Using Balancing Chemical Equations as a Key Starting Point To Create Green Chemistry Exercises Based on *Inorganic Syntheses* Examples

John Andraos*

CareerChem, 504-1129 Don Mills Road, Toronto, Ontario M3B 2W4, Canada

S *Supporting Information*

ABSTRACT: Following our previous work on introducing a database of tested chemical examples from *Organic Syntheses* that can be used as a repository for problem set development in green chemistry courses, in this paper we extend this idea to include over 1300 examples taken from *Inorganic Syntheses* covering 36 volumes. Examples are sorted according to the following 13 categories: asymmetric syntheses, syntheses involving catalyst preparation, chemoenzymatic reactions, classical resolutions, convergent synthesis plans, kinetic resolutions; multicomponent reactions, multistep linear synthesis plans, natural feedstocks as starting materials, reactions involving product distributions, reactions involving sacrificial reagents, reactions involving nonunity stoichiometric coefficients, and polymerization reactions. In this paper, we highlight the skill of balancing chemical equations as a mandatory prerequisite of green metrics analysis. Through a problem set containing 70 exercises, we selected challenging examples from *Inorganic Syntheses* to emphasize this point and link it to the understanding of reaction mechanisms. A number of these examples also contain errors or missing information that students are asked to correct. This is yet another good training ground to exercise their skills in problem solving.

KEYWORDS: *Upper-Division Undergraduate, Inorganic Chemistry, Problem Solving/Decision Making, Green Chemistry, Synthesis*

■ INTRODUCTION

The literature on experimental green chemistry for undergraduates is dominated by organic chemistry examples in comparison with the handful of ones published in the field of inorganic chemistry.[1−9] Moreover, to the best of our knowledge, there are no published inorganic chemistry examples that have been examined by green metrics analysis. In our previous work[10,11] on the application of green metrics calculations to organic reactions, we noted the fundamental issue of determining balanced chemical equations as a mandatory starting point to initiate any kind of computation. The understanding and application of reaction stoichiometry accounting for the fate of all input materials (reactants) and origin of all output materials (products) in any chemical reaction arises directly from Lavoisier's law of conservation of mass. This skill is even more important in inorganic chemistry since it is dominated by redox transformations of metallic or organometallic species that involve nonunity stoichiometric coefficients in their balanced equations. A reviewer has commented that appreciating the origins of co- and byproducts in chemical processing in mass balance calculations is fundamental to the education and training of all chemists and is central to understanding the origin of waste and hence to devise effective means to mitigate its minimization.

Once a properly balanced chemical equation is written out for a given chemical transformation, the determination of the fundamental green metric, atom economy, can be determined readily. In this paper, we present a database of over 1300 examples from *Inorganic Syntheses*,[12] which has the same venerable status as *Organic Syntheses* with respect to external checking of procedures and reliable disclosure of all materials used. Instructors may use this database as a repository of examples they can draw upon to construct insightful problem sets that utilize green metrics calculations. The database contains examples from 36 volumes covering the same 12 categories as before,[10] plus a new one on polymerization reactions. The number of examples are given in parentheses:

- Asymmetric syntheses (0)
- Syntheses involving catalyst preparation (0)
- Chemoenzymatic reactions (0)
- Classical resolutions (15)
- Convergent synthesis plans (26)
- Kinetic resolutions (0)
- Multicomponent reactions (96)
- Multistep linear synthesis plans (130)
- Natural feedstocks as starting materials (0)
- Reactions involving product distributions (6)
- Reactions involving sacrificial reagents (8)
- Reactions involving nonunity stoichiometric coefficients (1023)
- Polymerization reactions (3)

It is not surprising that the penultimate category has the most examples as it is dominated by redox reactions, which is the class of reactions that characterizes most inorganic transformations. Five of the 12 categories do not have any representative examples, and therefore, this scenario presents chemists with fresh opportunities to fill the gap. Unless otherwise specified, fully balanced chemical equations are

A

provided including corrections made to the original publications. The oxidation states of metals are explicitly specified. In addition, all acronyms of reagents, catalysts, and functional groups are defined where appropriate for each example.

