by means of \(syn\)/\(anti\) descriptors, one reference ligand can be chosen and the orientation of the other ligands (clockwise or counter-clockwise) relative to the first one be determined. The nomenclature is based on the rule of using as many \('anti\'-descriptors as possible, but actually, this restriction is not really necessary. Starting with any ligand and describing the others clockwise or counter-clockwise would be sufficient to know the structure of the complex, however, then there would be several names for one structure.

**Conclusion**

In summary, the concept of nomenclature presented here is an efficient method of describing square-planar complexes containing \(C_1\)-symmetrical ligands perpendicular to the square-plane of the complex. The previous examples were all based on only one kind of \(C_1\)-symmetrical ligands. However, an expansion including complexes with different ligands would be no problem.

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