

This article was downloaded by:

On: 28 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>

## Paramagnetic Phosphametalloenes

C. Burney<sup>a</sup>; D. Carmichael<sup>b</sup>; K. Forissier<sup>b</sup>; J. C. Green<sup>a</sup>; F. Mathey<sup>b</sup>; L. Ricard<sup>b</sup>; S. Wendicke<sup>b</sup>

<sup>a</sup> Ecole Polytechnique, France <sup>b</sup> University of Oxford, United Kingdom

Online publication date: 27 October 2010

**To cite this Article** Burney, C. , Carmichael, D. , Forissier, K. , Green, J. C. , Mathey, F. , Ricard, L. and Wendicke, S.(2002) 'Paramagnetic Phosphametalloenes', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 177: 8, 1999 – 2000

**To link to this Article:** DOI: 10.1080/10426500213308

**URL:** <http://dx.doi.org/10.1080/10426500213308>

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.

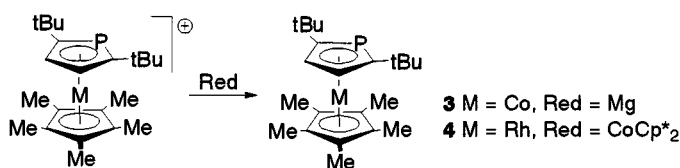
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any 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.

## PARAMAGNETIC PHOSPHAMETALLOCENES

*C. Burney,<sup>a</sup> D. Carmichael,<sup>b</sup> K. Forissier,<sup>b</sup> J. C. Green,<sup>a</sup>  
 F. Mathey,<sup>b</sup> L. Ricard,<sup>b</sup> and S. Wendicke<sup>b</sup>*  
*Ecole Polytechnique, France<sup>a</sup> and University of Oxford,  
 United Kingdom<sup>b</sup>*

(Received July 29, 2001; accepted December 25, 2001)

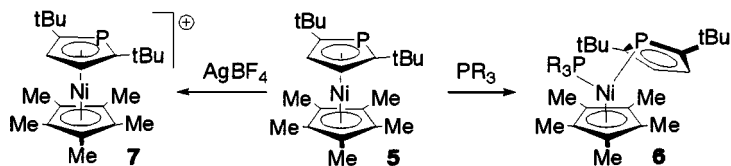
Reduction of monophosphacobaltocenium **1** ( $E_{1/2} = -0.74$  V in thf, SCE) and monophospharhodocenium **2** ( $E_{1/2} = -1.27$  V, thf) salts<sup>1,3</sup> leads cleanly to the corresponding purple (**3**, Co) and green (**4**, Rh) paramagnetic 19ve phosphametalloenes. Cyclic voltammetry (thf) implies that the corresponding monophosphairidocene is unstable. For **3**, NMR, x-ray, PES, and ADF analyses give a classical metallocene structure having a SOMO node at phosphorus. <sup>1</sup>H NMR suggests a similar structure for **4**.



SCHEME 1

Deep green monophosphanickelocene **5**, prepared from the corresponding lithium phospholide<sup>2</sup> with [NiCp\*(acac)], is a 20ve diradical. Treatment with 2e donors (PMe<sub>3</sub>, P(OMe)<sub>3</sub>) provokes an  $\eta^5$  to  $\eta^1$  ligation shift to form the 18ve complexe **6**. Mono-electronic oxidation ( $E_{1/2} = 0.03$  V, thf) using AgBF<sub>4</sub> gives an orange 19ve phosphanickelocenium sandwich complex **7**, whose SOMO is again nodal at P.

Address correspondence to K. Forissier, Laboratoire Hétéroéléments et Coordination, UMR CNRS 7653, Ecole Polytechnique, 91128 Palaiseau Cedex, France.



SCHEME 2

## REFERENCES

- [1] K. Forissier, L. Ricard, D. Carmichael, and F. Mathey, *Organometallics*, **19**, 954 (2000).
- [2] D. Carmichael, L. Ricard, and F. Mathey, *Chem. Commun.*, 1167 (1994).
- [3] G. Herberich and B. Ganter, *Inorg. Chem. Comm.*, **4**, 100 (2001).