PEDAGOGICAL BENEFITS FOR STUDENTS AND INSTRUCTORS

In creating the present *Inorganic Syntheses* database along the same categories as our previous *Organic Syntheses* database,[10,11] we give instructors maximum latitude in choosing experimentally checked examples that they can introduce into classroom or laboratory instruction. Examples can be selected that tie in directly with an instructor's current syllabus for introductory and advanced courses in inorganic chemistry where green chemistry principles may be introduced. The posed problem set questions are set up along the following structure. Students are first given a chemical transformation written out in the conventional manner where structures for substrates and products are shown, and reagents and reaction conditions are displayed above a reaction arrow. From this information, students are tasked to properly balance the chemical equation that accounts for all reaction byproducts. When dealing with redox (oxidation−reduction) reactions, which are frequently encountered in inorganic transformations, there are a number of pedagogical publications that have appeared over the years that can assist students and instructors in this task.[13−38] Next, students determine the atom economy as the ratio of molecular weight of the target product to the sum of the molecular weights of the reagents properly corrected for stoichiometric coefficients as prescribed by the balanced chemical equation. Depending on the level of sophistication of an instructor's green chemistry instruction, students may use the mass quantity details of the experimental procedure to determine process mass intensity and E-factor using the pedagogical algorithm previously described.[10,11] Because the assessment of reaction greenness is a comparative exercise, students can be asked to compare the performance of the worked out *Inorganic Syntheses* example with another example to the same product taken from the journal literature. This also gives students an opportunity to learn about literature searching and critiquing a given synthesis plan against another using well-developed metrics analysis.

To challenge students further, instructors may ask students to suggest alternative synthesis routes based on chemistry that they have learned in current or past courses. The amount of work that students are expected to do for any one thoroughly laid out example may at first be perceived as challenging; however, we argue that the benefits gained by integrating various interdisciplinary skills and chemical knowledge in telling a complete chemical story far outweigh this perception. In fact, the field of green chemistry is by its very nature interdisciplinary and demands the highest skill sets to be mastered. Integrated learning is emphasized in the study of green chemistry principles. The kinds of problem set questions posed in this paper and our previous work[10,11] emphasize this crucial point. The next section gives more detail into specific questions that can be posed which can be easily adapted by instructors to dovetail with other topics of interest. The exercises are composed of laddered concepts including connecting balancing chemical equations to conjecturing reaction mechanisms, identifying likely byproducts of a reaction when they are not explicitly stated (this can be directly tied to reaction mechanism), identifying chemical bonds made in a

target product to elucidate synthesis strategy, and identifying which atoms in substrate structures are oxidized and reduced in a redox transformation. Typically, these concepts are presented in various chemistry courses as isolated concepts which students are required to absorb by rote memory without seeing the "big picture".

From our teaching experience, we have found that effective learning takes place when concepts are woven together in an integrated way so that complete stories are told. This improves memory retention of basic facts, enhances problem solving skills through self-discovery, and increases student engagement in the subject since they see a worthwhile higher purpose in carrying out problem set exercises rather than viewing them as drudgery. Instructors may choose to leave out some features of laddered questions as they see fit; however, it is recommended that they be retained to strengthen integration of concepts as described. The reader is invited to peruse the Supporting Information to learn more. Following this teaching philosophy, we have received positive feedback both from undergraduate and graduate students taking elective green chemistry workshops offered by the Green Chemistry Initiative at the University of Toronto over the last three years.

TOPICS FOR PROBLEM SET EXERCISES

Beyond the standard questions on determination of atom economy (AE), reaction mass efficiency (RME), E-factor (E), and process mass intensity (PMI) for individual reactions and synthesis plans (linear and convergent) using the simplified algorithm and synthesis tree diagram tool described previously by us,[10] we present sample problem set exercises that focus on the chemistries of the reactions. These exercises give deeper insights into what is going on in the transformations and provide richer discussions about the application of green metrics analysis. The Supporting Information contains files of questions and worked solutions for 70 problems that focus on challenging reports published in *Inorganic Syntheses*. We briefly discuss the kinds of questions asked and their pedagogical value.

In the early volumes of the series, chemical equations were written out using molecular formulas employing compact parenthesis and bracket notation instead of drawing out explicit chemical structures in order to save space in printing. This gives an opportunity for instructors to ask students to carry out the task of deciphering the coded notation so that more advanced questions on synthesis strategy may be asked, such as identifying synthesis target bonds and sacrificial reagents. Once these steps are identified, they can be probed further from a green chemistry perspective by determining and comparing the fractions of waste arising from target bond forming and sacrificial steps, respectively. Clearly, synthesis plans that are dominated by target bond forming reactions are generally more efficient and produce less waste than those dominated by sacrificial ones, irrespective of whether they follow linear or convergent strategies.

