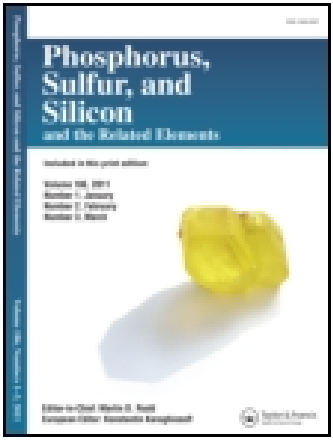

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

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Published online: 02 Apr 2008.

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 215-218
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New Chiral Ligands and Complexes from α-Amino Acids

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N-diphenylphosphinoamino methyl/ethyl esters, dppam, react with [$PtCl_2$(cod)] and [RhCl(cod)]$_2$ to give *cis*-[$PtCl_2$(dppam-P)$_2$] and [RhCl(cod)(dppam-P], while interaction of dppam with [$PdCl_2$(cod)] leads to different complexes.

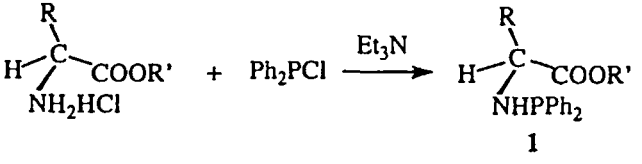
Keywords: N-diphenylphosphinoamino esters; [$PtCl_2$(cod)]; [RhCl(cod)]$_2$; [$PdCl_2$(cod)]

INTRODUCTION

Chiral Complexes are very important in catalytic asymmetric synthesis. As natural and readily available chiral compounds, amino acids are often employed as starting material for chiral ligands.[1-4] There are several reports[5-7] which involve N,N-bis(diphenylphosphino)amino esters, but no N-mono(diphenylphosphino)amino ester complexes are found except one report about the stereoselective synthesis of the N-phosphorus(V) substituted amino acids via the N-phosphorus(III) derivative of amino acids.[8] Here we present some new N-diphenylphosphinoamino esters and the corresponding chiral complexes of these ligands.

RESULTS AND DISCUSSION

S-α-amino esters react with one equivalent of chlorodiphenylphosphine to give S-N-diphenylphosphinoamino esters **1** in the presence of triethylamine in yields up to 90% (**SCHEME** 1).

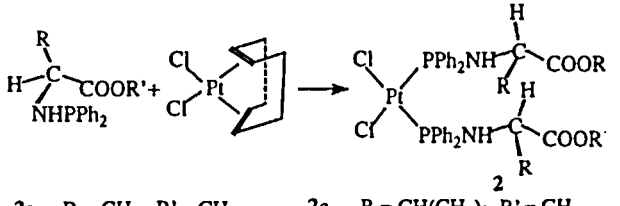


1

1a dppal $R = CH_3$, $R' = CH_3$ **1c** dppval $R = CH(CH_3)_2$, $R' = CH_3$
1b dppgl $R = CH_2CH_2CO_2CH_2CH_3$, $R' = CH_2CH_3$ **1d** dpppal $R = CH_2Ph$, $R' = CH_3$
1e dppmet $R = CH_2CH_2SCH_3$, $R' = Cl$

SCHEME 1

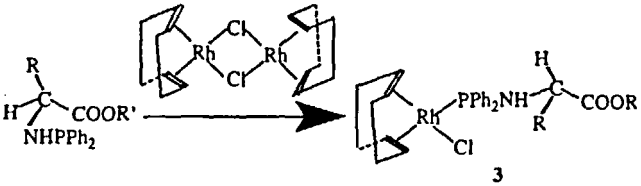
Compounds **1** react with $[PtCl_2(cod)]$ and $[RhCl(cod)]_2$ to give *cis*-$[PtCl_2(dppam\text{-}P)_2]$ **2**, $[RhCl(cod)(dppam\text{-}P)]$ **3** as expected (**SCHEME** 2 and **SCHEME** 3).



