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INORGANIC SYNTHESES

Volume 36

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PREFACE

This volume of *Inorganic Syntheses* spans the preparations of a wide range of important inorganic, organometallic, and solid-state compounds. Continuing a long-standing tradition, we have emphasized useful compounds and methods. Reflecting our own personal research interests, transition metal halides, complexes with cyclopentadienyl and substituted cyclopentadienyl ligands, and compounds with metal–metal bonds are featured. We have also included a chapter on pedagogically important compounds that we hope will find their way into undergraduate inorganic chemistry teaching laboratories.

The volume is divided into six chapters. Chapter 1 contains the syntheses of some key early transition metal halide clusters and the very useful mononuclear molybdenum(III) synthon, $MoCl_3(THF)_3$. This set of procedures was submitted by Lou Messerle and Rinaldo Poli. Chapter 2 covers the synthesis of a number of cyclopentadienyl compounds, including a novel route to sodium and potassium cyclopentadienide, MC_5H_5. Special thanks are due to John Bercaw, Endy Min, and Ged Parkin for the syntheses of the bis(pentamethylcyclopentadienyl) compounds of groups 3, 4, 5, and 6. Chapter 3 details synthetic procedures for a range of metal–metal bonded compounds, including several with metal–metal multiple bonds. Special thanks here are due to Al Cotton, Carlos Murillo, and Dick Walton. Chapter 4 contains procedures for a range of early and late transition metal compounds, each a useful synthon for further synthetic elaboration. Chapter 5 deals with the synthesis of a number of main group compounds and ligands, while Chapter 6 covers teaching laboratory experiments. The editors are grateful to Marcetta Darensbourg for suggesting the teaching chapter.

We would like to thank everyone who submitted syntheses for Volume 36 and the checkers who dedicated considerable time and effort in checking the procedures. We acknowledge the long delay in getting this volume published and thank the contributors and checkers for their patience. To those contributors who will not see their syntheses in this volume, we apologize for not being able to find an individual willing or able to check their syntheses. We wish to extend special thanks to Vera Mainz for her expert help in the preparation of the cumulative indices that appear at the end of this volume. We undertook this large project in the hope that readers will find this material to be useful aids to locating recipes that have appeared since the last cumulative index, which summarized content up through volume 30 of *Inorganic Syntheses*.

Finally, we would like to thank our friend and colleague Tom Rauchfuss for his tireless encouragement and advice, and our mentors Dick Andersen and Geoff Wilkinson (for GSG) and Ward Schaap and John Fackler (for APS) who taught us both the joys and challenges of synthetic inorganic chemistry.

ALFRED P. SATTELBERGER
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DEDICATION

This volume is dedicated to the memory of eight eminent chemists who made outstanding contributions to inorganic chemistry in general and to *Inorganic Syntheses* in particular. We also note the recent passing of two other inorganic chemists, Bill Lipscomb and Gordon Stone, who were not former volume editors but whose contributions to inorganic chemistry were significant. Each was a talented synthetic chemist in his own right, and all helped shape the discipline we know and love.

GEORGE THERALD MOELLER (EDITOR-IN-CHIEF, VOLUME V, 1957)

Therald Moeller was born in North Bend, Oregon, on April 3, 1913, and died in Broken Arrow, Oklahoma, on November 24, 1997, at the age of 84. In 1934, he graduated from Oregon State College (now Oregon State University) in Corvallis as the top student of his senior class, having majored in chemical engineering. In 1938, he received his Ph.D. degree in inorganic and physical chemistry from the University of Wisconsin, Madison, for a thesis titled “A Study of the Preparation and Certain Properties of Hydrous Lanthanum Oxide Sols,” carried out under the direction of Francis C. Krauskopf. Therald was Instructor in Chemistry at Michigan State College (now Michigan State University) at East Lansing (1938–1940), but in 1940 he moved to the University of Illinois, Urbana-Champaign. In 1969, Therald became Chair of the Department of Chemistry at Arizona State University in Tempe, serving in this capacity until 1975. He retired as Professor Emeritus in 1983.

