

Review

# Metal derivatives of poly(pyrazolyl)alkanes<sup>☆</sup>

## II. Bis(pyrazolyl)alkanes and related systems

Claudio Pettinari\*, Riccardo Pettinari

*Dipartimento di Scienze Chimiche, Università Degli Studi di Camerino, Via S. Agostino 1, MC 62032 Camerino, Italy*

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**Abbreviations:** acacH, 2,4-pentanedione; OAc, acetate; Bipy, 2,2'-bipyridyl; Bn, benzyl; Bp<sup>x</sup>, a general bis(pyrazolyl)borate; <sup>i</sup>Bu, iso-butyl; <sup>n</sup>Bu, normal-butyl; <sup>t</sup>Bu, tert-butyl; camphpzh, 7,8,8-trimethyl-4,5,6,7-tetrahydromethano-2-indazole; COD, 1,5-cyclooctadiene; Cp, a general cyclopentadienyl; cy, cyclohexyl; dme, 1,2-dimethoxyethane; dmf, dimethylformamide; dppe, 1,2-diphenylphosphinoethane; en, etilendiammina; Et, ethyl; Et<sub>2</sub>O, diethyl ether; EtOH, ethanol; Fo, formyl; Hin, indazole; hfacH, hexafluoroacetylacetone; H<sub>2</sub>C(pz)<sub>2</sub>, bis(pyrazolyl)methane; H<sub>2</sub>C(pz<sup>x</sup>)<sub>2</sub>, a general bis(pyrazolyl)methane; Ind, indenyl; Me, methyl; mim, 1-methylimidazol-2-yl; ox, oxalate; *o*-pd, orthophenylendiammine; phen, 1,10-phenanthroline; pip, piperidine; pzTp<sup>x</sup>, a general tetrakis(pyrazolyl)borates; py, pyridyl; pyr, pyridine; (R<sub>2</sub>C)<sub>n</sub>(pz<sup>x</sup>)<sub>2</sub> or RR'C(pz)<sub>2</sub>, a general bis(pyrazolyl)-*N,N'*-alkane; tfo, trifluoroacetate; tfs, trifluoromethanesulfonate; thi, thienyl; Htz, 1,2,4-triazole; THF, tetrahydrofuran; Tmed, tetramethylethylenediamine; tpm, tris(2-pyridyl)methoxymethane; Tp<sup>x</sup>, tris(pyrazolyl)borate

<sup>☆</sup> Part I is Ref. [1].

\* Corresponding author. Tel.: +39 0737 402234; fax: +39 0737 637345.

*E-mail address:* [claudio.pettinari@unicam.it](mailto:claudio.pettinari@unicam.it) (C. Pettinari).

## Abstract

This review summarizes the literature concerning metal complexes of bis(pyrazolyl)alkane ligands  $R_2C(pz^x)_2$  and follows a previous article describing the coordination chemistry of tris(pyrazolyl)alkanes [C. Pettinari, R. Pettinari, Coord. Chem. Rev., in press]. A comprehensive survey of bis(pyrazolyl)alkanes coordination chemistry, based on the nature of the metal, is presented, together with the main synthetic methods and spectroscopic and structural features of this important class of ligands.

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**Keywords:** Poly(pyrazolyl)alkane; Coordination chemistry; Metal derivatives

