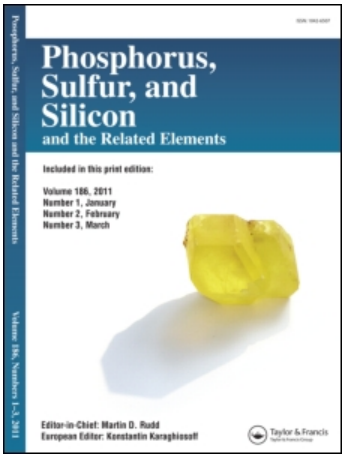

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Reactions of a Cyclenphosphoranide Platinum (II) Complex and the Role of Highly Nucleophilic Substituents at the Axial Positions of a Trigonal Bipyramid

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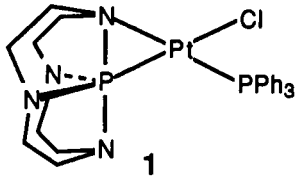
Abstract (η^2-cyclenP)Pt(Cl)PPh_3 **1** exhibits a large variety of selective reactions due to the platinum metal and cyclenphosphoranide ligand, cyclenP. Moreover, the cyclenP ligand is capable of altering many of the usual reactions and/or mechanisms at square planar platinum (II) complexes.

INTRODUCTION

(η^2-cyclenP)Pt(Cl)PPh_3 **1** undergoes reactions that involve the phosphoranide, $R_4P:^-$, ligand (cyclenP), the platinum, or a combination of both. Evidence shows that the cyclenP ligand is capable of altering many of the usual reactions and/or mechanisms at square planar platinum (II) complexes.



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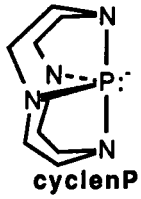
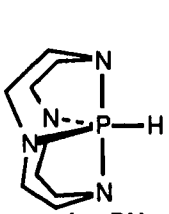


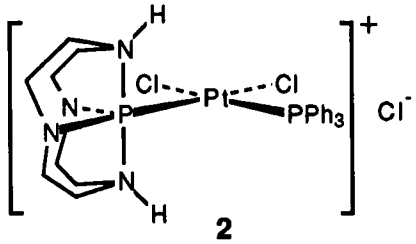
cyclenP

RESULTS AND DISCUSSION

We have previously reported the synthesis of **1** by the reaction of cyclenPH[1] with *cis*-$Cl_2Pt(PPh_3)_2$.[2] The addition of HCl to this complex results in cleavage of the Pt-N bond and dual protonation at the axial positions of the cyclenP ligand yielding *cis*-[$Cl_2Pt(H_2$cyclenP)PPh_3]X **2**. Attempts to isolate a monoprotonated intermediate in this reaction by addition of less than two equivalents of HCl led to only **2** and unreacted **1**. The usual mechanism of HCl addition to square planar platinum (II) complexes involves oxidative addition to the platinum, followed by reductive elimination. An alternative, or perhaps additional, possibility with **1** is the ability of the cyclenP ligand to

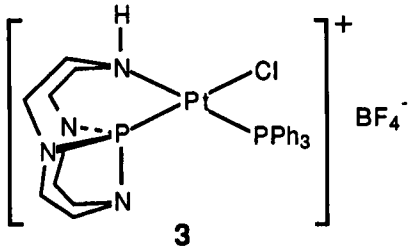


cyclenPH



2

open and close during reaction. In fact, protonation of **1** using HBF_4, an acid with a noncoordinating anion, allows isolation of $[(\eta^2\text{-HcyclenP})Pt(Cl)PPh_3]BF_4$ **3**, a complex



