

Optically Active Transition-metal Compounds.^{†,*} Stereochemistry and Crystal Structure Determination of $[(\eta^5\text{-C}_5\text{H}_5)\text{CoI-NC}_5\text{H}_4\text{-C(R)=N-CH(CH}_3\text{)(C}_6\text{H}_5\text{)}]^+\text{I}^-$, $\text{R} = \text{CH}_3$

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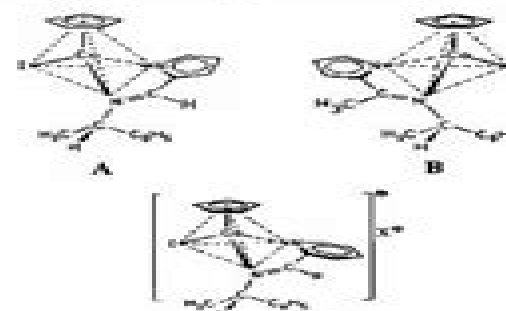
Abstract

The crystal structure and absolute configuration of the title compound has been determined by single-crystal X-ray diffraction. The crystals are orthorhombic with $a = 11.837(6)$, $b = 12.206(6)$ and $c = 14.523(7)$ Å, space group $P2_12_12_1$ and $d(\text{calc.}, Z = 4) = 1.91 \text{ gm cm}^{-3}$. The structure was refined to the final agreement factors of $R(F) = 0.061$ and $R_w(F) = 0.059$. The Co–I bond is 2.584(2) Å which is significantly shorter than that observed in related complexes where the metal is bonded to pyrrole instead of pyridine. The two Co–N bonds are quite different; the Co–N (imine) bond being longer (1.99(1) Å) than the Co–N (pyridine) one (1.91(1) Å). The configuration around the chiral carbon and the Co atom has been determined using the Bijvoet method. The conformation of the $\text{CH(CH}_3\text{)(C}_6\text{H}_5\text{)}$ substituent with respect to the plane of the chelate ring is in accord with the concept of minimal steric hindrance simultaneously allowing for phenyl/ C_5H_5 attraction.

Introduction

From the reaction of $(\text{C}_5\text{H}_5)\text{Co(CO)}\text{I}_2$ with the Schiff bases NN^* , derived from 2-pyridine-carbaldehyde, 2-acetylpyridine, 2-benzoylpyridine, 2-pyrrole-carbaldehyde, 2-acetylpyrrole, (–)-1-phenylethylamine, and (–)-3-aminomethylpiperane, a number of new complexes has been prepared and characterized [1]. The compounds derived from pyrrole Schiff bases NN^* are neutral molecules $\text{C}_5\text{H}_5\text{Co(NN}^*)\text{I}$ because the chelate ligands NN^* are incorporated

as anions, whereas the complexes derived from pyridine Schiff bases NN^* are salts $[\text{C}_5\text{H}_5\text{Co(NN}^*)\text{I}]^+\text{X}^-$ with $\text{X} = \text{I}^-$ or PF_6^- as counterions. Recently, we have determined the X-ray structures and absolute configurations of two neutral complexes **A** and **B** derived from the pyrrole Schiff bases differing only in the substituent at the imine carbon of the chelate ring (Scheme 1), and compared their conforma-



	I	II	III	IV	V	VI
R	H	H	CH ₃	CH ₃	C ₆ H ₅	C ₆ H ₅
X	I	PF ₆	I	PF ₆	I	PF ₆

Scheme 1.

tions with those found in solution [2]. We now report the crystal structure and absolute configuration of the ionic complex **III** obtained by the reaction between $\text{C}_5\text{H}_5\text{Co(CO)}\text{I}_2$ with the Schiff base, derived from 2-acetylpyridine and (S)(–)-1-phenylethylamine, having I^- as counterion. Compound **III** is one out of a set of six compounds differing

[†]Part 22 of Ivan Bernal's series. For part 22 see ref. 4.^{*}Simultaneously part 89 of Henri Brunner's series. For part 88 see ref. 4.^{**}Authors to whom correspondence should be addressed.

