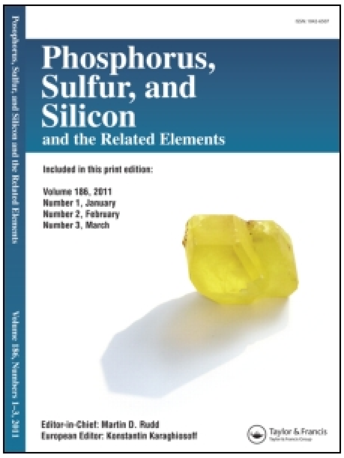
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Early Transition-Metal Complexes of Phosphorus-Nitrogen-Sulfur Heterocycles

Robert Hilts[a]; Xiaoliang Gao[a]; Masood Parvez[a]; Tristram Chivers[a]
[a] Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada

To cite this Article Hilts, Robert , Gao, Xiaoliang , Parvez, Masood and Chivers, Tristram(1994) 'Early Transition-Metal Complexes of Phosphorus-Nitrogen-Sulfur Heterocycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 431 — 432

To link to this Article: DOI: 10.1080/10426509408021889

URL: http://dx.doi.org/10.1080/10426509408021889

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 431–432
Reprints available directly from the publisher
Photocopying permitted by license only

EARLY TRANSITION-METAL COMPLEXES OF PHOSPHORUS-NITROGEN-SULFUR HETEROCYCLES

ROBERT HILTS, XIAOLIANG GAO, MASOOD PARVEZ AND TRISTRAM CHIVERS
Department of Chemistry, The University of Calgary, Calgary, Alberta, T2N 1N4, Canada

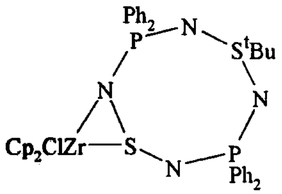
Abstract The preparation, structural characterization and some synthetic applications of the first early transition-metal complexes of the $P_2N_4S_2$ ring are presented.

INTRODUCTION

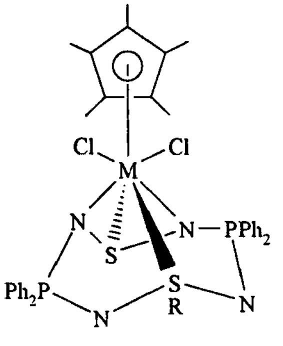
The $R_4P_2N_4S_2$ heterocycles are versatile ligands for a wide variety of transition metals owing to the presence of juxtaposed (hard) nitrogen and (soft) sulfur centers in the skeleton of the ring. Most of the early work with these ligands involved the oxidative-addition of the S-S bond in the neutral rings to electron-rich late transition-metal complexes.[1] The recent development of high yield syntheses for the anionic derivatives $[Li(Ph_4P_2N_4S_2R)(THF)]_2$ (R = alkyl, aryl)[2] and $M_2[Ph_4P_2N_4S_2]$ (M = Li, Na)[3,4] has facilitated a comprehensive study of the coordination chemistry of these ligand systems via metathetical reactions with transition-metal halide complexes. The present paper describes the synthesis, structures and synthetic utility of the first early transition-metal complexes of the $P_2N_4S_2$ ring.

SYNTHESIS AND STRUCTURES OF 1, 2 AND 3

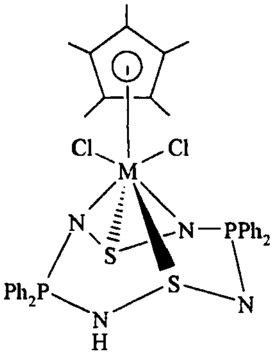
The novel zirconathiaziridene **1** was obtained by treating $ZrCp_2Cl_2$ with ½$[Li(Ph_4P_2N_4S_2{}^tBu)(THF)]$ in THF. When the less sterically crowded $[MCp^*Cl_3]$ (M = Zr, Hf) metal reagents are used in this reaction, complexes of the type **2** are formed. Unlike **1**, in which the heterocyclic ring is bound through adjacent sulfur and nitrogen atoms, the $[Ph_4P_2N_4S_2R]^-$ ligand in **2** is attached in a tetradentate fashion (η^4-N,N′,S,S′) to the metal. The reaction of $[MCp^*Cl_3]$ with $Na_2[Ph_4P_2N_4S_2]$, followed by acidification affords **3**. Like **2**, compound **3** possesses a tetradentate (η^4-N,N′,S,S′) $P_2N_4S_2$ ligand, but, in this case, the exocyclic R group is attached to nitrogen rather than sulfur. In the solid state **3** exists as a hydrogen-bonded dimer.



1



2 (M = Zr, Hf; R = Me, ^tBu)



3 (M = Zr, Hf)

REACTIONS OF 2 AND 3 WITH ELECTROPHILES AND NUCLEOPHILES

The complex **1** reacts with selected electrophiles to give $P_2N_4S_2$ rings with S-organo, S-halogeno or N-H functionalities. Hard electrophiles, such as H^+, are transferred regiospecifically to nitrogen atoms in the ring while soft electrophiles, such as Br^+ and CH_3^+, end up on sulfur. The nucleophilic attack of PMe_3 on **2** results in an unprecedented ring opening of the heterocyclic ligand and the eventual formation of the acyclic compound, $[Me_3P{=}NPPh_2NS(Me)NPPh_2NH_2]Cl$.

REFERENCES

1. See, for example: T. Chivers, M. Edwards, A. Meetsma, J. C. van de Grampel and A. van der Lee, Inorg. Chem., 31, 2156 (1991).
2. T. Chivers, M. Edwards, R. W. Hilts, M. Parvez and R. Vollmerhaus, J. Chem. Soc., Chem. Commun., 1483 (1993).
3. T. Chivers, M. Cowie, M. Edwards and R. W. Hilts, Inorg. Chem., 31, 3349 (1992).
4. T. Chivers, X. Gao and R. Vollmerhaus, unpublished results.