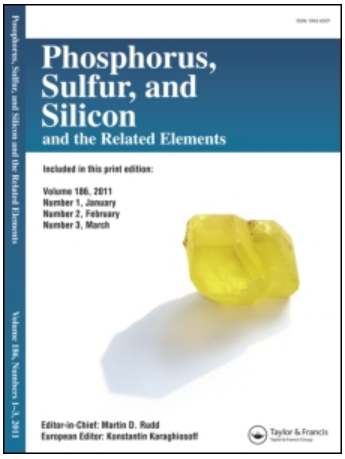

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Pentacoordinate Phosphorus in Transition-Metal Chemistry

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PENTACOORDINATE PHOSPHORUS IN TRANSITION-METAL CHEMISTRY

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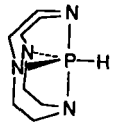
Abstract The pentacoordinate phosphorus molecule, cyclenphosphorane (cyclenPH), is found to be a useful and unique ligand in transition-metal chemistry. It reacts with metal-carbonyl dimers to cleave the dimers and yield covalent phosphoranide-metal complexes and metal carbonyl anions. With *cis*-$Cl_2Pt(PPh_3)_2$, two phosphoranide-metal complexes are formed, one ionic and the other covalent. A unique reaction occurs with $ClRh(PPh_3)_3$ where, initially, a product is obtained in which one of the P-N bonds of the cyclenP moiety is cleaved. This species undergoes a three-fragment oxidative addition of CH_2Cl_2 to reform the pentacoordinate phosphorus and also form a novel P-N-C-Rh metallocycle.

INTRODUCTION

The reactions of cyclenphosphorane, cyclenPH[1], with transition-metal carbonyl



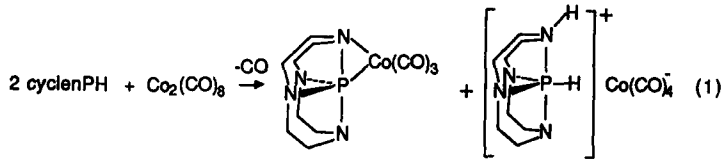
cyclenPH

dimers, $HWCp(CO)_3$ (Cp=η^5-C_5H_5), *cis*-$Cl_2Pt(PPh_3)_2$ (Ph=phenyl) and $ClRh(PPh_3)_3$ are reported.

RESULTS AND DISCUSSION

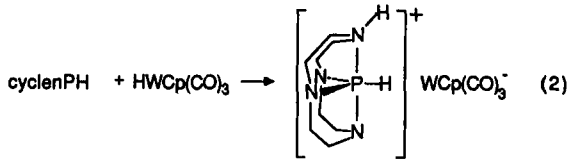
The reactions of cyclenPH with transition-metal carbonyl dimers proceeds, in general, to cleave the dimers yielding covalent phosphoranide-metal complexes and metal carbonyl anions. For example, the reaction of cyclenPH with $Co_2(CO)_8$

yields (η^2-cyclenP)$Co(CO)_3$ and (cyclenPH_2)[$Co(CO)_4$] according to reaction 1 at low temperatures.



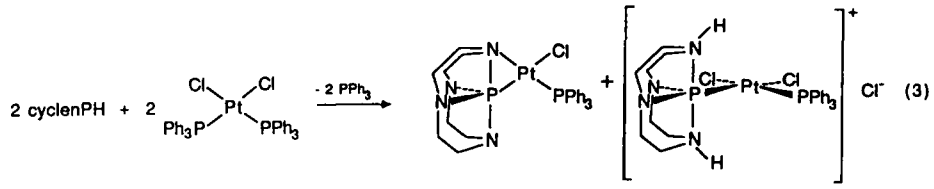
At elevated temperatures (in solution), (cyclenPH_2)[$Co(CO)_4$] loses H_2 and CO to give (η^2-cyclenP)$Co(CO)_3$. Similarly, (η^2-cyclenP)$MoCp(CO)_2$ and (cyclenPH_2)[$MoCp(CO)_3$] are formed by reaction of cyclenPH with [$MoCp(CO)_3$], except that elevated temperatures (refluxing THF) are necessary and the salt does not lose H_2 and CO. With $Mn_2(CO)_{10}$, no covalent compound could be isolated, only the salt (cyclenPH_2)[$Mn(CO)_5$] was obtained. No reaction is found with [$FeCp(CO)_2$]$_2$.

