



Review

Dynamic behavior in solution of seven-coordinated transition metal complexes



Fernando Villafañe*

GIR MIOMeT-IU Cinquima-Química Inorgánica, Facultad de Ciencias, Campus Miguel Delibes, Universidad de Valladolid, 47011 Valladolid, Spain

Contents

1. Introduction	87
2. Pentagonal bipyramidal (PBP) complexes	87
2.1. PBP [M(heptadentate)] complexes	87
2.2. PBP [M(pentadentate) ₂] complexes	87
2.3. PBP [M(mer-tridentate) ₄] complexes	88
2.4. PBP [M(bidentate) ₃ L] complexes	89
2.5. PBP [M(bidentate) ₂ L ₃] complexes	89
2.6. PBP [M(bidentate)L ₅] complexes	89
3. Capped octahedral (cO) complexes	89
3.1. cO [M(fac-tridentate) ₄] complexes	89
3.2. cO [M(bidentate) ₂ L ₃] complexes	90
3.3. cO [M(bidentate)L ₅] complexes	92
3.4. cO [ML ₇] complexes	93
4. Capped trigonal prismatic (cTP) complexes	94
4.1. cTP [M(tetradentate) ₃] complexes	94
4.2. cTP [M(bidentate) ₂ L ₃] complexes	94
4.3. cTP [M(bidentate)L ₅] complexes	95
5. Complexes with 4:3 geometry (4:3)	96
5.1. 4:3 [M(tetradentate)(bidentate)L] complexes	96
5.2. 4:3 [M(fac-tridentate) ₄] complexes	96
5.3. 4:3 [M(bidentate) ₂ L ₃] complexes	96
6. Final remarks	98
References	99

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ABSTRACT

This work reviews the dynamic behavior in solution of seven-coordinated complexes of different transition metals containing mono and polydentate monohapto ligands. The complexes are classified according to their geometry in the solid state, established by X-ray diffraction: pentagonal bipyramidal (PBP), capped octahedral (cO), capped trigonal prismatic (cTP), and complexes with 4:3 tetragonal base-trigonal base geometry (4:3). For each geometry, the processes are ordered from lower degrees of freedom to higher, thus going from complexes containing more polydentate ligands to those with more monodentate ligands. The processes detected in solution may be classified into two main groups: those implying changes

Abbreviations: 4:3, tetragonal base-trigonal base; allyl, CH₂CHCH₂; ax, axial; bpa, bis(pyridylmethyl)amine; cO, capped octahedron; Cp, cyclopentadienyl; cTP, capped trigonal prism; DFT, Density Functional Theory; diars, o-phenylenebis(dimethylarsine); dmahfb, cis-2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluoro-2-butene; cis-Me₂AsC(CF₃)=C(CF₃)AsMe₂; dmdepe, 1-dimethylphosphino-2-diethylphosphinoethane; dmdPhpe, 1-dimethyl-2-diphenylphosphinoethane; dmdppe, 1-dimethylphosphino-2-diisopropylphosphinoethane; dmedepe, 1-dimethyl-2-diethylphosphinoethane; dmpdmae, 1-dimethylphosphino-2-dimethylarsinoethane; dmpe, 1,2-bis(dimethylphosphino)ethane; dmsb, 1,2-bis(dimethylsilyl)benzene; dpae, 1,2-bis(diphenylarsino)ethane; dPhpdmae, 1-diphenylphosphino-2-dimethylarsinoethane; dppe, 1,2-bis(diphenylphosphino)ethane; dppm, bis(diphenylphosphino)methane; EAN, Effective Atomic Number; EHMO, Extended Hückel Molecular Orbital; eq, equatorial; Et₂mtc, N,N'-diethylmonothiocarbamate; Fc, [Fe(η⁵-C₅H₅)(η⁵-C₅H₄)], ferrocenyl; Me, methyl; Me₂mtc, N,N'-dimethylmonothiocarbamate; N-mtpp, N-methyl-meso-tetraphenylporphyrinato; NMR, Nuclear Magnetic Resonance; NNP, 2-(N,N-diethylaminomethyl)-6-(di-t-butylphosphinomethyl)pyridine; pbmpa, o-phenylenebis(methylphenylarsine); P₂N₂, PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh; PBP, pentagonal bipyramid; PNP-R₂, N,N'-bis(dialkyl- or diarylphosphino)-2,6-diaminopyridine; pz, pyrazolate; TBP, trigonal bipyramid; TfO⁻, triflate, trifluoromethylsulfonate; Tp, hydridotrispyrazolylborato; Tp', hydridotris(3,5-dimethylpyrazolyl)borato; Tp^{Pr}, hydrottris(3-isopropylpyrazol-1-yl)borato; UV, ultraviolet-visible; VT, variable temperature.

* Corresponding author. Tel.: +34 983184620.

E-mail address: fervilla@qi.uva.es

Seven-coordination
Transition metals
Coordination compounds
Ligand migration
Ligand scrambling

in the coordination geometry of the metals, and those affecting the positions of the ligands. No changes in the coordination geometry of the starting or final products of the dynamic process are usually observed, but the proposal of intermediates of different geometries to that of the starting or final products is common. Two main different types of processes may be differentiated considering the positions of the ligands involved in the dynamic processes: migration and scrambling, and both occur for most of the dynamic processes herein reviewed.