Therald became an internationally recognized authority on the chemistry of the rare earth elements (lanthanides) and published 94 research papers and books in this area alone. During his 45 years of teaching and research, he guided the laboratory research of 43 Ph.D. students, 20 postdoctoral fellows, and 11 M.S. and 25 B.S. students for a total of 99 research students in inorganic chemistry. Of these, at least 39 became professors themselves at universities in the United States, Taiwan, Spain, India, Japan, Brazil, England, and Finland. Several became Department Chairs and one a College President.

Therald’s 281 publications include 22 books and laboratory manuals authored or edited by him (32 books if Spanish, Russian, Japanese, Italian, and Polish editions are counted). One of these texts, *Inorganic Chemistry, An Advanced Text* (Wiley, 1952), was the “bible” of inorganic chemistry for decades, enjoying widespread adoption (I used it in my first inorganic chemistry class in 1956). Until its appearance, few U.S. universities taught inorganic courses more advanced than the freshman level because only foreign texts were available, and none of these were satisfactory. As soon as Therald's text appeared, universities began to teach advanced inorganic chemistry, which immensely influenced its development in the United States and around the world. Along with John C. Bailar Jr. (Editor-in-Chief, Volume IV, 1953), Therald cofounded the ACS Division of Inorganic Chemistry (1956), serving as its Chair in 1961–1962. He also served for many years as a member of the Board of Directors of *Inorganic Syntheses*, Inc.

EUGENE GEORGE ROCHOW (EDITOR-IN-CHIEF, VOLUME VI, 1960)

Gene Rochow was born in Newark, New Jersey, on October 4, 1909, and died in Fort Myers, Florida, on March 21, 2002, at the age of 92. He spent his childhood in Maplewood, New Jersey, where he displayed an interest in electricity and the early use of silicon as a crystal detector in radio sets. Gene followed his brother Theodore as a chemistry assistant both in high school and at Cornell University, Ithaca, New York. He was a lecture and laboratory assistant to Louis M. Dennis, Chairman of the Chemistry Department at Cornell, under whom he received his B.S. (1931) and Ph.D. degrees (1935), the latter for a thesis titled "Contributions to the Chemistry of Fluorine." Gene also worked as a special assistant to Alfred Stock, who spent several months in 1932 at Cornell as Baker Lecturer. From Stock he first learned about the chemistry of silicon hydrides, and in fact was responsible for drawing the diagrams for Stock's famous book, *The Hydrides of Boron and Silicon*, which was written during that time.

After a summer job as Research Chemist at the Halowax Corporation, New York City (1931–1932), and as a Lecture Assistant at Cornell (1932–1935), Gene found summer employment with the Hotpoint Company, a General Electric Company subsidiary. He later became a Research Associate at the General Electric Research Laboratory, Schenectady, New York (1935–1948). His most notable discovery there was a process to produce methylchlorosilanes, the precursors to silicones, from methyl chloride and a silicon/copper alloy, a process still used on a large scale today. He continued his research on silicone production until his transfer to Richland, Washington, where he conducted research on nuclear fission as a source of domestic energy. When the U.S. Government requested that GE work on nuclear propulsion for naval vessels, Gene, a Quaker, left in 1948 to teach chemistry at Harvard University, where he remained until retiring in 1970. His 1949 Baekeland address called for conservation, recycling, and the use of less wasteful alternatives long before these became fashionable. In the early 1950s, he became the first to apply broad-line NMR to the study of dynamic motion in silicone polymers. His interest in the differences in the chemistry of the group

14 elements led to work that culminated in the Allred–Rochow electronegativity scale, which can be found in many current textbooks.

Gene was the author or coauthor of several influential books, including *Chemistry of the Silicones* (1946, 1951), *General Chemistry—A Topical Introduction* (1954), *The Chemistry of Organometallic Compounds* (1956), *Unnatural Products* (1960), *Organometallic Chemistry* (1964), *Metalloids* (1966), *Chemistry—Molecules That Matter* (1974), and *Modern Descriptive Chemistry* (1977). The holder of numerous U.S. and foreign patents on chemical processes and organometallic substances, Gene received many awards, including the Baekeland Medal, American Chemical Society (1949); the Meyer Award, American Ceramic Society (1951); the Perkin Medal, Society of Chemical Industry (London, 1962); election to the American Academy of Arts and Sciences (1962); the Honor Scroll, American Institute of Chemists (1964); the Frederick Stanley Kipping Award, American Chemical Society (1965); the Chemical Pioneers Award, American Institute of Chemistry (1968); the Award for Excellence in Teaching, Manufacturing Chemists Association (1970); the James Flack Norris Award for the Teaching of Chemistry, American Chemical Society (1973); and the Alfred Stock Medal, German Chemical Society (1983).

