

to that for simple thiolate ligands.¹⁸ The novel Pt-S-S-CH(CH₃)₂ grouping features a sulfur-sulfur distance of 2.037 (4) Å and a torsion angle of 89.5°. In the tungsten complex^{19,20} the W-S-S-C₆H₄CH₃ fragment has a sulfur-sulfur distance of 2.053 (4) Å and a torsion angle of 63.1°. The sulfur-sulfur bond distances in these two complexes are in the range found for most organic and inorganic disulfides.²¹ However, while the PtSSC torsion angle is close to that found for open-chain organic disulfides (85 ± 20°)²² the WSSC angle is much smaller²³ and outside this range.

(17) Crystal Data: C₁₅H₁₂O₃S₂W, *M_r* = 1904.53, red, brick-shaped, monoclinic, space group *P*2₁/*c*, *Z* = 4, *D*_{calcd} = 2.032 g cm⁻³, *a* = 10.640 (3) Å, *b* = 11.400 (3) Å, *c* = 12.872 (3) Å, β = 94.58 (2)°, *U* = 1556.3 Å³. The structure was solved by using 1672 reflections with *I* > 3σ(*I*) collected in the range 3.5° < 2θ < 45.0°. The final residuals are *R_F* = 4.0% and *R_{wF}* = 5.5%.

(18) Bird, P. H.; Lai, R. D.; Shaver, A.; Siriwardane, U. *Can. J. Chem.* 1982, 60, 2075-2081.

(19) The W-S1 distance is 2.506 (2) Å. The Cp ring is tilted slightly: C12 is farthest from W (2.397 (9) Å), while C14 and C15 are nearest (2.304 (9) and 2.313 (9) Å, respectively). Similar tilting has been observed for the complexes CpM(CO)₃Cl, M = Mo and W: Bueno, C.; Churchill, M. R. *Inorg. Chem.* 1981, 20, 2197-2202 and is predicted on the basis of molecular orbital calculations.²⁰

(20) The conformation of the S1-S2 bond with respect to the CpW(CO)₃ fragment is as predicted: Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* 1982, 1, 180-188.

(21) (a) Sutton, L. E. "Tables of Interatomic Distances and Configurations in Molecules and Ions"; The Chemical Society: Burlington House, London, 1958; *Spec. Publ.—Chem. Soc. No. 11*; 1965; *Spec. Publ.—Chem. Soc. No. 18*; Suppl. (1956-1959). (b) Laur, P. H. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 3.

(22) (a) Van Wart, H. E.; Scheraga, H. A. *Proc. Natl. Acad. Sci. U.S.A.* 1977, 74, 13-17 and references therein. (b) Guttenberger, H. G.; Bestmann, H. J.; Dickert, F. L.; Jorgensen, F. S.; Snyder, J. P. *J. Am. Chem. Soc.* 1981, 103, 159-168 and references therein.

(23) No significant intermolecular contacts were observed.

These compounds are among the first linear representatives of a potentially large new class of complexes containing catenated-sulfur ligands. The preparative routes reported here are suitable for general application.