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1. Introduction

When compared with other common geometries such as square planar or octahedral, seven-coordinated complexes are less significant, considering both the number of compounds described and their possible applications. In fact, an excellent review by Alvarez et al. in 2003 revealed that crystal structures of seven-coordinated complexes represented less than 2% of all the structures reported [1]. Furthermore, the number of reports covering their possible applications is relatively scarce, although they include different areas of noteworthy interest, such as catalytic activity [2–21], magnetic and electronic properties [22–33], or bioactivity [34–37].

The relatively low activity research on seven-coordinated complexes might be a function of the difficulty of preparing these complexes, but is mainly related with the limitations associated with the limitations related to the characterization of the complexes, and therefore to the difficulties to propose an undeniable structure for them. This is a consequence of the small differences of energy between the possible geometries: pentagonal bipyramidal (*PBP*), capped octahedral (*cO*), capped trigonal prismatic (*cTP*), and tetragonal base–trigonal base (4:3). This energetic similarity has been supported both experimentally and theoretically. Besides, many of the seven-coordinated complexes reported are dynamic in solution, what makes even more difficult their complete characterization. In fact, only one example of seven-coordinated complex rigid on the NMR time scale even at elevated temperatures, $[\text{ReH}_2(\text{EPh}_3)(\text{CO})(\text{PMe}_2\text{Ph})_3]$ ($\text{E} = \text{Si}, \text{Sn}$), has been found [38]. These complexes were structurally characterized by single-crystal X-ray crystallography both in solvated and in unsolvated forms, but no simple ideal seven-coordinate polyhedron could be accounted for the observed bond angles.

The first aspect, that is, their different solid state structures and their geometric and energetic relationships has been profusely discussed [1,39–50]. However, their dynamic behavior in solution has not been so far previously reviewed, and this is the first attempt to fill this gap.

The processes reviewed are herein ordered starting from more symmetric complexes and then going into those of lower symmetry. Therefore *PBP* complexes (D_{5h}) are treated first, then *cO* (C_{3v}), *cTP* (C_{2v}), and finally 4:3 (C_s).¹ The increase in the degrees of freedom imposed by the ligands present is considered for each geometry. Thus each section starts reviewing the complexes containing more polydentate ligands, and then those with more monodentate ligands. Given the complexity of the topic, only dynamic processes of monometallic species of crystallographically characterized complexes are reviewed. However, there are many other reports in the literature of processes described by the authors as fluxional, but they are not collected in this review when no mechanistic support is provided. On the other hand, free energies (in kJ mol^{-1}) and other thermodynamic or kinetic data of the processes reviewed are included in schemes, in order to facilitate the overview of these data.

All the complexes herein reviewed contain monohapto ligands, either mono- or polydentate. Organometallic complexes (which usually fulfill the EAN rule) containing η^3 -allyl and/or η^5 -Cp ligands are formally seven-coordinated when the metal has a d^4 configuration. They give rise to dynamic processes in solution which are well established, such as intramolecular trigonal twist for allyl complexes [51], *cis*–*trans* isomerization for those containing Cp ligands [52,53], or *endo*–*exo* equilibrium for complexes containing both allyl and Cp ligands [54–56]. Therefore, they are not included herein.

2. Pentagonal bipyramidal (*PBP*) complexes

2.1. *PBP* [*M*(heptadentate)] complexes

Lonnon et al. recently described a high-spin ($S=2$) seven-coordinate iron(II) cationic complex containing the heptadentate ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)-2,6-bis(aminomethyl)pyridine [57]. The crystal structure showed that the coordination environment about the iron atom is better described as *cTP* (C_s) rather than *PBP* (C_2). However, all the NMR data were concordant with the latter geometry in solution, in which one pyridylmethyl “arm” of each bpa domain are in equatorial positions and the other in an axial position (Scheme 1). The data supported a dynamic process in solution occurring with dissociation of a pyridylmethyl arm, to afford a strained six-coordinate species. This was followed by rebinding of the arm in a different position, giving now a new seven-coordinate transition state, in which the pyridylmethyl arms within each bpa domain are essentially equivalent. Therefore, the intramolecular process occurred by exchanging the enantiomers of the seven-coordinate complex ion, by pairwise-interchanging the nonequivalent pyridylmethyl arms of the two bpa domains. NMR experiments allowed one to calculate the activation parameters for the exchange, indicated in Scheme 1. DFT (B3LYP) calculation of the energy barrier for this process was 53.5 kJ mol^{-1} , in good agreement with the experimental observations.

2.2. *PBP* [*M*(pentadentate) L_2] complexes

Iron(II) complexes containing the pentadentate ligand 2,6-bis[(methyl(2-pyridylmethyl)amino)-*N*-methyl]pyridine and two additional ligands, such as MeCN or triflate, have been very recently reported by Grau et al. [58]. They are seven-coordinated complexes at low temperature, whereas at high temperature five-coordinate complexes with *TBP* geometry are formed upon loss of two ligands (Scheme 2). The solid state structure revealed a seven-coordinate iron(II) complex with a *PBP* geometry. The proposed 7–5 equilibrium was based on VT NMR and UV–vis studies, which provided evidence for the thermodynamic parameters collected in Scheme 2. However, the rate of the 7–5 interconversions could not be fully established, although they appear to be much slower than the well known 6–4 and 4–4 coordination equilibria. This is the first example of a 7–5 coordination equilibrium, and this discovery generates several new directions, such as whether other similar coordination equilibria (for instance, 5–3 or 8–6) are yet to be discovered.

¹ This symmetry label refers to a homoleptic [ML_7] complex.

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