JACOB KLEINBERG (EDITOR-IN-CHIEF, VOLUME VII, 1963)

Jake Kleinberg was born on February 14, 1914, in Passaic, New Jersey, and died on January 12, 2004, in Lawrence, Kansas, at the age of 89. He lost his father at the age of 3 and put himself through college by working part-time. Although initially enrolled at the City College of New York, he transferred to Randolph-Macon College, Ashland, Virginia, from which he received his B.S. degree in 1934. He earned his M.S. (1937) and Ph.D. degrees (1939) from the University of Illinois, Urbana-Champaign, under Ludwig F. Audrieth (Editor-in-Chief, Volume III, 1950), one of the founders and most prolific contributors to *Inorganic Syntheses* and a member of its Board of Editors (1934–1967). His thesis involved the ammonolysis of esters and the use of sulfamic acid in the separation of the rare earths. Jake was Assistant Professor at James Millikin University, Decatur, Illinois (1940–1943), and the College of Pharmacy at the University of Illinois, Chicago (1943–1946). In 1946, he joined the chemistry faculty of the University of Kansas, becoming Professor in 1951 and serving as Department Chairman from 1963 to 1970 before retiring in 1984. He was a Resident Lecturer for the National Science Foundation's summer institutes for high school chemistry teachers, led two committees that selected two Chancellors, and was President of the local chapter of Phi Beta Kappa.

Jake was the author of 95 scientific articles. He was the first to synthesize the ReH_9^{2-} anion (although its composition would remain mysterious for many years), and carried out many studies of the electrochemical reduction of both inorganic and organic substances. The titles of his books reflect his primary interests: *Unfamiliar Oxidation States and Their Stabilization* (1950); *Non-Aqueous Solvents: Applications as Media for Chemical Reactions* (with Ludwig F. Audrieth, 1953); *Inorganic Chemistry* (with William James Argersinger Jr. and Ernest Griswold, 1960); *University Chemistry* (with John C. Bailar Jr. and Therald Moeller, 1965); *Chemistry with Inorganic Qualitative Analysis* (with Therald Moeller and John C. Bailar Jr., 1965); *Introductory Analytical Chemistry* (with Alexander I. Popov and Ronald T. Pflaum, 1966); and *Radiochemistry of Iodine* (with Milton Kahn, 1977).

The winner of the ACS Midwest Award and the Amoco Foundation Award for Distinguished Teaching, Jake was a consultant for the Los Alamos National Laboratory and a member of the Editorial Board of *Chemical Reviews* (1951–1953), the *Journal of Inorganic & Nuclear Chemistry* (founded in 1955), and *Inorganic Chemistry* (1961–1964).

HENRY FULLER HOLTZCLAW JR. (EDITOR-IN-CHIEF, VOLUME VIII, 1966)

Henry Holtzclaw was born on July 30, 1921, in Stillwater, Oklahoma, and died in Lincoln, Nebraska, on May 24, 2001, after a long illness at the age of 79. He earned his A.B. degree in chemistry from the University of Kansas, Lawrence, in 1942, where his father was a Professor of Economics. While still a student, he was employed at the Eastman Kodak Company in Rochester, New York (summers of 1941 and 1942). He obtained his M.S. (1946) and Ph.D. degrees (1947) from the University of Illinois, Urbana-Champaign, under John C. Bailar Jr. (Editor-in-Chief, Volume IV, 1953). He participated in the Manhattan Project with the Tennessee Eastman Corporation in Oak Ridge, Tennessee (1944–1945), and his doctoral thesis was entitled "Polarographic Reduction of Cobaltic Coordination Complexes." In 1947, Henry joined the Chemistry Department of the University of Nebraska, Lincoln, and rose through the ranks to become Professor. He was appointed Foundation Professor of Chemistry in 1967 and Dean of Graduate Studies from 1976 to 1985. He spent a sabbatical leave as Guest Professor to teach and carry out research at the Universität Konstanz in Germany. He retired from the University of Nebraska in 1988.

