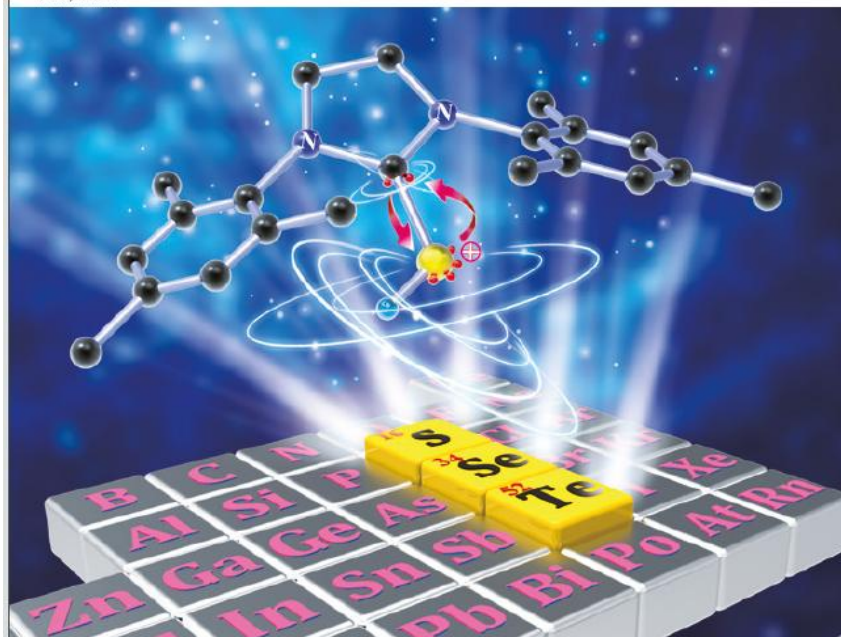


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#### COMMUNICATION

Douglas W. Stephen *et al.*  
N-Heterocyclic carbene stabilized parent sulfenyl, selenenyl,  
and tellurenyl cations (X<sup>+</sup>, X = S, Se, Te)

## Diamidophosphites from $\beta$ -Hydroxyamides: Readily Assembled Ligands for Pd-Catalyzed Asymmetric Allylic Substitution

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**Abstract** Two groups of modular chiral diamidophosphite ligands were easily synthesised from accessible *N*-Boc-amino alcohols and pseudodipeptides. The reaction of these compounds with [Pd(allyl)Cl]<sub>2</sub> in the presence of AgBF<sub>4</sub> yielded complexes [Pd(allyl)(L)<sub>2</sub>]BF<sub>4</sub>. In addition, metalchelates [Pd(allyl)(L)]BF<sub>4</sub> with (*S*)-methioninol-based *P,S*-bidentate ligands were prepared. The structures of the novel ligands and complexes were elucidated by means of 2D-NMR and were confirmed by single-crystal X-ray diffraction, as well as by DFT calculations. Asymmetric inducers of this type exhibited high enantioselectivities in the Pd-mediated allylic substitution of (*E*)-1,3-diphenylallyl ethyl carbonate with CH<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub> (up to 98% *ee*) and (CH<sub>2</sub>)<sub>4</sub>NH (up to 92% *ee*). *Ee* values of up to 86% and 73% obtained in the Pd-catalyzed allylic alkylation of cinnamyl acetate with ethyl 2-oxocyclohexane-1-carboxylate and ethyl 2-oxocyclopentane-1-carboxylate, respectively. The effects of the structural modules, such as the nature of the phosphorus-containing ring or exocyclic substituent, on the catalytic activity and enantioselectivity were investigated.