A possible mechanism for these reactions could involve formation of a metal-hydride intermediate [similar to the reaction of Me_3SiH with $Co_2(CO)_8$[2]. We do find cyclenPH to cleanly abstract a proton from $HWCp(CO)_3$ to yield (cyclenPH_2)[$WCp(CO)_3$]:



The structures of (η^2-cyclenP)$Co(CO)_3$ and (η^2-cyclenP)$MoCp(CO)_2$ have been confirmed by X-ray crystallography. The N_4P skeletal geometry is very close to trigonal bipyramidal with one long P-N bond of about 1.85 Å (in the metallocycle) and three shorter P-N bonds of about 1.70 Å each.

A covalent and ionic product are formed from the reaction of cyclenPH with *cis*-$Cl_2Pt(PPh_3)_2$ (reaction 3).



(3)

The X-ray structure of (η^2-cyclenP)PtCl(PPh_3) shows the bidentate nature of the cyclenP moiety and the *cis* arrangement of phosphorus atoms. The geometry of the cyclenP group is almost identical to that in (η^2-cyclenP)$Co(CO)_3$ and (η^2-cyclenP)$MoCp(CO)_3$.

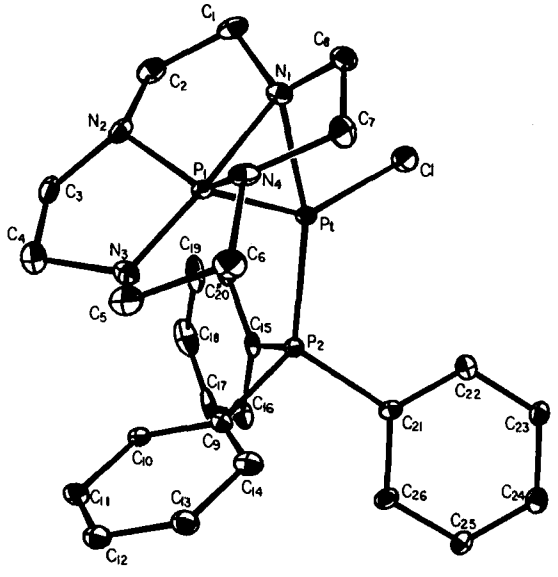
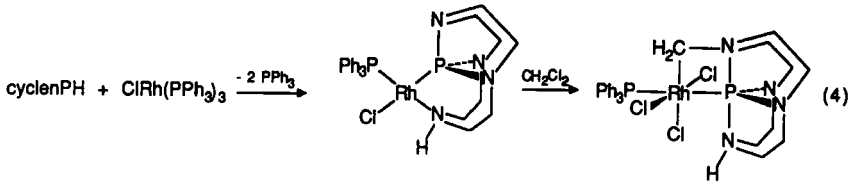


FIGURE 1 The structure of (η^2-cyclenP)PtCl(PPh_3).

Cleavage of one P-N bond is initially observed in the reaction of cyclenPH with Wilkinson's catalyst. However, this product undergoes a three-fragment oxidative addition of dichloromethane to reform the P-N bond and give a phosphoranide-metal complex with a novel P-N-C-Rh metallocycle (reaction 4).



The structure of the final product was confirmed by X-ray crystallography.

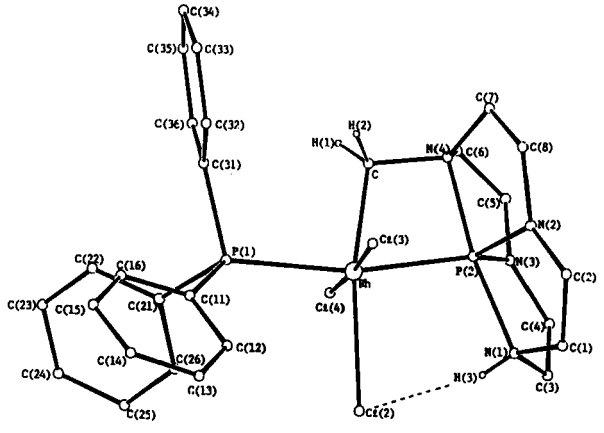


FIGURE 2 The structure of (cyclenPH)(CH_2)$RhCl_3$(PPh_3).

ACKNOWLEDGEMENT

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