Henry's research interests encompassed mass spectroscopy, proton magnetic resonance, and polarography of coordination compounds especially metal complexes of chelates such as β-diketonates. He was the coauthor of three popular freshman chemistry textbooks, some of which went through as many as 10 editions: *College Chemistry: With Qualitative Analysis* (1963), *General Chemistry* (1972), and *Basic Laboratory Studies in College Chemistry with Semi-Micro Quantitative Analysis* (1986).

Henry served as Chair of the Test of English as a Foreign Language Research Committee of the Educational Testing Services in the 1980s. In 1995, he received the James A. Lake Academic Freedom Award in recognition of his role as Chairman of a committee investigating a faculty member who helped lead a student anti-war demonstration in 1971.

WILLIAM LEE JOLLY (EDITOR-IN-CHIEF, VOLUME XI, 1968)

Bill Jolly was born in Chicago, Illinois, on December 27, 1927, and passed away at the age of 86 in Berkeley, California, on January 10, 2014. Bill received his B.S. (1948) and M.S. (1949) degrees from the University of Illinois at Urbana-Champaign, where he studied phosphate and hydrazine chemistry under the inorganic chemist Ludwig Audrieth (Editor-in-Chief, Volume III, 1950). He then moved to the University of California at Berkeley, where he obtained his Ph.D. degree under Wendell Latimer for work on the physical properties of germanium compounds. He was appointed for 1 year as an instructor at Berkeley in 1952 and then served as the Head of the Physical Chemistry and Inorganic Chemistry Division at the Radiation Laboratory in Livermore from 1952 until 1955. In the latter year, he returned to Berkeley as an Assistant Professor in the Chemistry Department, and was promoted to Associate Professor in 1957 and to Professor in 1962. He became Professor Emeritus in 1991.

Bill's research interests included thermodynamic and spectroscopic studies of liquid ammonia solutions, the synthesis of main group hydrides, and the chemistry of sulfur–nitrogen compounds, especially S_4N_4. In addition to work on the mechanism of hydrolysis of the borohydride ion, Bill developed improved routes to germane, stannane, arsine, and stibine. In the late 1960s and for the next 15 years, he carried out extensive and widely cited X-ray photoelectron spectroscopy (ESCA) studies of the chemical structure and bonding of inorganic compounds (especially those containing nitrogen and phosphorus) and organometallic compounds (especially metal carbonyls).

Among his other achievements, Bill wrote a highly entertaining history of the Chemistry Department at Berkeley called *From Retorts to Lasers* (1987). He was an expert in the chemistry of photography and invented a developer for the "solarization" of film, a technique that creates partly negative, partly positive photographic images. Among his awards was a Guggenheim Fellowship in 1959–1960, which he spent at the Chemical Institute of the University of Heidelberg, Germany. He was elected a fellow of the American Association for the Advancement of Science in 1984.

He was a prodigious author, especially in the area of preparative inorganic chemistry, where his textbooks were widely used and influential. Among his books are *Synthetic Inorganic Chemistry* (1960), *The Inorganic Chemistry of Nitrogen* (1964), *Preparative Inorganic Reactions* (editor, 7 volumes, 1964–1971), *The*

Chemistry of the Non-Metals (1966), *The Synthesis and Characterization of Inorganic Compounds* (1970), *Metal-Ammonia Solutions* (compiler, 1972), *Encounters in Experimental Chemistry* (1972, 1985), *Principles of Inorganic Chemistry* (1976), *Modern Inorganic Chemistry* (1985, 1991, 1998), and *Solarization Demystified* (unpublished, 1997).