Exercises in Writing out Full Structures of Reaction Products

Questions Q4 (thiodithiazyl dichloride, thiotrithiazyl chloride, trithiazyl chloride, thiodithiazyl chloride), Q16 ((1-3:6-7:10-12-η-2,6,10-dodecatriene-1,12-diyl)nickel), Q32 ([[(1,2,5,6-η)-1,5,-cyclooctadiene] [(1,2,3-η)-2-cycloocten-1-yl]cobalt), Q33 (dodecacarbonyltetrarhodium), Q34 (*meso-* and racemic-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)

hydrate (5,5,7,12,1 2,14-Me$_6$[14] ane-1,4,8,11-N4·x H$_2$O), Q35 (dodecacarbonyltetra-μ-hydrido-*tetrahedro*-tetrarhenium), Q42 (octahydridotetrakis(triphenylphosphine)-dirhenium(IV)), Q43 (decakis(acetonitrile)dirhodium(II) tetrafluoroborate), Q47 (polycyclic borazine), Q50 (ruthenium cluster compounds), Q52 (2,2′-bis(1,3,2-benzodioxaborole)), Q54 (sodium 2-(5-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide), Q56 (diiridium(0,II) tris(bis(bis(trifluoroethoxy)-phosphino)methylamine)dichloride), Q60 (diethylammonium *cyclo*-octathiotetraphosphate(III)), Q61 (various sulfur−nitrogen compounds), and Q66 (various iron−sulfur and iron−tellurium compounds) show examples of target products that are written out in a manner that masks the tracing of what is occurring in the reactions.

Exercises in Redox Reaction Balancing

Many examples given in *Inorganic Syntheses* either do not give fully balanced chemical equations identifying all reaction byproducts or contain errors in stoichiometric coefficients. This is particularly true of redox reactions. Questions Q1, Q10, Q11, Q12, Q15, Q17, Q25, Q36, Q38, Q39, Q46, Q53, Q55, and Q64 deal with situations of incorrect balancing, and questions Q13, Q14, Q19, Q21, Q25, Q26, Q31, Q32, Q33, Q37, Q40, Q42, Q43, Q44, Q50, Q62, and Q65 deal with situations of incomplete identification of byproducts. For the latter case, a useful question to pose is the rationalization of byproduct identity via a reaction mechanism that accounts for both it and the target product as is done in questions Q2, Q5, Q7, Q49, and Q58. In question 41, the identities of byproducts are designated as unknown by the authors, yet it is possible to speculate what they may be based on writing out possible redox half reactions. In this example, it is trivial to recognize that the ruthenium and osmium metal ions are being reduced. The challenge is to identify what is being oxidized, either chloride ion to chlorine gas, or dimethylformamide to dimethylamine and carbon dioxide. Clearly, separate experimental evidence is needed to determine which route is operative. Redox reactions are also interesting with respect to the identification of which atoms are oxidized and which atoms are reduced by determination of their respective oxidation numbers. Questions Q1, Q8, Q18, Q22, Q24, and Q33 are of this type. The example highlighted in question 42 is at first paradoxical because it involves reducing a rhenium(III) complex to a rhenium(IV) complex with sodium borohydride which begs the question as to which atom is being reduced. Furthermore, there are three cases for the stoichiometry of the reaction depending on what byproducts are used in the equation balancing. Careful bookkeeping of the oxidation number changes in each kind of element from reactants to products indicates that it is the protic hydrogen atoms in ethanol, acting both as a reactant and solvent, that are reduced either to diatomic hydrogen for cases I and II, or to hydride ion for case III when hydrogen gas is absent as a byproduct in its balanced chemical equation. The experimental molar ratio of 16.8 to 1 for sodium borohydride to rhenium(III) complex is consistent with the corresponding stoichiometric molar ratios of 6 to 1 and 14 to 1 for cases I and II, respectively, whereas it is inconsistent with the value of 1.75 to 1 predicted by case III. This is good evidence to rule out case III as a possible balanced equation and suggests that hydrogen gas is indeed one of the byproducts of the reaction. Question 67 is an excellent example that combines both chemical knowledge and elementary algebra to work out the balanced chemical equation for the permanganate oxidation of