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Registry No. CpW(CO)₃SH, 51187-51-0; NphtSCH₂C₆H₅, 14204-26-3; NphtS-*p*-C₆H₄CH₃, 15199-26-5; NphtSSCH₂C₆H₅, 33704-38-0; NphtSS-*p*-C₆H₄CH₃, 33704-37-9; NphtS(=O)-CH₂C₆H₅, 40167-14-4; NphtS(=O)-*p*-C₆H₄CH₃, 42300-58-3; CpW(CO)₃SCH₂C₆H₅, 85882-86-6; CpW(CO)₃S-*p*-C₆H₄CH₃, 58057-63-9; CpW(CO)₃SSCH₂C₆H₅, 85882-87-7; CpW(CO)₃SS-*p*-C₆H₄CH₃, 85882-88-8; CpW(CO)₃S(=O)CH₂C₆H₅, 85893-30-7; CpW(CO)₃S(=O)-*p*-C₆H₄CH₃, 85893-31-8; NphtSNpht, 7764-29-6; CH₃CH₂CH₂SNpht, 17796-71-3; (CH₃)₂CHSNpht, 17796-72-4; NphtS₂Npht, 7764-30-9; CH₃CH₂CH₂S₂Npht, 30912-77-7; (CH₃)₂CHS₂Npht, 33704-40-4; *cis*-(PPh₃)₂Pt(Npht)-(SCH₂CH₂CH₃), 85882-89-9; *cis*-(PPh₃)₂Pt(Npht)(S₂CH₂CH₂CH₃), 85882-90-2; *cis*-(PPh₃)₂Pt(Npht)(SCH(CH₃)₂), 85882-91-3; *cis*-(PPh₃)₂Pt(Npht)(S₂CH(CH₃)₂), 85882-92-4; *cis*-(PPh₃)₂Pt(Npht)(SCH₂C₆H₅), 85882-93-5; *cis*-(PPh₃)₂Pt(Npht)(S₂CH₂C₆H₅), 85882-94-6; *cis*-(PPh₃)₂Pt(Npht)(S-*p*-C₆H₄CH₃), 85882-95-7; *cis*-(PPh₃)₂Pt(Npht)(S₂-*p*-C₆H₄CH₃), 85882-96-8; *cis*-(PPh₃)₂Pt(Npht)(SNpht), 85882-97-9; *cis*-(PPh₃)₂Pt(Npht)(S₂Npht), 85882-98-0; (PPh₃)₂PtC₂H₄, 85882-99-1; PPh₃, 603-35-0.

Supplementary Material Available: Positional and thermal parameters, bond distances and bond angles with their estimated standard deviations, and listings of structure factor amplitudes for the complexes *cis*-(PPh₃)₂Pt(Npht)SSCH(CH₃)₂ and CpW(CO)₃SS-*p*-C₆H₄CH₃ (29 pages). Ordering information is given on any current masthead page.

Book Reviews

Multiple Bonds Between Metal Atoms. By F. A. Cotton and R. A. Walton. Wiley-Interscience, New York. 1982. xiv + 466 pages. \$47.50.

This book, with a foreword by R. Hoffmann, is the first to be published dealing only with compounds containing multiple bonds between metal atoms and is written by two accomplished practitioners in the field. The authors have covered the literature through 1980, and some of the early literature of 1981 is also included. Spot checks against this reviewer's files indicate that the coverage is exceptionally complete.

The book covers all aspects of the chemistry of compounds with metal-metal multiple bonds as indicated by the chapter headings: Chapter 1, Introduction and Survey (35 pp); Chapter 2, Quadruple Bonds Between Rhenium and Technetium (48 pp); Chapter 3, Quadruple Bonds between Molybdenum and Tungsten (66 pp); Chapter 4, Quadruple Bonds between Chromium Atoms (33 pp); Chapter 5, Triple Bonds between Metal Atoms (82 pp); Chapter 6, Double Bonds between Metal Atoms (46 pp); Chapter 7, Dirhodium and Isoelectronic Compounds (28 pp); Chapter 8, Physical, Spectroscopic, and Theoretical Results (114 pp). Within each of the chapters, 2-7, the synthesis, structures, and reactivity of the various compounds are presented and discussed. Where possible, reactivity-structure correlations are made and tied in with the theoretical results.

The organization of the material is built primarily around structural classes, which is understandable given the importance (indeed, necessity) of structural results to the field and the paucity of *systematic* reactivity studies. The text is clearly written, although in places the sheer rapidity with which the reader is bombarded with information makes casual reading difficult. Much of the first chapter is an interesting history of "How It All Began" and a polemic on "non-Wernerian" chemistry.

The book is remarkably free of error (only two minor ones were noted). Material is readily accessible via the adequate index or the detailed Table of Contents. This book is highly recommended to anyone who would like to see what the field of metal-metal multiple bonds entails, to teachers and students of inorganic chemistry, and to researchers in the field. For the latter, a perspicacious reading will reveal many areas of potentially rewarding research.