JOHN KEEN RUFF (CO-EDITOR-IN-CHIEF, VOLUME XIV, 1973)

John was born on February 19, 1932, in New York City and died on January 6, 2004, in Athens, Georgia, of cancer at the age of 71. He received his B.S. degree in 1954 from Haverford College in Haverford, Pennsylvania, where he worked on hormones in his honors work. He obtained his Ph.D. degree from the University of North Carolina, Chapel Hill, in 1959 for a dissertation, "Light-Scattering of Aqueous Aluminum Nitrate and Gallium Perchlorate Solutions," that was supervised by S. Young Tyree (Editor-in-Chief, Volume IX, 1967). He then worked for 10 years at Redstone Arsenal, a research unit at Huntsville, Alabama, operated by the Rohm & Haas Company. In 1969, he moved to the University of Georgia, Athens, where he was a faculty member for 27 years.

John specialized in fluorine, boron, sulfur, phosphorus, and metal carbonyl chemistry. With M. Frederick Hawthorne, he discovered a series of amine complexes of aluminum trihydride and showed that some of them give aluminum metal when heated; this process later became useful for the formation of aluminum thin films by chemical vapor deposition. One of his notable achievements was the discovery that the PPN cation, bis(triphenylphosphoranylidene) ammonium, forms air-stable salts with many air-sensitive anions such as $[Co(CO)_4]^-$. He also discovered that cesium fluoride can serve as a catalyst for the synthesis of organic fluoroxy compounds (R_FOF) by the fluorination of acyl halides.

He wrote three editions (1995, 1998, 2001) of the laboratory manual *Experiments in General, Organic and Biological Chemistry* (coauthor Bobby Stanton). John was awarded a Sloan Research fellowship in 1969 and was a longtime member of the Atlanta Yacht Club.

DUWARD FELIX SHRIVER (EDITOR-IN-CHIEF, VOLUME XIX, 1979)

Duward ("Du") F. Shriver was born on November 20, 1934, in Glendale, California, and died on March 6, 2013, in Evanston, Illinois. He was raised on Oahu in the Hawaiian Islands, received his undergraduate degree in 1958 from the University of California, Berkeley, working with William L. Jolly (Editor-in-Chief, Volume XI, 1968), and his Ph.D. degree in 1961 from the University of Michigan, working with Robert W. Parry (Editor-in-Chief, Volume XIII, 1972). Du spent his entire academic career at Northwestern, beginning in 1961. He was named Morrison Professor of Chemistry in 1987 and served as Chemistry Department Chair from 1992 to 1995.

Du published more than 400 scientific articles spanning inorganic and organometallic synthesis, bioinorganic, solid-state and polymer chemistry, and vibrational spectroscopy. Some of his more notable achievements were the stepwise protonation of a carbonyl ligand to form methane and the isolation of cluster compounds containing the ketenylidene ligand; both of these systems are relevant to the industrially important Fischer–Tropsch process. He also made significant contributions to the design and synthesis of new polymers for lithium ion batteries and the vibrational signature of metal dioxygen compounds.

Du's book *The Manipulation of Air-Sensitive Compounds* (1969, 1986) is a standard reference in the field of organometallic chemistry, and he coedited *The Chemistry of Metal Cluster Compounds* (1990) with Herbert D. Kaesz (Editor-in-Chief, Volume XXVI, 1989) and Richard D. Adams. His highly successful undergraduate textbook *Inorganic Chemistry* (1990, 1994, 1999, 2006), coauthored with Peter W. Atkins, has been translated into 10 languages and is used to teach this very broad and important subject to students around the world. Du mentored more than 150 students and postdoctoral students who went on to pursue careers in industry and government and at national laboratories, colleges, and universities.

He received many professional awards, including a Guggenheim Fellowship, an Alfred P. Sloan Research Fellowship, the Royal Society of Chemistry Ludwig Mond Medal, the Materials Research Society Medal, and the American Chemical Society Award for Distinguished Service in Inorganic Chemistry. He was a fellow of the American Association for the Advancement of Science.

