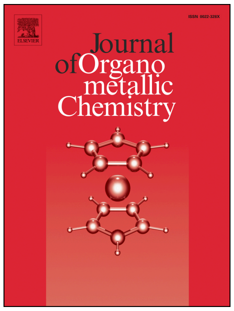

Synthesis, structure, and reactivity of doubly *trans*-spanning bis(dialkyl selenide) complexes; a new route to diselenamacrocycles via alkene metathesis in metal coordination spheres

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!!** REVISED **!!

Synthesis, Structure, and Reactivity of Doubly *trans*-Spanning bis(dialkyl selenide) Complexes; A New Route to Diselenamacrocycles via Alkene Metathesis in Metal Coordination Spheres

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Abstract: The reaction of selenium with $NaBH_4$ and $Br(CH_2)_6CH{=}CH_2$ (2.0 equiv each) gives the dialkyl selenide $Se((CH_2)_6CH{=}CH_2)_2$ (91% after workup) which is combined with $PtCl_2$ (0.5 equiv, toluene) to give *trans*-$PtCl_2(Se((CH_2)_6CH{=}CH_2)_2)_2$ (**10**, 85%). The reaction of **10** and Grubbs' first generation catalyst yields macrocyclic *trans*-$PtCl_2(Se((CH_2)_6CH{=}CH(CH_2)_6)_2$-$Se)$ (**11**, 60%) as a mixture of *syn*/*anti* isomers with respect to the selenium lone pairs. The reaction of **11** and Ph_2Zn gives the diphenyl complex *trans*-$PtPh_2(Se((CH_2)_6CH{=}CH(CH_2)_6)_2Se)$ (**12**, 86%; mixture of isomers). When **11** is treated with H_2 under conditions that hydrogenate related diphosphine complexes (5 bar, 50 °C, $(Ph_3P)_3RhCl$ or PtO_2, CH_2Cl_2), no reaction occurs. Under more forcing conditions, (8 bar, 85 °C, Pd/C, C_2H_5OH), **11** and **12** give the demetalated diselenamacrocycle $Se(C_{14}H_{28})_2Se$ (**13**; 72-67%). The crystal structures of **11** and **12** show *anti* selenium lone pairs and *trans* C=C linkages; that of **13** exhibits columns of extended macrocycles.

Keywords: platinum, selenium, Grubbs' first generation catalyst, alkene metathesis, hydrogenation, crystal structures

Highlights

A diselenamacrocycle is assembled in a platinum coordination sphere by C=C metathesis
Substitution of the chloride ligands of the platinum diselenamacrocycle is possible
Attempted hydrogenation of the diselenamacrocycle detaches it from platinum
All solid state molecular structures of these species exhibit inversion centers

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