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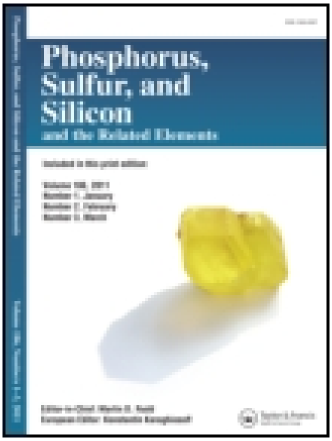

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Novel Heterocyclic P-Ligands: Synthesis and Application in Pt(II) Complexes

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Novel Heterocyclic P-Ligands: Synthesis and Application in Pt(II) Complexes

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3-Diphenylphosphino-1,2,3,6-tetrahydro- and 1,2,3,4,5,6-hexahydro-phosphinines, as well as dibenzo[c,e][1,2]oxaphosphorines (L) were prepared and used in the synthesis of the corresponding cis chelate Pt(II) complexes and $PtCl_2L_2$ complexes, respectively. The latter family of compounds includes 7-membered ring Pt(II) complexes.

Keywords P-heterocycles; monodental and bidental P-ligands; Pt(II) complexes; ring Pt(II) complexes; stereospecific ^{3}J(P-Pt) NMR couplings

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INTRODUCTION

In this article, we summarize our recent results on P-ligands and their platinum complexes. It was found earlier that the interaction of arylphospholes and dichlorodibenzonitrile platinum formed a mixture of a monophosphole and a diphosphole complex, this latter with *trans* orientation of the hetero rings.[1] As a comparison, an analogous reaction of the Mathey-phosphole led, almost exclusively, to the *cis* diphosphole complex. The difference is due to the presence or lack of steric hindrance. Other P-heterocycles, such as phosphabicyclo[3.1.0]hexanes, 1,2-dihydrophosphinines and 1,4-dihydrophosphinines were converted to Rh(III) or Pd(II) complexes.[2]

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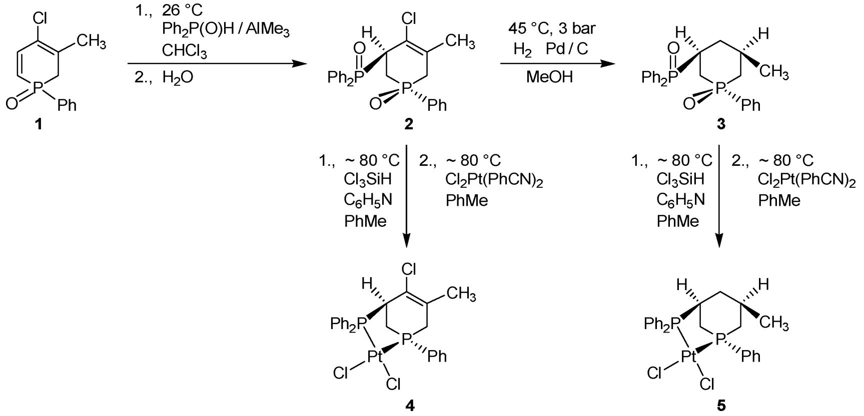
New phosphinine derivatives with exocyclic P-functions were developed by us (Scheme 1). The Michael-addition of diphenylphosphine oxide to 1-phenyl-1,2-dihydrophosphinine oxide (**1**) afforded a 3-diphenylphosphinoxido-1,2,3,6-tetrahydrophosphinine oxide (**2**)[3] that was converted to the corresponding 1,2,3,4,5,6-hexahydrophosphinine oxide (**3**).[4] Both bis(phosphine oxides) were formed in a diastereoselective manner, whose stereostructures were evaluated by DFT calculations and/or stereospecific NMR couplings. The phosphinoxido-tetrahydrophosphinine oxide (**2**) was subjected to double deoxygenation to provide the corresponding bis(phosphine) with preserved stereochemistry that on reaction with the platinum precursor led to a *cis* chelate complex (**4**).[5] The phosphinoxido-hexahydrophospinine oxide (**3**) was taken in a similar sequence of reactions to furnish another *cis* chelate complex (**5**) as the final outcome.[6]