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**Ernest L. Eliel, Samuel H.
Wilen, Norman L. Allinger**



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Bodie E. Douglas, Yoshihiko Saito, 1980-01-01 **STEREOCHEMISTRY OF OPTICALLY ACTIVE TRANSITION METAL**

COMPOUNDS. B.E. DOUGLAS (ED.), *Topics in Stereochemistry* Ernest L. Eliel, Samuel H. Wilen, Norman L.

Allinger, 2009-09-17 This seminal series first edited by Ernest Eliel responsible for some of the major advances in stereochemistry and the winner of the ACS Priestley Medal in 1996 provides coverage of the major developments of the field of stereochemistry The scope of this series is broadly defined to encompass all fields of chemical and biological sciences that are founded on molecular and supramolecular interactions Insofar as chemical physical and biological properties are determined by molecular shape and structure the importance of stereochemistry is fundamental to and consequential for all natural sciences Topics in Stereochemistry serves as a multidisciplinary series that enriches all of chemistry Aimed at advanced students university professors and teachers as well as researchers in pharmaceutical agricultural biotechnological polymer materials and fine chemical industries Topics in Stereochemistry publishes definitive and scholarly reviews in stereochemistry and has long been recognized as the gold standard reference work in this field Covering the effect of chirality on all aspects of molecular interaction from the fundamental physical chemical properties of molecules and their molecular physics to the application of chirality in new areas such as its applications in materials science Topics in Stereochemistry explores a wide variety of properties both physical and chemical of isomers with a view to their applications in a number of disciplines from biochemistry to materials science **Molecular Optical Activity and the Chiral**

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Spectroscopy and Transition Metal Chemistry P. Gülich, R. Link, A. Trautwein, 2013-11-11 Two decades have passed since the original discovery of recoilless nuclear gamma resonance by Rudolf Mossbauer the spectroscopic method based on this resonance effect referred to as Mossbauer spectroscopy has developed into a powerful tool in solid state research The users are chemists physicists biologists geologists and scientists from other disciplines and the spectrum of problems amenable to this method has become extraordinarily broad In the present volume we have confined ourselves to applications of Mossbauer spectroscopy to the area of transition elements We hope that the book will be useful not only to non Mossbauer specialists with problem Oriented activities in the chemistry and physics of transition elements but also to those actively working in the field of Mossbauer spectroscopy on systems compounds as well as alloys of transition elements The first five

chapters are directed to introducing the reader who is not familiar with the technique to the principles of the recoilless nuclear resonance effect the hyperfine interactions between nuclei and electronic properties such as electric and magnetic fields some essential aspects about measurements and the evaluation of Mossbauer spectra Chapter 6 deals with the interpretation of Mossbauer parameters of iron compounds Here we have placed emphasis on the information about the electronic structure in correlation with quantum chemical methods because of its importance for chemical bonding and magnetic properties

Advances in Organometallic Chemistry, 2025-05-01 Advances in Organometallic Chemistry Volume 83 the latest release in this longstanding serial is known for its comprehensive coverage of topics in organometallic synthesis reactions mechanisms homogeneous catalysis and more Chapters in this new release include Pd catalysis a useful tool in the field of polymer synthesis Recent advances and applications Modern Mechanistic Approaches for the Depolymerization of Commodity Plastics via Homogeneous Metal Catalysis Functionalization of fullerenes by transition metal catalyzed cyclization reactions and Synergistic Metal Ligand Reactivity in Half Sandwich Complexes of Fe Co and Ni for Bond Activation and Catalysis Contains contributions from leading authorities in the field of organometallic chemistry Covers topics in organometallic synthesis reactions mechanisms homogeneous catalysis and more Informs and updates readers on the latest developments in the field Carefully edited to provide easy to read material