HERBERT DAVID KAESZ (EDITOR-IN-CHIEF, VOLUME XXVI, 1989)

Herb Kaesz was born on January 4, 1933, in Alexandria, Egypt, to Austrian parents and died on February 26, 2012, in Los Angeles, California, at the age of 79, about a month after he had been diagnosed with cancer. His father, a chemist, had joined his wife's family business, Kurz Optical, to run the Alexandria branch. When Herb was 7, the family emigrated to the United States. He received his A.B. degree from New York University in 1954 with Phi Beta Kappa honors. He earned his M.A. (1956) and Ph.D. degrees (1959) from Harvard University under the supervision of F. Gordon Stone for work on molecular addition compounds of boron. In August 1960, Herb joined the Inorganic Division of the University of California, Los Angeles (UCLA), where he served until his retirement in 2003. He remained an active Professor Emeritus until his death.

Herb's research centered on the synthesis and applications of organometallic compounds, especially metal carbonyls. In 1961, he synthesized $Tc_2(CO)_{10}$, which completed the list of elements, 14 in number, that form isolable binary carbonyls in the zero oxidation state. He discovered many new metal hydride and cluster compounds, and carried out elegant investigations of the nucleophilic activation of coordinated CO ligands under mild conditions. His book, *The Chemistry of Metal Cluster Complexes* (1990), coauthored with Duward F. Shriver (Editor-in-Chief, Volume XIX, 1979) and Richard D. Adams, became the premier reference text on the topic. He also studied main group element compounds and, later in his career, he investigated the development of pyrolytic and photolytic methods of metal film deposition for electronic applications.

He served as Chair of the International Union of Pure and Applied Chemistry (IUPAC) Commission on the Nomenclature of Inorganic Chemistry, was President of *Inorganic Syntheses*, Inc., and served for more than three decades as Associate Editor of the ACS journal, *Inorganic Chemistry* (1969–2001). Herb's honors included the ACS Southern California Section's Tolman Medal (1981), a Fellowship of the American Association for the Advancement of Science (1988), and the ACS Award for Distinguished Service in the Advancement of Inorganic Chemistry (1998). In 2009, the inaugural year of the program, he was elected an ACS Fellow. Herb held two foreign fellowships—a Fellowship from the Japan Society for the Promotion of Science (1978) and a Senior U.S. Scientist Award from the Alexander von Humboldt Foundation in Germany (1988). He also twice held the post of Professeur Invité in France, once in Toulouse (1992) and once in Paris (1995).

GEORGE B. KAUFFMAN
California State University, Fresno, CA

NOTICE TO CONTRIBUTORS AND CHECKERS

The *Inorganic Syntheses* series (www.inorgsynth.com) publishes detailed and independently checked procedures for making important inorganic and organometallic compounds. Thus, the series is the concern of the entire scientific community. The Editorial Board hopes that many chemists will share in the responsibility of producing *Inorganic Syntheses* by offering their advice and assistance in both the formulation and the laboratory evaluation of outstanding syntheses.

The major criterion by which syntheses are judged is their potential value to the scientific community. We hope that the syntheses will be widely used and provide access to a broad range of compounds of importance in current research. The syntheses represent the best available procedures, and new or improved syntheses of well-established compounds are often featured. Syntheses of compounds that are available commercially at reasonable prices are ordinarily not included, however, unless the procedure illustrates some useful technique. *Inorganic Syntheses* is not a repository of primary research data, and therefore submitted syntheses should have already appeared in some form in the primary peer-reviewed literature and, at least to some extent, passed the "test of time." The series offers authors the chance to describe the intricacies of synthesis and purification in greater detail than possible in the original literature, as well as to provide updates of an established synthesis.

Authors wishing to submit syntheses for possible publication should write their manuscripts in a style that conforms with that of previous volumes of *Inorganic Syntheses* (a style guide is available from the Board Secretary). The manuscript should be in English and submitted as an editable electronic document. Nomenclature should be consistent and should follow the recommendations presented in *Nomenclature of Inorganic Chemistry, IUPAC Recommendations 2005*, published for the International Union of Pure and Applied Chemistry by The Royal Society of Chemistry, Cambridge, 2005. This document is available online (as of 2012) at http://www.iupac.org/fileadmin/user_upload/databases/Red_Book_2005.pdf. Abbreviations should conform to those used in publications of the American Chemical Society, particularly *Inorganic Chemistry*.

