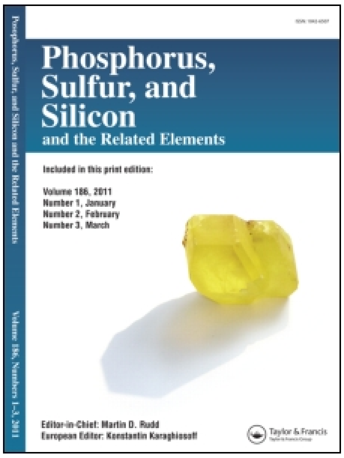

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# Cationic Pd<i>II</i> Complexes of Fesulphos Ligands: Highly Efficient Catalysts for the Enantioselective Ring Opening of Oxa- and Azabicyclic Alkenes with Dialkylzinc Reagents

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# Cationic Pd$^{II}$ Complexes of Fesulphos Ligands: Highly Efficient Catalysts for the Enantioselective Ring Opening of Oxa- and Azabicyclic Alkenes with Dialkylzinc Reagents

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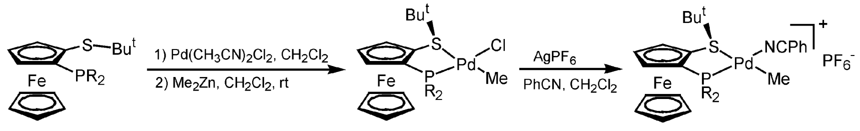
**Keywords** Cationic palladium catalyst; heterobicyclic alkenes; planar chirality; ring-opening; sulfur ligand

## INTRODUCTION

The Pd-catalyzed enantioselective ring-opening reaction of meso oxa- and azabicyclic alkenes with dialkylzinc reagents reported by Lautens et al.[1] constitutes a synthetically outstanding C—C bond-forming desymmetrization reaction. Herein we describe that cationic methyl Pd$^{II}$ complexes of Fesulphos ligands[2] serve as excellent catalysts for this asymmetric transformation, allowing the performance of the reaction at very low-catalyst loading.



***Fesulphos***

R = Ph, **1a**-Pd (Cl)(Me), 80%
R = Cy, **1a**-Pd (Cl)(Me), 94%

[**1a**-Pd(Me)(NCPh)]$^+$PF$_6^-$, 81%

**SCHEME 1**

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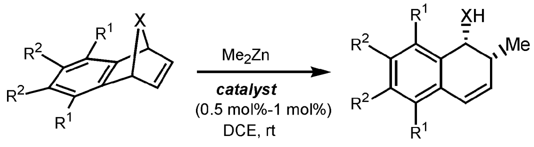

***catalyst***: [**1a**-Pd(Cl)(Me)]+ $Ar_4BNa$ for X=O
[**1a**-Pd(Me)(NCPh)]$PF_6$ for X= NTos

**SCHEME 2**

**TABLE I Ring-Opening Reaction of Oxa- and Azabicyclic Alkenes**

| $R^1$ | $R^2$ | X | Yield (%) | ee (%) |
|---|---|---|---|---|
| H | O | O | 88 | 97 |
| H | $O(CH_2)_2O$ | O | 71 | >99 |
| H | F | O | 95 | 95 |
| OMe | H | O | 98 | 97 |
| H | H | NTs | 50 | 99 |

## RESULTS

The cationic methyl $Pd^{II}$ complexes were easily obtained from Fe-sulphos ligands by initial treatment with $Pd(CH_3CN)_2Cl_2$, followed by transmetalation with $Me_2Zn$ and removal of the second chlorine atom by reaction with $AgPF_6$/benzonitrile. The cationic P,S-Pd complex was isolated as a single isomer having the methyl group *trans* to sulphur as proved by X-ray diffraction analysis (Scheme 1).[3]

Complete conversions, good chemical yields (50–98%), and excellent enantioselectivities (95–>99% ee) were obtained at room temperature in the opening of a wide variety of meso benzobicyclic alkenes, including the much less-reactive aza analogues (Scheme 2 and Table I).

Theoretical studies by DFT methods of the complexation to the alkene have been done to understand the excellent asymmetric induction exerted by these novel catalysts.

## REFERENCES

[1] M. Lautens, and S. Hiebert, *J. Am. Chem. Soc.*, **126,** 1437–1447 (2004).

[2] O. García Mancheño, J. Priego, S. Cabrera, R. Gómez Arrayás, T. Llamas, and J. C. Carretero, *J. Org. Chem.*, **68,** 3679–3686 (2003).

[3] S. Cabrera, R. Gómez Arrayás, and J. C. Carretero, *Angew. Chem., Int. Ed. Engl.*, **43,** 3944–3947 (2004).