## 1. Introduction

Bis(pyrazolyl)alkanes  $(R_2C)_n(pz^x)_2$  (Fig. 1) constitute a family of stable and flexible bidentate ligands, isoelectronic and isosteric with the well-known bis(pyrazolyl)borates, also discovered by Trofimenko [2]. These molecules form a variety of coordination compounds with main group and transition metals. Their coordinating behaviour is often very different from that shown by  $Bp^x$ ,  $(R_2C)_n(pz^x)_2$  being able to yield stable adducts containing six  $M-N-N-C-N-N$  and seven  $M-N-N-C-C-N-N$  membered rings (Fig. 2), basic salts, mercuriated products, cleavage of the carbon ( $sp^3$ )–N bond and “agostic” interaction  $M \cdots H-C$  between the metal center and protons of the bridging methylene groups. While bipy or phen metal adducts are likely to contain an approximately planar, five membered  $-M-N-C-C-N$  moiety, upon coordination of  $(R_2C)_n(pz^x)_2$  to a metal, a six- or a seven-membered cycle is formed for which a boat conformation is forecast. Nevertheless, both the internal and external angles of the formally related  $M-(N-N)_2-E$  moieties (where E is not carbon) are known to be able to undergo wide variations. X-ray studies, carried out on several  $\mu$ -pyrazolato- $N,N'$ -derivatives [3–5], showed that the six-membered ring is not always in the boat conformation, but can undergo

a severe folding as in bis(3,5-dimethylpyrazolyl)borato- $N,N'$ -( $\eta^3$ -cycloheptatrienyl)(dicarbonyl)molybdenum [4], or can be a distorted chair as in dimeric [bis(cyclopentadienyl)titanium( $\mu$ -pyrazolato- $N,N'$ )]<sub>2</sub> [5a] or dihydrobis(3,5-dimethylpyrazolyl)borate( $\eta^3$ -allyl)dicarbonylmolybdenum [5b]. Related studies with pyrazaboles showed that energy differences between chair, boat, or planar conformations of a  $M-(N-N)_2-E$  ( $M = E =$  boron) are small, and that the solid state configuration is mainly determined by packing effects [3].

The  $(R_2C)_n(pz^x)_2$  ligands can be readily prepared and various substituents may replace each hydrogen atom, so that electronic and steric effects can be varied nearly at will. A steady stream of new derivatives was recently reported, however at this moment no complete and systematic review has appeared. We report a comprehensive survey of the coordination chemistry of bis(pyrazolyl)alkanes (and related systems containing only two pyrazolyl rings), based on the nature of the metal, together the principal synthetic methods and spectroscopic and structural properties of this class of ligands.

## 2. Syntheses and properties of bis(pyrazolyl)alkanes

The synthesis of  $H_2C(pz)_2$  was first reported by Trofimenko [2]. This ligand can be prepared by reaction of Hpz with  $CH_2Cl_2$  in an autoclave at  $150^\circ C$ . At  $200^\circ C$  this reaction leads to 4,4'-dipyrazolylmethane, which upon reaction with boranes, forms a pyrazabole polymer. Some  $R_2C(pz^x)_2$  have also been prepared from the reaction of potassium salts of the azole with methylene iodide. The use of strong bases often has allowed higher yields [6].

Elguero and co-workers improved the Trofimenko method some years later. They showed that  $N,N'$ -pyrazolylmethanes can be prepared by reaction of azoles with  $CH_2Cl_2$  under phase transfer catalysis (PTC) conditions [7]. Substituted bis(pyrazolyl)alkanes  $(H_2C)_n(pz^x)_2$  ( $x = H, NO_2, 4-Br, 4-NO_2, NH_2, 5-NH_2$ ) were prepared by reaction of the correspondingly substituted pyrazoles with  $CH_2Cl_2$  or by direct attack on the pyrazolyl rings [8].

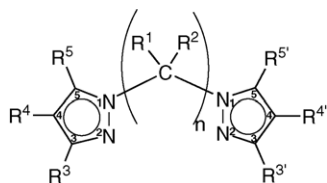


Fig. 1. General structure of bis(pyrazol-1-yl)alkane ligands.

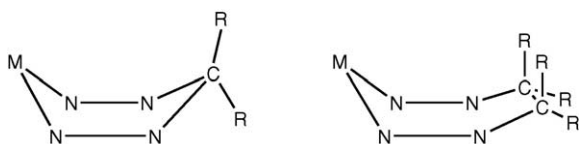


Fig. 2. Six and seven-membered rings formed by bis(pyrazolyl)alkanes after metal coordination.

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