Submissions should consist of four sections: Introduction, Procedure, Properties, and References. The Introduction should include an indication of the importance and utility of the product(s) in question, and a concise and critical summary of the available procedures for making them and what advantage(s) the chosen method has over the alternatives. The Procedure should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. It should contain an admonition if any potential hazards are associated with the procedure, and what safety precautions should be taken. Sources of unusual starting materials must be given, and, if possible, minimal standards of purity of reagents and solvents should be stated. Ideally, all reagents are readily available commercially or have been described in earlier volumes of *Inorganic Syntheses*. The scale should be reasonable for normal laboratory operation, and problems involved in scaling the procedure either up or down should be discussed if known. Unusual equipment or procedures should be clearly described and, if necessary for clarity, illustrated in line drawings. The yield should be given both in mass and in percentage based on theory. The Procedure section normally will conclude with calculated and found microanalytical data. The Properties section should supply and discuss those physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an intelligent manner. Under References, pertinent literature citations should be listed in the order they appear in the text.

Manuscripts should be submitted electronically to the Secretary of the Editorial Board, Professor Stanton Ching, sschi@conncoll.edu. The Editorial Board determines whether submitted syntheses meet the general specifications outlined above. Every procedure will be checked in an independent laboratory, and publication is contingent on satisfactory duplication of the syntheses. For online access to information and requirements, see www.inorgsynth.com.

Chemists willing to check syntheses should contact the editor of a future volume or make this information known to Professor Ching.

TOXIC SUBSTANCES AND LABORATORY HAZARDS

Chemicals and chemistry are by their very nature hazardous. The obvious hazards in the syntheses reported in this volume are delineated, where appropriate, in the experimental procedure. It is impossible, however, to foresee every eventuality, such as a new biological effect of a common laboratory reagent. As a consequence, all chemicals used and all reactions described in this volume should be viewed as potentially hazardous. Care should be taken to avoid inhalation or other physical contact with reagents and solvents used in this volume. In addition, particular attention should be paid to avoiding sparks, open flames, or other potential sources that could set fire to combustible vapors or gases.

The following sources are especially recommended for guidance:

NIOSH Pocket Guide to Chemical Hazards, U.S. Government Printing Office, Washington, DC, 2005 (ISBN-13: 978-1-59804-052-4), is available free at http://www.cdc.gov/niosh/npg/ and can be purchased in paperback and spiral bound format. It contains information and data for 677 common compounds and classes of compounds.

Organic Syntheses, which is available online at http://www.orgsyn.org, has a concise but useful section "Handling Hazardous Chemicals."

Prudent Practices in the Laboratory: Handling and Disposal of Chemicals, National Academy Press, 1995 (ISBN-13: 978-0-30905-229-0), is available free at http://www.nap.edu/catalog.php?record_id=4911.

W. L. F. Amarego and C. Chai, *Purification of Laboratory Chemicals*, 6th ed., Butterworth-Heinemann, Oxford, 2009 (ISBN-13: 978-1-85617-567-8), is the standard reference for the purification of reagents and solvents. Special attention should be paid to the purification and storage of ethers.

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Chapter One

TRANSITION METAL HALIDE COMPOUNDS

1. OCTAHEDRAL HEXATANTALUM HALIDE CLUSTERS

Submitted by THIRUMALAI DURAISAMY,[*] DANIEL N. T. HAY,[*] and LOUIS MESSERLE[*]
Checked by ABDESSADEK LACHGAR[†]

Octahedral hexatantalum halide clusters usually exist as extended structures of the form $Ta_6(\mu\text{-}X)_{12}X_2$ with terminal (outer) and bridging (inner) halogen atoms shared between clusters, or as discrete clusters such as $Ta_6(\mu\text{-}X)_{12}X_2 \cdot 8H_2O$ that are better formulated as $Ta_6(\mu\text{-}X)_{12}X_2(OH_2)_4 \cdot 4H_2O$. These clusters consist of six tantalums linked through Ta—Ta bonding to form a Ta_6 octahedron with a halide bridge along each of the 12 octahedral edges and one terminal ligand (halide, water, etc.) located apically on each tantalum.[1] A range of cluster oxidation states have been reported.[2]

