Additions and Corrections

Interligand Hypervalent Interaction in the Bis(silyl) Hydride Derivatives of Niobocene [*J. Am. Chem. Soc.* **1995**, *117*, 10133]. GEORGII I. NIKONOV,* LUDMILA G. KUZMINA, DMITRY A. LEMENOVSKII, AND VASILY V. KOTOV

We have found that the centrosymmetric space group *Pnma* is the more appropriate one for the crystal structure of $Cp_2Nb(SiClMe_2)_2H$ (**3**), affording better esd's. The crystal data are as follows: $C_{14}H_{23}Cl_2Si_2Nb$, orthorhombic, *Pnma*, $a = 16.584(3)$ Å, $b = 13.214(3)$ Å, $c = 8.419(2)$ Å, $V = 1844.9(6)$ Å^3, $Z = 4$, $\mu = 10.6$ cm^{-1}, $D_{calc} = 1.481$ g/cm^3, $\Delta\rho_{max} = 1.03$, $\Delta\rho_{min} = -2.04$ e/Å^3, 2221 unique reflections, 2214 used, $R_1 = 0.035$, $wR_2 = 0.1027$, GOF = 1.24. A similar, independent, discovery has been made by Dr. J. W. Kampf of the University of Michigan.

In *Pnma*, the two silicon centers are related by mirror symmetry. Thus the explanation of asymmetry is not required. However, the anomalously long Si−Cl [2.1633(13) Å] and short Nb−Si [2.5974(10) Å] bond lengths, together with an uncommonly small Si−Nb−Si′ bond angle of 104.27(5)° and two short H−Si contacts of 2.056 Å, agree with the proposed interligand hypervalent interaction in **3**.

Supporting Information Availabile: Corrected Tables 1−4 of the supporting information giving atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **3** (5 pages). See any current masthead page for ordering and Internet access instructions.

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Book Reviews

Ferrocenes−Homogeneous Catalysis−Organic Synthesis−Materials Science. Edited by A. Togni (ETH, Switzerland) and T. Hayashi (Kyoto University, Japan). VCH: New York. 1994. xix + 540 pp. $145.00. ISBN 3-527-29048-6.

This book is "intended to provide an overview of the main areas of research where ferrocene plays a key role, because of both its chemical and physical properties". It consists of 10 chapters, each prepared by experts currently active in the area. These chapters are loosely grouped under the headings: "Homogeneous Catalysis" (1−3), "Organic Synthesis−Selected Aspects" (4−7), and "Materials Science" (8−10).

Chapter 1, 1,1′-Bis(diphenylphosphino)ferrocene−Coordination Chemistry, Organic Synthesis, and Catalysis, by K.-S. Gan and T. S. A. Hor, includes introductory sections on the preparation of "dppf"-ligated complexes of group 5−14 metals, their structural properties and modes of coordination, their Mossbauer, ^{31}P-NMR, and ^{1}H-NMR spectra, and their fluxionality. Most of the chapter is devoted to catalysis by dppf-ligated metals of various couplings and cross-couplings, alkylations, arylations, carboxylations and carboxylative coupling reactions, and nucleophilic substitutions. Briefer sections follow on condensations and polymerizations, hydroformylations, hydrogenations, reductions, hydroborations, hydrosilylations, and some isomerizations. The sections on coupling reactions are particularly well written and referenced with many data tables. This is an ideal first chapter for a book such as this because the introductory sections in particular and the synthetic methods and catalytic mechanisms which follow set the stage for discussions of related topics in the later chapters.

Chapter 2, Asymmetric Catalysis with Chiral Ferrocenylphosphine Ligands, by T. Hayashi, describes the design, synthesis, testing, and utilization of carbon-central and ferrocene-planar chiral 1,2- and 1,2,1′-ferrocenylphosphine and -diphosphine ligands with group 9−11 transition metals as stereoselective catalysts for cross-coupling of organometallics with halides, for allylic substitutions via π-allyl complexes, and for the hydrogenation and the hydrosilylation of olefins and ketones. Many examples with the observed e/e's are cited. The section detailing the authors' own investigations of chiral 2-(α-aminoethyl)-1,1′-bis(diphenylphosphino)ferrocenyl-ligated gold complexes as catalysts for highly stereoselective aldol condensations with α-isocyanocarboxylates is particularly elegant.

Chapter 3, Enantioselective Addition of Dialkylzinc to Aldehydes Catalyzed by Chiral Ferrocenyl Aminoalcohols, by Y. Butsugan, S. Araki, and M. Watanabe, recounts attempts by the authors to design effective chiral-ferrocene-containing catalysts for enantioselective addition of zinc alkyls to aldehydes. It is more restricted in scope and less selective in coverage than the two preceding chapters but includes more experimental detail. A final section on the enantio- and diastereoselective addition of diethylzinc to racemic α-thio- and α-selenoaldehydes is of particular interest.

Chapter 4, Chiral Ferrocene Derivatives. An Introduction, by G. Wagner and R. Herrmann, begins with brief discussions of "central" and "planar" chirality in metallocenes, and the structure, stability, and stereochemistry of α-ferrocenylalkyl carbocations then follows with extensive and detailed accounts of the synthetic approaches to all types of both central-chiral and planar-chiral ferrocenes. This chapter concludes with a few well-chosen examples of the use of ferrocene derivatives as chiral starting materials in the synthesis of prostaglandin analogues, as chiral auxiliaries in four component condensations to synthesize (*S,S,S,S*)-tetravaline or to form a (*S,R*)-glutathione derivative, and as fugitive chiral auxiliaries in the synthesis of (+)-corynoline and in C−C coupling, hydrogenation, hydrosilylation, allylations, and aldol-type reactions. This is an excellent chapter with many well-chosen examples and leading references. Anyone contemplating the synthesis of a chiral ferrocene catalyst might do well to begin here.

