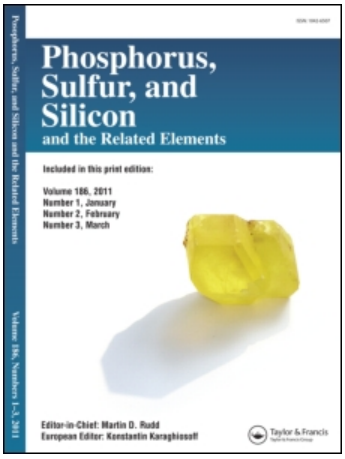

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Paramagnetic Phosphametallocenes

C. Burney[a]; D. Carmichael[b]; K. Forissier[b]; J. C. Green[a]; F. Mathey[b]; L. Ricard[b]; S. Wendicke[b]
[a] Ecole Polytechnique, France [b] University of Oxford, United Kingdom

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PARAMAGNETIC PHOSPHAMETALLOCENES

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

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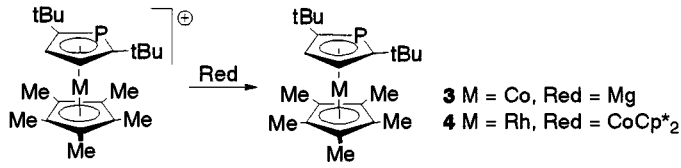
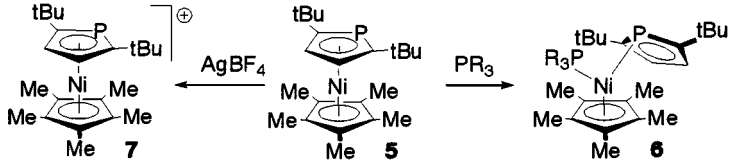
Reduction of monophosphacobaltocenium **1** ($E_{1/2} = -0.74$ V in thf, SCE) and monophospharhodocenium **2** ($E_{1/2} = -1.27$ V, thf) salts[1,3] leads cleanly to the corresponding purple (**3**, Co) and green (**4**, Rh) paramagnetic 19ve phosphametallocenes. Cyclic voltammetry (thf) implies that 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. ^{1}H NMR suggests a similar structure for **4**.



SCHEME 1

Deep green monophosphanickelocene **5**, prepared from the corresponding lithium phospholide[2] with [NiCp*(acac)], is a 20ve diradical. Treatment with 2e donors (PMe_3, $P(OMe)_3$) provokes an η^5 to η^1 ligation shift to form the 18ve complexe **6**. Monoelectronic oxidation ($E_{1/2} = 0.03$ V, thf) using $AgBF_4$ gives an orange 19ve phosphanickelocenium sandwich complex **7**, whose SOMO is again nodal at P.

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



SCHEME 2

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