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## Phosphorus, Sulfur, and Silicon and the Related Elements

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

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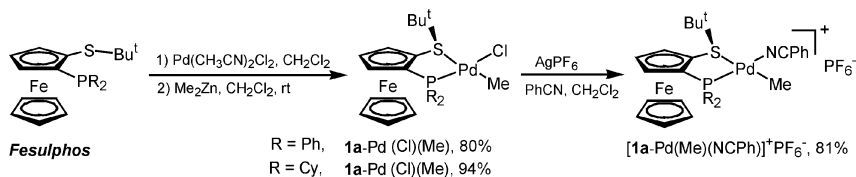
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**Keywords** Cationic palladium catalyst; heterobicyclic alkenes; planar chirality; ring-opening; sulfur ligand

### INTRODUCTION

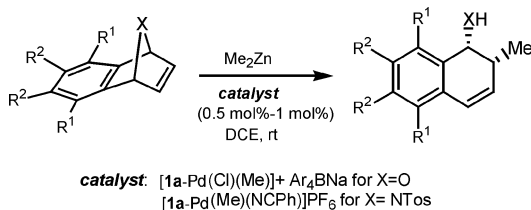
The Pd-catalyzed enantioselective ring-opening reaction of meso oxa- and azabicyclic alkenes with dialkylzinc reagents reported by Lautens et al.<sup>1</sup> constitutes a synthetically outstanding C–C bond-forming desymmetrization reaction. Herein we describe that cationic methyl Pd<sup>II</sup> complexes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



### SCHEME 1

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## SCHEME 2

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

R <sup>1</sup>	R <sup>2</sup>	X	Yield (%)	ee (%)
H	O	O	88	97
H	O(CH <sub>2</sub> ) <sub>2</sub> O	O	71	>99
H	F	O	95	95
OMe	H	O	98	97
H	H	NTs	50	99

## RESULTS

The cationic methyl Pd<sup>II</sup> complexes were easily obtained from Fe-sulphos ligands by initial treatment with Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>, followed by transmetalation with Me<sub>2</sub>Zn and removal of the second chlorine atom by reaction with AgPF<sub>6</sub>/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).<sup>3</sup>

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.

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