Chapter 5, Ferrocene Compounds Containing Heteroelements (external to the Cp rings), by M. Herberhold, covers the synthesis and chemistry of a wide variety of ferrocenyl derivatives which fall in this category. Several tables of data are included and many references, few of them recent, are cited.

Chapter 6, Macrocycles and Cryptands Containing the Ferrocene Unit, by C. D. Hall, focuses "on macrocycles and cryptands that contain... a redox-active... ferrocene unit... [which] by suitable variation of the size and structure of the host cavity... can bind cationic, anion or... guest species by means of electrostatic interactions". Such supramolecular complexes have potential application in electronics, as chemical catalysts, or as mimics for metalloenzymes. For the most part the complexes are ferrocenophanes, cryptands containing a ferrocene unit, or macrocyclic cryptand and cavitand derivatives of ferrocene. The chapter is replete with examples and some tables of metal-ion binding by these complexes as evinced by X-ray crystallography, partition coefficients, cyclic voltammetry, and/or IR, UV, and NMR measurements. Most of the studies cited are relatively recent; indeed, the entire area is relatively new in so far as ferrocenes are concerned.

Chapter 7, Electrochemical and X-ray Structural Aspects of Transition Metal Complexes Containing Redox-Active Ferrocene Ligands, by P. Zanello, was written on the premise that "the metallocene centers [of ferrocene-containing heterometallic complexes might] offer the unique opportunity to evaluate the stereodynamic effects accompanying redox changes, not only... of bonding angles and distances, but through two geometrical parameters peculiar to their assembly of cyclopentadienyl rings:" (i) rotation between the eclipsed and staggered conformation and (ii) their tilting from parallel. "Both of these motions tend to relieve molecular steric strain induced by electronic perturbation." Unfortunately, although this long (115 pages), nicely written, up-to-date (241 references, more than 40% since 1990) chapter overflows with X-ray structures and cyclic voltammagrams, the original expectation could not be realized for, in the words of the author, "... in spite of the fact that electrochemistry allows access to redox congeners of many heterometallic complexes that could be isolated, we were unable to find examples of solid-state structures of redox congeners". Any investigator looking for leading references to the redox chemistry of substituted ferrocene complexes would do well to start by consulting this chapter.

Chapter 8, Ferrocene-Containing Charge-Transfer Complexes. Conducting and Magnetic Materials, by A. Togni, begins with a brief discussion of the nature of charge-transfer complexes in general and of the chemical and structural characteristics expected to confer insulating, semiconducting, or metallic character as well as ferromagnetic or antiferromagnetic properties to organic solids. A concise, but in-depth, summary of X-ray structures and electrical and magnetic properties of a number of crystalline charge-transfer complexes involving ferrocenes and substituted ferrocenes, particularly decamethylferrocene, follows. The studies cited are generally quite recent, more than one-third published since 1991. The author concludes that, in spite of the fact that optimal matching of donors and acceptors can lead some 1D CT complexes to display 3D bulk ferromagnetic properties, "rational design of organic/organometallic ferromagnetic materials with given structure and given physical properties still remains an essentially unattained goal".

Chapter 9, Ferrocene-Containing Thermotropic Liquid Crystals, by R. Deschenaux and J. W. Goodby, is rather like the preceding chapter in the sense that both exemplify the sort of educated trial-and-error approach required by any relatively new area of experimental science—in this case, specifically, the search for novel new ferrocene-containing liquid crystals. In spite of a brief introductory discussion of thermotropic liquid crystals as pertains to ferrocene containing structures in general, this chapter, like the preceding one, is not for the uninitiated. More than one-half of the references in this fairly short chapter cite work published since 1990, much of it by Deschenaux *et al.*

Chapter 10, Synthesis and Characterization of Ferrocene-Containing Polymers, by K. E. Gonsalves and X. Chen, discusses addition and condensation polymers of vinyl ferrocene and some ring-opening polymerizations of ferroceneophanes, 1,1′-ferrocenylphosphazenes, and 5-ferrocenylnorbornenes. It concludes with a brief discussion of methods used to attach a ferrocenyl group to preformed organic polymers and an interesting section on the use of electropolymerization to modify electrode surfaces.

What's to be said about this nicely produced volume as a whole? The editors state that the work is not intended to be comprehensive but rather to provide a recent single volume source delineating current trends in ferrocene chemistry and its applications. It certainly does this, but, as it is written by many specialists, the coverage is necessarily uneven and at times quite specialized. It does contain, however, a lot of recent data, many pertinent examples, and a large number of leading references.

Few chemists these days would claim to "specialize" in ferrocenes *per se*; who then might consult this book? While it is still fairly current, those seeking a quick reference to the literature in a particular area might do so although its utility in this sense is restricted somewhat by the lack of an author index. Those contemplating a new research field potentially involving ferrocenes might helpfully consult it for a quick background in, or overview of, one or more of the areas covered therein. However, those with but a cursory knowledge of magnetic materials, liquid crystals, or polymers are probably not going to get much out of the final three chapters unless they are prepared also to consult other literature for definitions, notational conventions, and further introductory background material.

Much of the work detailed in this book concerns attempts to develop precise ferrocene-containing structures/materials tailored for use as stereoselective catalysts, liquid crystals, semiconductors, bulk ferromagnets, and polymers. Given this emphasis on *function* as a consequence of *structure*, it is surprising to this reviewer, that no mention is made of molecular modeling. This technique is now routinely used in many areas of chemical, pharmaceutical, and biochemical research. Might it not also be helpful in some of the specialties covered here?

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