Physical Inorganic Chemistry Andreja Bakac, 2010-04-19 Physical Inorganic Chemistry contains the fundamentals of physical inorganic chemistry including information on reaction types and treatments of reaction mechanisms Additionally the text explores complex reactions and processes in terms of energy environment and health This valuable resource closely examines mechanisms an under discussed topic Divided into two sections researchers professors and students will find the wide range of topics including the most cutting edge topics in chemistry like the future of solar energy catalysis environmental issues climate changes atmosphere and human health essential to understanding chemistry

Topics in Stereochemistry, Volume 25 Scott E. Denmark, Jay A. Siegel, 2006-05-05 Diese Reihe zur Stereochemie wendet sich an fortgeschrittene Studenten und praktisch tätige Naturwissenschaftler in erster Linie organische Chemiker mit Interesse an Fragen der Physikochemie und Molek lphysik Themen sind vielf ltige Aspekte der Stereochemie der r umlichen Anordnung organischer und biologischer Molek le sowie die Auswirkungen der Orientierung auf die Eigenschaften der Verbindungen

Topics in Inorganic and Organometallic Stereochemistry Gregory L. Geoffroy, 2009-09-17 This volume is devoted entirely to inorganic and organometallic stereochemical subjects Discusses the systematic notations that have been developed to satisfy the needs for a rational and systematic stereochemical nomenclature Reviews the stereochemical aspects of the changes of bonding at carbon centers induced by metals either catalytically or stoichiometrically Also reviews the major achievements in current stereochemical research the synthesis of asymmetric compounds mediated by transition metals Discusses the structures of transition metal carbonyl clusters summarizing recent progress in this expanding area and providing a semiquantitative rationalization of the

structures for these clusters **Ligand Exchange Chromatography** Vadim A. Davankov, 2018-01-18 This book presents a systematic and comprehensive review of the information on chromatographic processes that involve the formation of coordination compounds aiming not only to demonstrate the achievements that have been made in the theory of praxis of chromatography but also to point out as far as possible the future of potential of ligand exchange chromatography Topics in Stereochemistry, Volume 20 Ernest L. Eliel, Samuel H. Wilen, Norman L. Allinger, 2009-09-17 This seminal series first edited by Ernest Eliel responsible for some of the major advances in stereochemistry and the winner of the ACS Priestley Medal in 1996 provides coverage of the major developments of the field of stereochemistry The scope of this series is broadly defined to encompass all fields of chemical and biological sciences that are founded on molecular and supramolecular interactions Insofar as chemical physical and biological properties are determined by molecular shape and structure the importance of stereochemistry is fundamental to and consequential for all natural sciences Topics in Stereochemistry serves as a multidisciplinary series that enriches all of chemistry Aimed at advanced students university professors and teachers as well as researchers in pharmaceutical agricultural biotechnological polymer materials and fine chemical industries Topics in Stereochemistry publishes definitive and scholarly reviews in stereochemistry and has long been recognized as the gold standard reference work in this field Covering the effect of chirality on all aspects of molecular interaction from the fundamental physical chemical properties of molecules and their molecular physics to the application of chirality in new areas such as its applications in materials science Topics in Stereochemistry explores a wide variety of properties both physical and chemical of isomers with a view to their applications in a number of disciplines from biochemistry to materials science *Handbook of Microbial Iron Chelates (1991)* Gunther Winkelmann, 2017-11-22 Handbook of Microbial Iron Chelates emphasizes the various microbial compounds and synthetic analogues functioning as siderophores in microbes and as potential drugs in human iron metabolism There are chapters describing the isolation chemical characterization synthesis and physicochemical properties of microbial iron chelates Other chapters deal with the physiology and genetics of transport and receptors involved in iron uptake Chemists biologists biochemists pharmacologists and medical doctors interested in the general aspects of iron metabolism siderophores receptors and iron complex formation should consider this book a rich information source *Chirality in Transition Metal Chemistry* Hani Amouri, Michel Gruselle, 2008-11-20 Chirality in Transition Metal Chemistry is an essential introduction to this increasingly important field for students and researchers in inorganic chemistry Emphasising applications and real world examples the book begins with an overview of chirality with a discussion of absolute configurations and system descriptors physical properties of enantiomers and principles of resolution and preparation of enantiomers The subsequent chapters deal with the the specifics of chirality as it applies to transition metals Some reviews of Chirality in Transition Metal Chemistry useful to students taking an advanced undergraduate course and particularly to postgraduates and academics undertaking research in the areas of chiral inorganic supramolecular