M. David Curtis, *The University of Michigan*

Chemically Modified Surfaces in Catalysis and Electroanalysis. Edited by J. S. Miller. ACS Symposium Series No. 192. American Chemical Society, Washington, D.C. 1982. ix + 301 pp. \$36.95.

This volume contains 17 articles containing material that was presented at the American Chemical Society Meeting in New York

in August, 1981. Aspects of catalysis at or near conducting or semiconducting electrode surfaces receive essentially as much attention as do nonelectrochemical catalytic processes. The electrochemical subjects addressed include the properties and behavior of conducting polymeric films on electrodes, digital simulation of cyclic voltammograms for second-order catalytic reactions, attachment of electroactive derivatives to semiconducting photoelectrodes, attachment of various ruthenium polypyridine complexes to electrode surfaces, electropolymerization techniques for depositing metallopolymers, and electrochromic applications of chemically modified electrodes. The nonelectrochemical articles span the range from several examples of catalysts attached to polymeric supports, chemically derivatized solids based on layered phosphonates, catalysts derived from intercalation in layered silicates, deposited metal clusters in Fischer-Tropsch synthesis, the behavior of organometallic catalysts deposited on refractory supports, and a new class of immobilized phase-transfer catalysts.

A fair fraction of the most active groups in the rapidly expanding field of chemically modified electrodes and surfaces are represented by contributions to this volume. The articles vary considerably in length and apparent objective. A few occupy 25–35 pages and present reasonably comprehensive discussions at some depth. Others are as brief as 8–10 pages and come closer to previews or extended abstracts than full-fledged articles. Overall, the volume provides a good account of representative activity in a field that has attracted considerable recent attention. It can be recommended to those seeking a perspective in the field.

Fred C. Anson, *California Institute of Technology*

Gmelin Handbook of Inorganic Chemistry. 8th Edition. Rh—Rhodium. Supplement Volume B1. Compounds of Rhodium. W. P. Griffith, H. Jehn, J. A. McCleverty, C. J. Raub, and S. D. Robinson, volume authors. W. P. Griffith and K. Swars, volume editors. Gmelin Institut für Anorganische Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften and Springer-Verlag, Berlin/Heidelberg/New York. 1982. x + 221 pages. DM 720, \$300.30.

Considering the current high interest in various aspects of rhodium chemistry, it is welcome news that the Gmelin Institute is now updating its coverage of this element (the previous coverage is only through 1938). Although the progress in the area will undoubtedly leave the remaining volumes in the series somewhat dated, their completion will certainly fill a large gap in literature coverage and their appearance will be welcome. The arrangement of material follows the standard Gmelin system and the present volume is concerned primarily with binary and ternary species although some classical coordination compounds are also included. Evidently the majority of coordination complexes including those with phosphines, arsines, and stibines will be covered in Supplement Volume B2.

Beginning with a short section on the rhodium-hydrogen system, Volume B1 continues with 15 more sections covering binary compounds and complexes with oxygen, nitrogen, the halogens, the chalcogens, boron, carbon, silicon, and phosphorus, and arsenic, antimony, and bismuth. Within each section is listed first binary systems of rhodium with the element in question followed by listings of stoichiometric compounds and/or complexes. Thus for example with oxygen coverage begins with binary oxides, including nonstoichiometric phases, and continues with a large array of rhodates of various metals. The section closes with listings of hydroxides and hydroxo and aquo complexes. The coverage is through 1981 with some more recent references and the authors and publishers are to be commended for the despatch with which the volume has been produced.

The authors generally do a good job of indicating when there is doubt as to the proper formulation of species listed and have included considerable cross-references. There does seem to be some inconsistency in coverage in that a number of groups of coordination complexes are included but other closely related ones are not. Thus, for example, nitrate complexes are included but nitro complexes are to be left for a later volume. Also sulfoxide, sulfite, and sulfate complexes appear, but complexes of other sulfur-containing ligands do not. This is probably not a serious fault, but it is likely to cause some confusion for the person using the series for the first time.