3

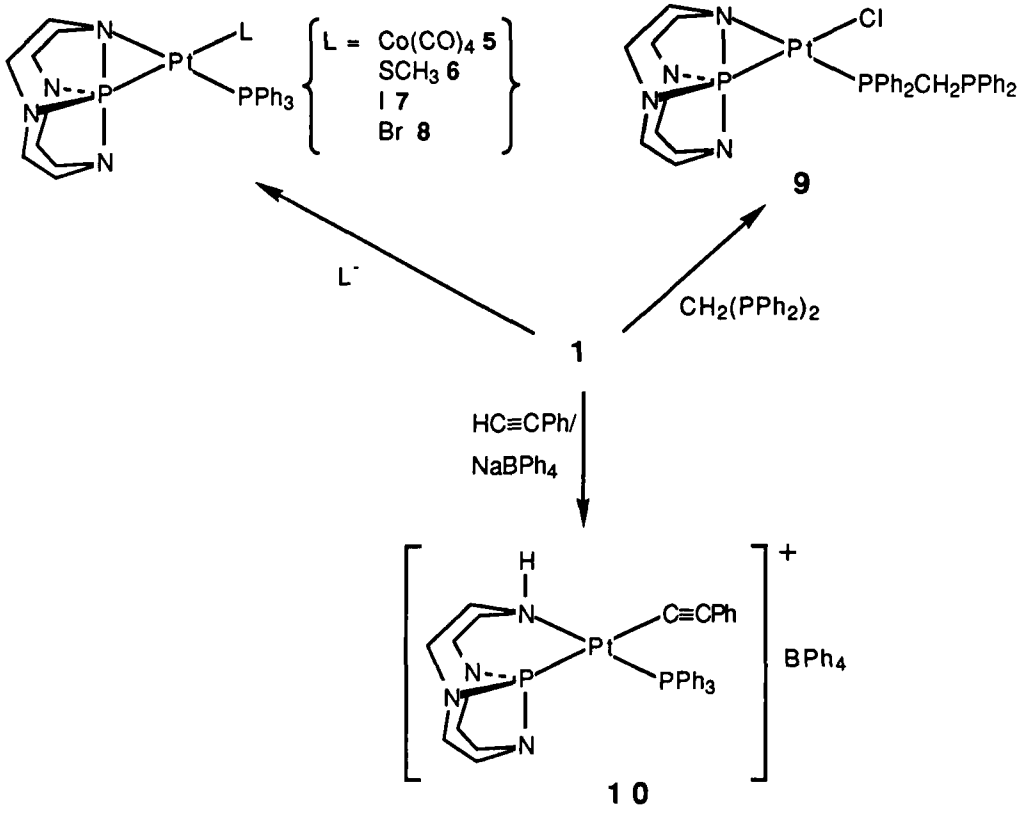
in which cyclenP is ligated in the "open" form. Support for the open form of cyclenP comes from the large downfield ^{31}P chemical shift of the cyclenP phosphorus, + 94 ppm in **3** compared to - 55 ppm (in **1**) and - 59 ppm (in **2**). The disappearance of the upfield negative resonance and the appearance of a downfield one is consistent with coordination of the open form of the cyclenP ligand and has been observed before with rhodium complexes.[3] The ^1H NMR spectrum shows (in addition to the expected phenyl and methylene resonances) a broad peak at δ 6.06 which integrates to one proton. These spectra are consistent with P-N bond cleavage and coordination of the open form of cyclenP with one of the nitrogens protonated.

Support for the intermediacy of **3** in the conversion of **1** to **2** comes from the further reaction of **3** with HCl which yields $[(H_2cyclenP)PtCl_2PPh_3]BF_4$ **4**, which is the BF_4 salt of the cation of **2**. Interestingly, treatment of **3** with another equivalent of HCl results in disproportionation, yielding **1** and **2**.

While very strong electrophiles, such as the above protic acids, attack the cyclenP ring, nucleophiles lead to ligand substitution at platinum. For example, reactions of **1** with $Na[Co(CO)_4]$, NaSMe, KI, and KBr, gave the chloride substitution products, (η^2-cyclenP)PtLPPh$_3$, where L = $Co(CO)_4$ **5**, SMe **6**, I **7**, and Br **8**. Neutral donors, on the other hand, appear to favor PPh_3 displacement: reaction of **1** with $CH_2(PPh_2)_2$ (dppm) led to (η^2-cyclenP)Pt(Cl)$PPh_2CH_2PPh_2$ **9**, in which the dppm is monodentate.

Very weak electrophiles do not appear to react directly with **1**. For example, no reaction was observed between **1** and HC≡CPh, even in refluxing THF. However, addition of $NaBPh_4$ to the reaction led to both P-N bond cleavage and Pt-C bond formation, yielding $[(\eta^2$-HcyclenP)Pt(C≡CPh)$PPh_3]BPh_4$ **10**. In this case, the sodium helps displace the chloride, while the nitrogen on the cyclenP ligand leads to C-H activation of the alkyne. This reaction again illustrates the ability of the cyclenP ligand to alter the usual products and/or mechanisms at square planar platinum (II) centers: the expected reaction would lead to either π-coordination of the alkyne or oxidative addition of the alkyne fragments to the metal. The reactions leading to products **5** through **10** are summarized in Scheme 1.

Scheme 1



Several mechanisms are consistent with the formation of **10**. One is Pt-Cl bond rupture, followed by π-coordination of the alkyne, then C-H bond cleavage and

rearrangement to a terminal alkyne. Another is N-protonation, followed by displacement of Cl^- by $C{\equiv}CPh^-$. The fact that we found no reaction when **1** was treated with $PhC{\equiv}CPh$ and $NaBPh_4$ suggests that the π-bonding mechanism may not be involved in the synthesis of **10** and that N-protonation may occur before alkyne coordination.

The above reactions demonstrate, not only the remarkable range of reactivity of metal complexes containing the cyclenP ligand, but also the selectivity. Thus, anionic nucleophiles displace chloride, while neutral donors favor PPh_3 substitution. Cationic electrophiles with noncoordinating anions attack nitrogen leading to P-N bond cleavage; those with coordinating anions lead to N-Pt bond cleavage (leading to **2**). Moreover, the synthesis of **10** shows that, by a suitable choice of reagents, combinations of these reactivities (such as P-N bond cleavage and chloride substitution) can be achieved in one reaction, here leading to the activation of C-H bonds.

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