2

2a $R = CH_3$, $R' = CH_3$ **2c** $R = CH(CH_3)_2$, $R' = CH_3$
2b $R = CH_2CH_2CO_2CH_2CH_3$, $R' = CH_2CH_3$ **2d** $R = CH_2Ph$, $R' = CH_3$
2e $R = CH_2CH_2SCH_3$, $R' = CH$

SCHEME 2

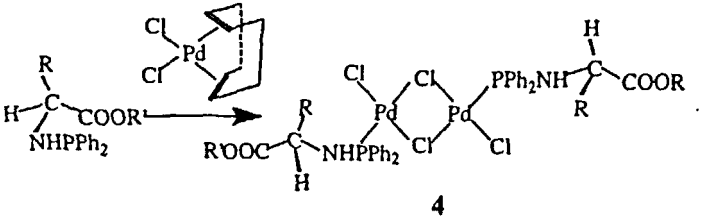


3

3a	$R = CH_3$, $R' = CH_3$	**3c**	$R = CH(CH_3)_2$, $R' = CH_3$
3b	$R = CH_2CH_2CO_2CH_2CH_3$, $R' = CH_2CH_3$	**3d**	$R = CH_2Ph$, $R' = CH_3$
		3e	$R = CH_2CH_2SCH_3$, $R' = CH_3$

SCHEME 3

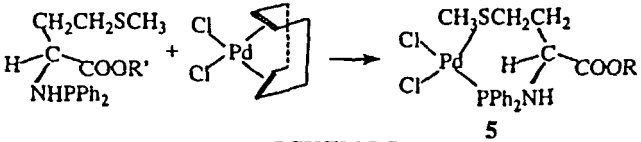
It is surprising that **1** and $[PdCl_2(cod)]$ lead to different products. As shown by **SCHEME 4**, **1a** and **1c** coordinate with $[PdCl_2(cod)]$ to give the surprising chloro-bridged binuclear complexes **4**. But **1e** and $[PdCl_2(cod)]$ gave a chelate hemilabile complex *cis*-$[PdCl_2(dppme\text{-}P,S)]$ **5** (**SCHEME 5**). Other ligands react with $[PdCl_2(cod)]$ to result in rather complicated mixtures which are difficult to separate.



4

4a	$R = CH_3$, $R' = CH_3$	**4c**	$R = CH(CH_3)_2$, $R' = CH_3$

SCHEME 4



5

SCHEME 5

Complexes **2a**, **4a**, and **5** have been confirmed by X-ray crystallographic analysis.

ACKNOWLEDGEMENTS

We wish to thank Johnson Matthey plc for loan of precious metals. Qingzhi Zhang is indebted to St Andrews University and Prof. J. D. Woollins as well as the Chinese Scholarship Council for financial support.

References

[1] F. Agbossou, J-F. Carpentier, F. Hapiot; I. Suisse and A. Mortreux, *Coord. Chem. Rev.*, 1998, **221**, 1615.
[2] L. R. Falvello, S. Fernandez, R. Navarro and A. Urriolabeitia, *New J. Chem.*, 1997, **21**, 909.
[3] P. W. Lednor, W. Beck, H.G. Fick and H H. Zippel *Chem. Ber.*,1978, **111**, 615.
[4] P. W. Lednor, W. Beck and H.G. Fick, *J. Organometall. Chem.*, 1978, **113**, 19.
[5] Trampisch and W. Beck, *Z. Naturforsch; B: Anorg. Chem. Org. Chem.*, 1983, **38**, 365.
[6] N. C. Payne and D. W. Stephan, *J. Organomet. Chem.*, 1981, **221**, 203, 223.
[7] A. Badia, L. R. Falvello, R. Navarro and E. P. Urriolabeitia *J. Organomet. Chem.*, 1998, **554**, 105.
[8] O. I. Kolodiazhnyi, E. V. Grishkun, S. V. Galushko and O. R. Golovatyi, *Phosphorus, Sulfur, and Silicon*, 1995, **103**, 183.