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Pentacoordinate Phosphorus in Transition-Metal Chemistry

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PENTACOORDINATE PHOSPHORUS IN TRANSITION-METAL CHEMISTRY

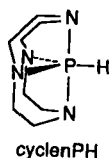
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Abstract The pentacoordinate phosphorus molecule, cyclenphosphorane (cyclenPH), is found to be a useful and unique ligand in transition-metal chemistry. It reacts with metal-carbonyl dimers to cleave the dimers and yield covalent phosphoranide-metal complexes and metal carbonyl anions. With *cis*-Cl₂Pt(PPh₃)₂, two phosphoranide-metal complexes are formed, one ionic and the other covalent. A unique reaction occurs with ClRh(PPh₃)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 CH₂Cl₂ to reform the pentacoordinate phosphorus and also form a novel P-N-C-Rh metallocycle.

INTRODUCTION

The reactions of cyclenphosphorane, cyclenPH¹, with transition-metal carbonyl

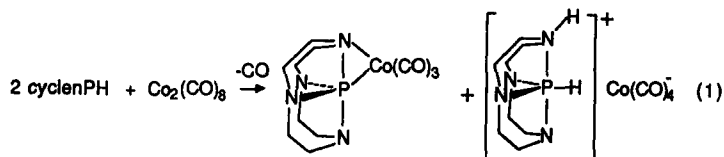


dimers, HW Cp(CO)₃ (Cp=η⁵-C₅H₅), *cis*-Cl₂Pt(PPh₃)₂ (Ph=phenyl) and ClRh(PPh₃)₃ are reported.

RESULTS AND DISCUSSION

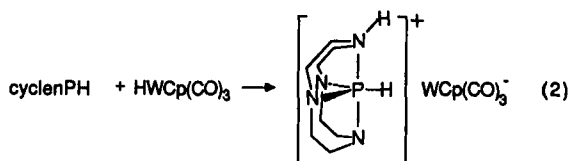
The reactions of cyclenPH with transition-metal carbonyl dimers proceeds, in general, to cleave the dimers yielding covalent phosphoranide-metal complexes and metal carbonyl anions. For example, the reaction of cyclenPH with Co₂(CO)₈

yields $(\eta^2\text{-cyclenP})\text{Co}(\text{CO})_3$ and $(\text{cyclenPH}_2)[\text{Co}(\text{CO})_4]$ according to reaction 1 at low temperatures.



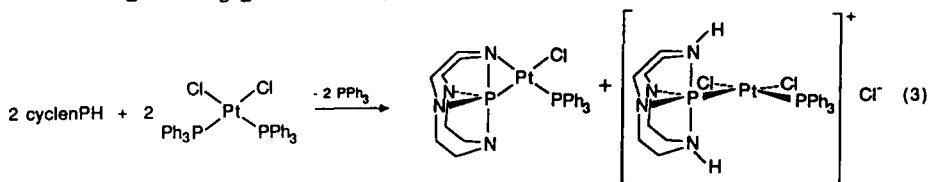
At elevated temperatures (in solution), $(\text{cyclenPH}_2)[\text{Co}(\text{CO})_4]$ loses H_2 and CO to give $(\eta^2\text{-cyclenP})\text{Co}(\text{CO})_3$. Similarly, $(\eta^2\text{-cyclenP})\text{MoCp}(\text{CO})_2$ and $(\text{cyclenPH}_2)[\text{MoCp}(\text{CO})_3]$ are formed by reaction of cyclenPH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

A possible mechanism for these reactions could involve formation of a metal-hydride intermediate [similar to the reaction of Me_3SiH with $\text{Co}_2(\text{CO})_8^2$]. We do find cyclenPH to cleanly abstract a proton from $\text{HWCp}(\text{CO})_3$ to yield $(\text{cyclenPH}_2)[\text{WCp}(\text{CO})_3]$:



The structures of $(\eta^2\text{-cyclenP})\text{Co}(\text{CO})_3$ and $(\eta^2\text{-cyclenP})\text{MoCp}(\text{CO})_2$ 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*-Cl₂Pt(PPh₃)₂ (reaction 3).



The X-ray structure of (η²-cyclenP)PtCl(PPh₃) 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 (η²-cyclenP)Co(CO)₃ and (η²-cyclenP)MoCp(CO)₃.

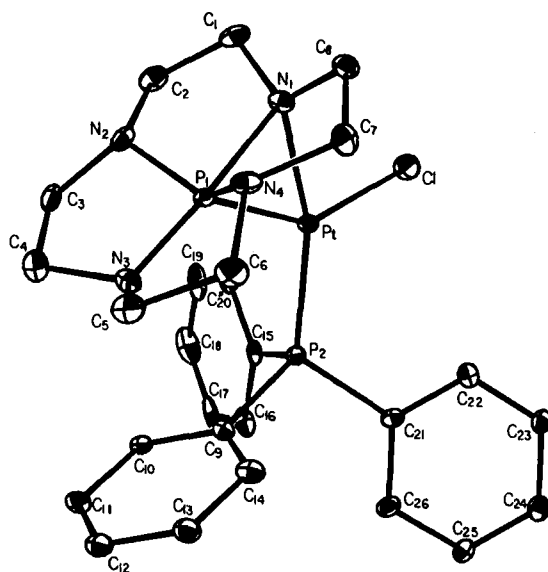
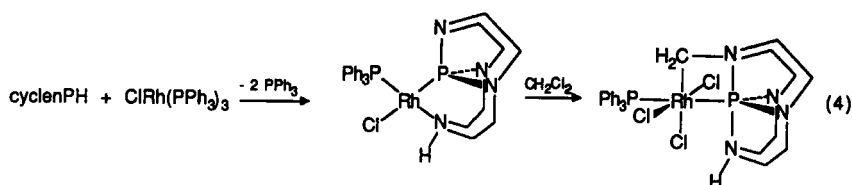


FIGURE 1 The structure of (η²-cyclenP)PtCl(PPh₃).

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.

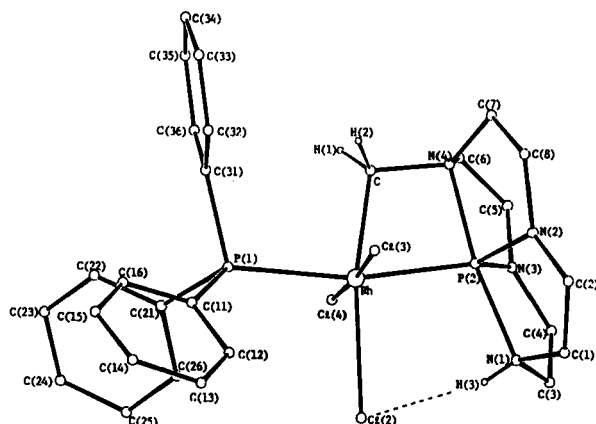


FIGURE 2 The structure of $(\text{cyclenPH})(\text{CH}_2)\text{RhCl}_3(\text{PPh}_3)$.

ACKNOWLEDGEMENT

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