SCHEME 1

On a related topic, dibenzo-oxaphosphorines with a variety of P-substituents were synthesized and used in complexations. In the first place, aryl-dibenzooxaphosporines (**7**) were made available from the P-chloro derivative (**6**), and than converted to the platinum complexes containing only one heterocyclic unit. It was interesting to find, on the basis of stereospecific Pt–P couplings, that in the case of phenyl substituent a *cis* complex (**8**), while in the case of triisopropylphenyl group a *trans* complex (**9**) was formed (Scheme 2).[7]

Then a few P-alkoxy and P-amino dibenzooxaphosphorines (**10**) were prepared and transformed to the corresponding platinum complexes (**11**) that in this particular case contained two heterocyclic P-ligands, moreover in position *cis*.[8] In the next stage, α-phenylethylamino- and menthyl-dibenzooxaphosphorines (**12** and **14**)[8] with optical activity and

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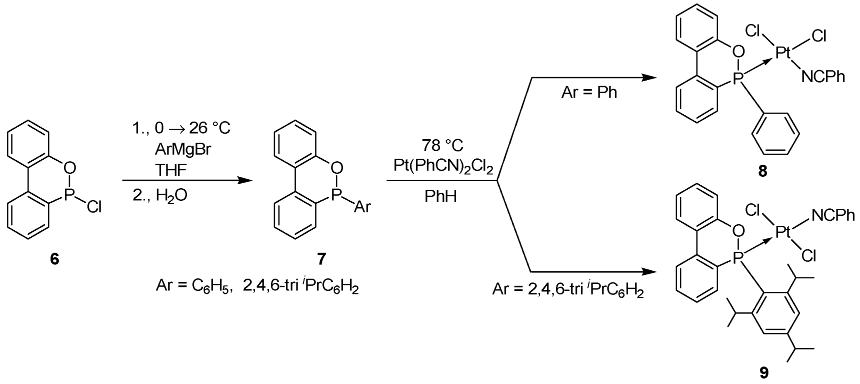
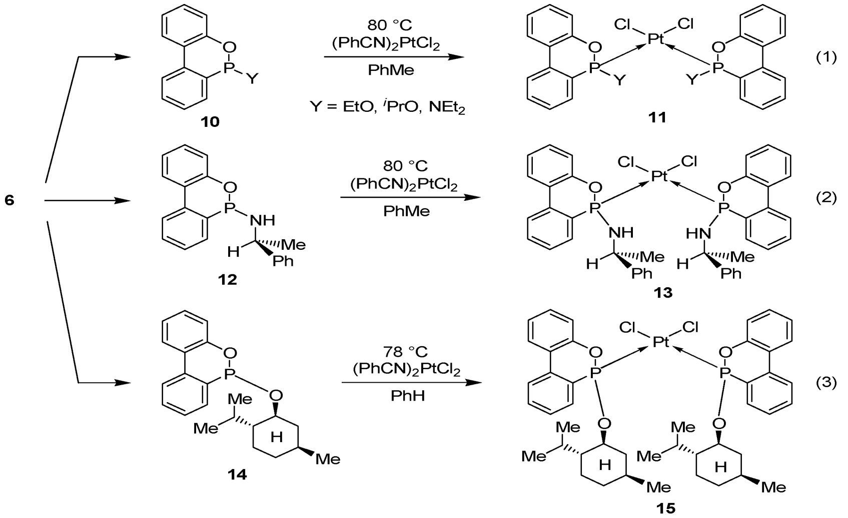


SCHEME 2

the related complexes (**13** and **15**)[9] were synthesized (Scheme 3). In the first case, the complex (**11**) was formed in a homo- and a heterochiral form, while in the other two cases, the complexes (**13** and **15**) were obtained in two homochiral forms and a heterochiral form.



SCHEME 3

The L-prolin methyl ester served as an additional reagent for the P-substitution of the chloro-dibenzooxaphosphorine (**6**). Complexation of the prolino-dibenzooxaphosphorine (**16**) led to the *cis* form of the bis(dibenzooxaphosphorino) platinum complex (**17**) (Scheme 4).