complexes and materials Chemistry World August 2009 the book offers an extremely exciting new addition to the study of inorganic chemistry and should be compulsory reading for students entering their final year of undergraduate studies or starting a Ph D in structural inorganic chemistry Applied Organometallic Chemistry Volume 23 Issue 5 May 2009 In conclusion the book gives a wonderful overview of the topic It is helpful for anyone entering the field through systematic and detailed introduction of basic information It was time to publish a new and topical text book covering the important aspect of coordination chemistry It builds bridges between Inorganic organic and supramolecular chemistry I can recommend the book to everybody who is interested in the chemistry of chiral coordination compounds Angew chem Volume 48 Issue 18 April 2009 About the Series Chirality in Transition Metal Chemistry is the latest addition to the Wiley Inorganic Chemistry Advanced Textbook series This series reflects the pivotal role of modern inorganic and physical chemistry in a whole range of emerging areas such as materials chemistry green chemistry and bioinorganic chemistry as well as providing a solid grounding in established areas such as solid state chemistry coordination chemistry main group chemistry and physical inorganic chemistry

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Materials-Chirality Mark M. Green, R. J. M. Nolte, E. W. Meijer, 2004-05-07 Dieser Sonderband der Reihe Topics in Stereochemistry besch ftigt sich mit der Chiralit t von Werkstoffen und der Bedeutung der Stereochemie f r bestimmte Polymere Fl ssigkristalle und andere spezielle Materialien Die Grundlage daf r bilden die ausf hrlich dargestellten Prinzipien der organischen Stereochemie Das aktuellste derzeit erh ltliche Buch zur Chiralit t

Chirality in Drug Design and Synthesis C. Brown, 2013-10-22 Chirality in Drug Design and Synthesis is a collection of papers that discusses the property of asymmetry in the structural and synthetic chemistry of natural products including the significance of chirality in medicinal

chemistry These papers examine the need for the preparation and study of pure enantiomers of chiral drug substances and their mechanism of interaction with enzymes and receptors These papers also investigate the techniques in studying these interactions as well as analyze the methods for their synthesis in enantiomerically pure form One paper discusses the pharmacological and pharmacokinetic analyses made that point to the differences in the activity and disposition of enantiometric pairs Another paper reviews the implications of the neglect of stereoselectivity at the different levels during the examination process of racemic drugs Since no general guidelines exists for the development of drugs with chiral centers one paper suggests a case by case approach in evaluating the safety and efficacy of drugs particularly as regards how isomers differ in their effects This collection is suitable for the pharmacologist medicinal chemists toxicologists mechanistic chemists and synthetic organic chemists

Fundamental Research in Homogeneous Catalysis M. Tsutsui, 2012-12-06 During the 70 s it has become drastically apparent that our natural resources including energy are not in unlimited supply This realization is strongly felt in the economic turmoil that is occurring but its effects will penetrate into other areas even causing moderate social changes Chemists play a major role in converting the world's natural resources into products The public consumes these products and now depends upon them to keep the high standard of living to which they have become accustomed This topic could easily be expounded into a whole article but it is sufficient to say that almost everything from the use of lightweight strong polymers which are replacing the use of metals in today's automobiles to the curing of diseases with asymmetrically synthesized drugs is related to the endeavors of chemistry Catalysts have played a major role in transforming resources to useful products Since a catalyst lowers the activation energy required for a particular reaction and often for only one specific pathway where normally many exist it is not surprising within the extant climate that researchers are now increasing their efforts and focusing their priorities on improving and discovering more efficient and selective catalysts

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