manganese(II)acetate to a cluster compound of manganese that contains two kinds of oxidized manganese ions, III and IV. Question 24 is a simpler version of the same kind of idea where a potassium 13-vanadomanganate(IV) 18-hydrate cluster compound, composed of 12 vanadium atoms with an oxidation state of +5 and one vanadium atom with an oxidation state of +4, is made by oxidizing potassium vanadate(V) with potassium peroxydisulfate. Yet another example of a compound containing one kind of metal atom in two different oxidation states is the Nocera complex involving iridium(0) and iridium(II) in the same structure (see Q56).

Exercises on Challenging Redox Reactions

Question 26 deals with a curious situation of redox balancing where more than one set of stoichiometric coefficients can satisfy the elemental balancing for the same set of substrates and products. Equations that are satisfied by multiple integer solutions are known as Diophantine equations and have been noted in connection with balancing redox reactions.[39−41] This situation can arise when there is more than one oxidation or reduction half reaction occurring, rather than having a single redox couple. In one case, osmium(IV) and hydrazine are reduced to osmium(II) and ammonia, respectively, and hydrazine is also oxidized to nitrogen gas. In the other case, ruthenium(II) and ammonia are oxidized to ruthenium(III) and nitric oxide, respectively, and chlorine gas is reduced to chloride ion. Examples of unusual redox reactions are given in questions Q27−30 where the assignment of which atoms are oxidized and which atoms are reduced is more challenging. In question 68, the structure of peroxotungstic acid, H$_2$W$_2$O$_{11}$, is not given in the reference, yet it is possible to deduce it by a combination of oxidation number analysis, determination of the number of rings and/or unsaturations, and the number of each kind of element. The insights gained in this question may be used to explore the application of the rings and unsaturations formula[42,43] to structures that contain more rings than the formula predicts, such as bicyclic compounds. For example, norbornane (C$_7$H$_{12}$) has 3 rings that can be traced out along its skeleton, yet the formula yields 2. Similarly, for adamantane (C$_{10}$H$_{16}$), there are 4 rings, yet the formula yields 3. Therefore, it may be deduced that the formula predicts the *minimum* of rings found in these structures rather than the total number of rings. This deeper insight is appreciated when the exercise is repeated on the Lindqvist ion (W$_6$O$_{19}^{-2}$), also described in the reference pertaining to question 68, where the rings and unsaturations formula predicts a value of 12 (4 unsaturations and 8 rings), yet there are a total of 30 rings that can be enumerated across its structure.

Exercises on Determining Stoichiometric Coefficients for Ill-Defined Reactions

Two examples found in the database, not given as problem set questions, involve situations of uncertainty where in one case the stoichiometry of the reaction has not been verified by experiment (Part 3, p. 138, Ex. 46[44]), and in the other, byproducts are not identified although nonunity stoichiometric coefficients are still specified for the reactants (Part 3, p. 171, Ex. 162[45]).

Exercises on Polymerization Reactions

Questions 69 and 70 deal with determinations of overall atom economies for synthesis plans that involve a polymerization step. The atom economies are expressed as a function of the chain length, n, and the limiting atom economy value is sought

after. In both cases, the balanced chemical equations as written in the *Inorganic Syntheses* references are true only for the monomer, *n* = 1.

The most recent 36th volume, for the first time since its inception in 1939, lists entries that are designated as teaching laboratory experiments appropriate to undergraduate students studying inorganic chemistry in the laboratory. These examples are highlighted in question 57. These entries in *Inorganic Syntheses* also contain laboratory questions and exercises made up by the authors that are unrelated to green chemistry issues. By contrast, the *Organic Syntheses* series to date has not yet made such a specific designation for undergraduate instruction though many of the examples published in the first five collective volumes have been used in a number of under-graduate laboratory reference books such as *Vogel's Textbook of Practical Organic Chemistry*.[46]

■ CONCLUDING REMARKS

We have extended our coverage of problem set questions for green chemistry exercises to include over 1300 examples from inorganic chemistry taken from the *Inorganic Syntheses* series. Apart from the standard questions based on determination of material efficiency metrics for reactions and synthesis plans, we have highlighted examples that showcase both interesting and challenging aspects of the chemistries involved. The skill of balancing chemical equations, particularly redox reactions, is emphasized along with identifying byproducts that may be rationalized with reaction mechanisms.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00770.