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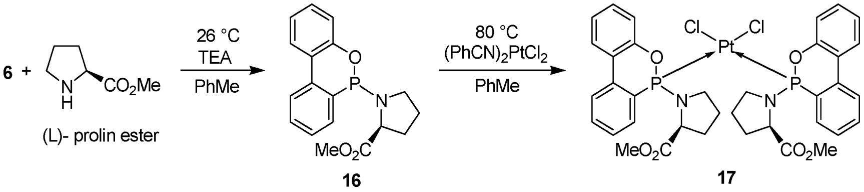
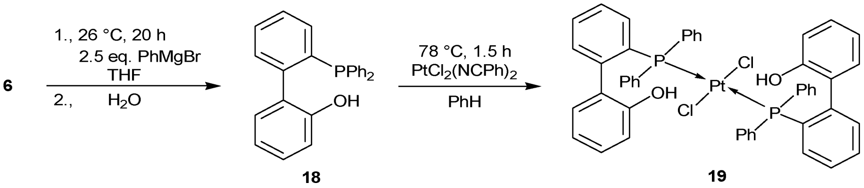


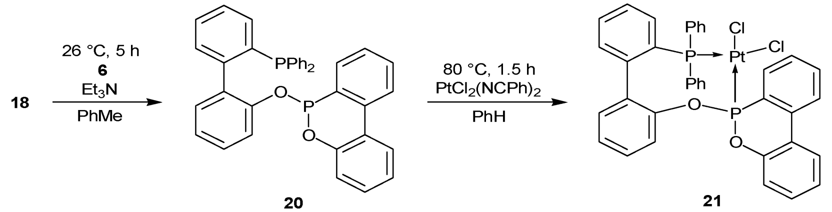
SCHEME 4

Ring opening reaction accompanying the substitution of the starting dibenzooxaphosphorine (**6**) furnished a new P-ligand (**18**), which on reaction with the platinum precursor gave a bis(triarylphosphino) complex (**19**) (Scheme 5). In this case, the substituents were, however, in the *trans* disposition, as suggested by sterospecific Pt–P couplings.[10]



SCHEME 5

Phosphorylation of the 1-hydroxy-1′-diphenylphosphino-biphenyl (**18**) with chloro-dibenzooxaphosphorine offered a newer possibility for ligand modification. Complexation of the special bidentate P-ligand (**20**) so obtained, led to a special ring Pt-complex (**21**) (Scheme 6).[10]



SCHEME 6

Aiming at the synthesis of further bidental P-ligands, methylaminoethanol was reacted with two equivalents of chloro-dibenzooxaphosphorine (**6**). The reaction took place smoothly and the resulting bisdibenzooxaphosphorine (**22**) was utilized in the preparation of a ring platinum complex (**23**) (Scheme 7).

L-Ephedrine was taken in a similar sequence of reactions to afford, eventually, an analogous 7-ring platinum complex (**25**) (Scheme 8).

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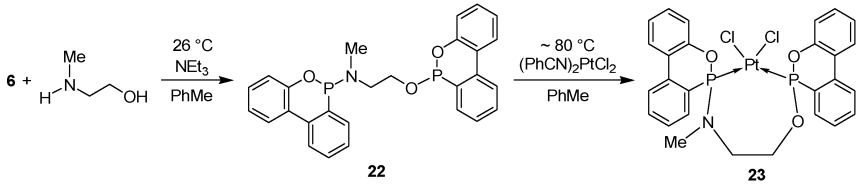
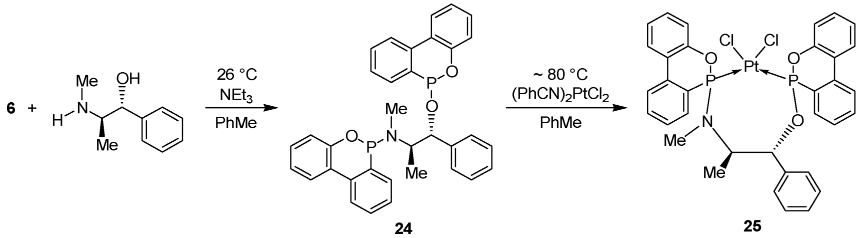


SCHEME 7



SCHEME 8

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