Ta_6Cl_{14} was first reported in 1907 from the reduction of Ta_2Cl_{10} (denoted as $TaCl_5$ hereafter) with sodium amalgam,[3] and its structure was determined in 1950.[4] It is prepared typically by high-temperature, solid-state reduction of $TaCl_5$ in vacuum-sealed quartz ampules.[5] Microwave heating has also been employed.[6] Extraction with large volumes of water gives good yields of the discrete cluster[7] $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ after aqueous reduction of oxidized cluster contaminants with $SnCl_2$. The most commonly used approach is that developed by Koknat et al., involving reduction at 700°C of $TaCl_5$ with a four-fold excess of Ta powder.[8]

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Ta_6Br_{14} was first prepared in 1910 by sodium amalgam reduction of $TaBr_5$.[3b] It has since been prepared by using the reductants aluminum[5a] and excess tantalum[8a] and can be isolated by aqueous extraction as the discrete cluster $Ta_6(\mu\text{-}Br)_{12}Br_2(OH_2)_4 \cdot 4H_2O$.[2a,b] A sample was structurally characterized as $[Ta_6(\mu\text{-}Br)_{12}(OH_2)_6](OH)Br \cdot 4H_2O$,[9] and another structure of the hexaaquo ion $[Ta_6(\mu\text{-}Br)_{12}(OH_2)_6]^{2+}$ was recently reported.[10]

There is considerable interest in the coordination[11] and catalytic[12] chemistries of these discrete clusters. Because of its high electron count, the hexaaquo ion $[Ta_6(\mu\text{-}Br)_{12}(OH_2)_6]^{2+}$ has been used frequently for phase determination[9,13] of isomorphous protein derivatives by SIR, MIR, SIRAS/MIRAS, and SAD/MAD methods in biomacromolecular crystallography. This use is growing as larger biomacromolecular structures and assemblies (e.g., membrane proteins, ribosomes, proteasomes) are studied.

We have found that the main group metal and metalloid reductants mercury, bismuth, and antimony are highly effective[14] in reducing WCl_6 or $MoCl_5$ at surprisingly lower temperatures than commonly used in the solid-state synthesis of early transition metal cluster halides. Borosilicate ampules can be substituted for the more expensive and less easily sealed quartz ampules at these lower temperatures, and the metals and metalloids are not as impacted by oxide coatings that inhibit solid-state reactions with more active metals. These lower temperatures may allow access to kinetic products, such as trinuclear clusters, instead of thermodynamic products.

We report here an extension of this reduction methodology to the convenient preparation[15] of $Ta_6(\mu\text{-}X)_{12}X_2(OH_2)_4 \cdot 4H_2O$ by reduction of TaX_5 with gallium dichloride, $Ga^+GaCl_4^-$ (for X = Cl), or gallium (for X = Br). Gallium dichloride has not been used as a preparative-scale reductant in transition metal chemistry. Gallium is an effective reductant, but because of its tendency to agglomerate and to adhere to glass, reductions employing Ga need to be agitated several times during the course of the reaction in order to optimize yields by homogenization of reactants. We have not yet tested the use of gallium dibromide as a reductant for $TaBr_5$, but expect that it would eliminate the need to homogenize reactants in gallium-based reductions and might improve the yield. The aquated hexatantalum clusters are liberated from the solid-state products by Soxhlet extraction with water, which greatly simplifies the isolation procedure. We also describe the straightforward preparation of a tetraalkylammonium derivative of the $[Ta_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$ anion that has solubility in a broader array of organic solvents than the aquated clusters.

General Procedures

TaX_5 (X = Cl, Br; Materion Advanced Chemicals, Milwaukee, WI), hydrochloric acid (12 M, Fisher Scientific), Ga (99.99%, Atlantic Equipment Engineers, Bergenfield, NJ), NaCl (Fisher), KBr (Aldrich Chemical), $SnCl_2 \cdot 2H_2O$ (Fisher), $SnBr_2$ (99.5%, Alfa Aesar), HBr (48%, Fisher), and diethyl ether (anhydrous, Fisher) are used as received. $Ga^+GaCl_4^-$ is purchased and used as received from