Database of reactions and references from *Inorganic Syntheses* (Parts 1, 2, and 3); example problem set exercises with worked solutions (ZIP)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: c1000@careerchem.com.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Huheey, J. E. In *Green Chemistry: Designing Chemistry for the Environment*; Anastas, P. T., Williamson, T. C., Eds.; American Chemical Society Symposium Series 626; American Chemical Society: Washington, D.C., 1996; Vol. *626*, pp 232−238.

(2) Uffelman, E. S.; Doherty, J. R.; Schultze, C.; Burke, A. L.; Bonnema, K. R.; Watson, T. T.; Lee, D. W., III Microscale syntheses, reactions, and ^{1}H NMR spectroscopic investigations of square planar macrocyclic tetraamido-N Cu(III) complexes relevant to green chemistry. *J. Chem. Educ.* **2004**, *81*, 182−185.

(3) Uffelman, E. S.; Doherty, J. R.; Schultze, C.; Burke, A. L.; Bonnema, K. R.; Watson, T. T.; Lee, D. W., III Microscale syntheses, reactions, and ^{1}H NMR spectroscopic investigations of square planar macrocyclic tetraamido-N Co(III) complexes relevant to green chemistry. *J. Chem. Educ.* **2004**, *81*, 325−329.

(4) Sidhwani, I. T.; Chowdhury, S. Greener alternative to qualitative analysis for cations without H_2S and other sulfur-containing compounds. *J. Chem. Educ.* **2008**, *85*, 1099−1101.

(5) Canal, J. P. An inorganic green chemistry experiment: the preparation and analysis of Group II metal oxalate hydrates. *Chem. Educator* **2009**, *14*, 26−29.

(6) Sharma, R. K.; Sharma, C.; Sidhwani, I. T. Solventless and one-pot synthesis of Cu(II) phthalocyanine complex: a green chemistry experiment. *J. Chem. Educ.* **2011**, *88*, 86−87.

(7) Clark, R. A.; Stock, A. E.; Zovinka, E. P. Metalloporphyrins as oxidation catalysts: moving toward "greener" chemistry in the inorganic chemistry laboratory. *J. Chem. Educ.* **2012**, *89*, 271−275.

(8) Birdwhistell, K. R.; Conroy, K. J.; Schulz, B. E. Greening the inorganic lab: combining microwaves and phase transfer catalysis for the rapid syntheses of Group VI carbonyl complexes. *Chem. Educator* **2014**, *19*, 133−137.

(9) Paluri, S. L. A.; Edwards, M. L.; Lam, N. H.; Williams, E. M.; Meyerhoefer, A.; Sizemore, I. E. P. Introducing "Green" and "Nongreen" Aspects of noble metal nanoparticle synthesis: an inquiry-based laboratory experiment for chemistry and engineering students. *J. Chem. Educ.* **2015**, *92*, 350−354.

(10) Andraos, J.; Hent, A. Simplified application of material efficiency green metrics to synthesis plans − pedagogical case studies selected from. *J. Chem. Educ.* **2015**, *92*, 1820−1830.

(11) Andraos, J.; Hent, A. Useful material efficiency green metrics problem set exercises for lecture and laboratory. *J. Chem. Educ.* **2015**, *92*, 1831−1839.

(12) Inorganic Syntheses Volumes. http://www.inorgsynth.com/volumes.php (accessed Mar 2016).

(13) Bottomley, J. Note on a method for determining the coefficients in chemical equations. *Chemical News* **1878**, *37*, 110−111.

(14) Johnson, O. C. Negative bonds and rule for balancing equations. *Chemical News* **1880**, *42*, 51.

(15) Karlslake, W. J. Balancing of ionic chemical equations. *Chemical News* **1907**, *69*, 41−43.

(16) Morris, K. B. The balancing of oxidation-reduction equations. *J. Chem. Educ.* **1938**, *15*, 538−540.

(17) Steinbach, O. F. Non-stoichiometric equations. *J. Chem. Educ.* **1944**, *21* (2), 66−69.

(18) Vanderwerf, C. A.; Davidson, A. W.; Sisler, H. H. Oxidation-reduction − a re-evaluation. *J. Chem. Educ.* **1945**, *22*, 450−457.