All told, this volume does a good job of pulling together a lot of information from a wide variety of sources, listing it with a critical evaluation of its reliability and thereby indicating where the area could benefit from further investigation. It is rather dry reading but that is not unusual for an encyclopedic work. The number of errors found by this reviewer was very small and in their context should be readily recognized as such. Finally while the fact that it is published in English will undoubtedly increase its utility, the price (\$300!!!) will almost certainly restrict its appearance to libraries.

Joel T. Mague, *Tulane University*

Topics in Current Chemistry. Vol. 105. Organic Chemistry. F. Boschke, Managing Editor. Springer-Verlag, Berlin/Heidelberg/New York. 1982. 158 pp. \$38.00.

This book contains three chapters: (i) "Prostereoisomerism (Prochirality)" (E. L. Eliel), (ii) "Asymmetric Hydroformylation" (G. Consiglio, P. Pino), and "The Group 5 Heterobenzenes—Arsabenzene, Stibabenzene, and Bismabenzene" (A. J. Ashe, III).

The first chapter on prostereoisomerism is an excellent contribution to the current review literature on stereochemistry (76 pages, 178 references). Beginning with the terminology of prochirality and historical significance, this chapter describes "Homotopic and Heterotopic Ligands and Faces" (17 pages), "Prochirality and Nuclear Magnetic Resonance" (21 pages), "Prostereoisomerism in Enzyme-Catalyzed Reactions" (35 pages), and "Prochirality and Two-Dimensional Chirality" (2 pages). Each section is comprehensive and very useful for the chemists who are engaged in studies on asymmetric organic and biological reactions. Among these sections which are all of high quality the section dealing with "Prostereoisomerism in Enzyme-Catalyzed Reactions" is the highlight of the chapter, in that it covers many well chosen enzymatic asymmetric reactions. This section will give many good suggestions not only to bioorganic chemists but also to organic and organometallic chemists.

The second chapter is a complete review of asymmetric hydroformylation, which compiles literature up to early 1981 (46 pages, 87 references). Although the latest reports of high optical yields by Pittman's and Knowles's groups were not included, this chapter describes and discusses all aspects of asymmetric hydroformylation catalyzed by chiral transition-metal complexes. The chapter includes sections describing (i) formation of optically active aldehydes, (ii) regularities observed in asymmetric hydroformylation, (iii) a model for the diastereomeric transition states controlling asymmetric induction, and (iv) the possible significance of the observed regularities. From the mechanistic discussions mentioned here readers will be able to obtain the requisite information about the controlling factors which should be taken into account in catalytic asymmetric reactions.

The last chapter is a high quality comprehensive review of a unique class of aromatics, the group 5 heterobenzenes (31 pages, 120 references). This chapter compiles work of the author, Märkl, and Bickelhaupt on arsabenzene, stibabenzene, and bismabenzene and describes the synthesis and spectral, physical, and chemical properties of these interesting compounds. In the chemical property section, Diels-Alder reactions, basicity, transition-metal complexation, electrophilic aromatic substitution, free radical rearrangements, reactions with alkyl lithium reagents, and miscellaneous functional group chemistry are reviewed.

Although this book does not necessarily consist of topics in the same field, it is obvious that each chapter is of great value to the organic, bioorganic, or organometallic chemists who are interested in that particular field.

Iwao Ojima, *Sagami Chemical Research Center*

Topics in Current Chemistry. Vol. 106. Synthesis and Structural Problems. F. L. Boschke, managing editor, Springer-Verlag, Berlin/Heidelberg/New York. 1982. 178 pages. \$39.00.

We have here another volume of Springer-Verlag's hard cover review journal. It is brought to our readers' attention because two of the four reviews which it contains deal with organometallic topics.

In his chapter entitled "Organotitanium Reagents in Organic Synthesis. A Simple Means to Adjust Reactivity and Selectivity