(19) Vanderwerf, C. A. A consistent treatment of oxidation-reduction. *J. Chem. Educ.* **1948**, *25*, 547−551.

(20) Bennett, G. W. Material balances and redox equations. *J. Chem. Educ.* **1954**, *31*, 324−325.

(21) Bennett, G. W. Otis Coe Johnson and redox equations. *J. Chem. Educ.* **1954**, *31*, 157−158.

(22) Yalman, R. G. Writing oxidation-reduction equations − a review of textbook methods. *J. Chem. Educ.* **1959**, *36*, 215−218.

(23) Burrell, H. P. C. Balancing organic redox equations. *J. Chem. Educ.* **1959**, *36*, 77−79.

(24) Lockwood, K. L. Redox revisited. *J. Chem. Educ.* **1961**, *38*, 326−329.

(25) Hudlicky, M. Reduction and oxidation tables. *J. Chem. Educ.* **1977**, *54*, 100−106.

(26) Kolb, D. The chemical equation. Part 1: simple reactions. *J. Chem. Educ.* **1978**, *55*, 184−189.

(27) Kolb, D. The chemical equation. Part 2: oxidation-reduction reactions. *J. Chem. Educ.* **1978**, *55*, 326−331.

(28) Carrano, S. A. Balancing an atypical redox equation. *J. Chem. Educ.* **1978**, *55*, 382.

(29) Kolb, D. More on balancing redox reactions. *J. Chem. Educ.* **1979**, *56*, 181−184.

(30) Kolb, D. Balancing complex redox equations by inspection. *J. Chem. Educ.* **1981**, *58*, 642−645.

(31) Cook, D.; Morrison, R. J. Oxidation numbers in organic chemistry. *Educ. Chem.* **1990**, *September*, 141−143.

(32) Davis, E. A revised approach to solving redox equations. *J. Chem. Educ.* **1990**, *67*, 671−672.

(33) Stout, R. Redox challenges: good times for puzzle fanatics. *J. Chem. Educ.* **1995**, *72*, 1125.

(34) Klemm, L. H. A classification of organic redox reactions and writing balanced equations for them, with special attention to heteroatoms and heterocyclic compounds. *J. Heterocycl. Chem.* **1996**, *33*, 569−574.

(35) Ludwig, O. G. On balancing "redox challenges. *J. Chem. Educ.* **1996**, *73*, 507.

(36) Guo, C. A new inspection method for balancing redox equations. *J. Chem. Educ.* **1997**, *74*, 1365−1366.

(37) Ten Hoor, M. J. Redox balancing without puzzling. *J. Chem. Educ.* **1997**, *74*, 1367−1368.

(38) Anselme, J. P. Understanding oxidation-reduction in organic chemistry. *J. Chem. Educ.* **1997**, *74*, 69−72.

(39) Crocker, R. Application of Diophantine equations to problems in chemistry. *J. Chem. Educ.* **1968**, *45*, 731−733.

(40) Balasubramanian, K. Linear variational Diophantine techniques in mass balance of chemical reactions. *J. Math. Chem.* **2001**, *30*, 219−225.

(41) Papp, D.; Vizvari, B. Effective solution of linear Diophantine equation systems with an application in chemistry. *J. Math. Chem.* **2006**, *39*, 15−31.

(42) Lodge, O. J. On nodes and loops in connexion with chemical formulae. *Philos. Mag.* **1875**, *50* (4), 367−376.

(43) Rouvray, D. H. Some reflections on the topological structure of covalent molecules. *J. Chem. Educ.* **1975**, *52*, 768−773.

(44) Wang, H. H.; Mueting, A. M.; Casalnuovo, J. A.; Yan, S.; Barthelmes, J. K. H.; Pignolet, L. H. Tris[1,3-bis(diphenylphosphino)-propane]-heptahydridotriiridium(2+) bis(tetrafluoroborate) and bis-[1,3-bis-(diphenylphosphino)propane]-pentahydridodiiridium(1+) tetrafluoroborate. *Inorganic Syntheses* **1990**, *27*, 22−26.

(45) Jain, K. C.; Agarwala, U. C. Thionitrosyl complexes of ruthenium(II). *Inorganic Syntheses* **1992**, *29*, 161−164.

(46) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Wiley: New York, 1989.

E