

Accepted Manuscript

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PII: S0022-328X(18)30685-5

DOI: [10.1016/j.jorganchem.2018.08.029](https://doi.org/10.1016/j.jorganchem.2018.08.029)

Reference: JOM 20556

To appear in: *Journal of Organometallic Chemistry*

Received Date: 4 August 2018

Revised Date: 25 August 2018

Accepted Date: 29 August 2018

Please cite this article as: H. Joshi, S. Kharel, N. Bhuvanesh, J.A. Gladysz, Synthesis, structure, and reactivity of doubly *trans*-spanning bis(dialkyl selenide) complexes; a new route to diselenamacrocycles via alkene metathesis in metal coordination spheres, *Journal of Organometallic Chemistry* (2018), doi: 10.1016/j.jorganchem.2018.08.029.

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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 NaBH₄ and Br(CH₂)₆CH=CH₂ (2.0 equiv each) gives the dialkyl selenide Se((CH₂)₆CH=CH₂)₂ (91% after workup) which is combined with PtCl₂ (0.5 equiv, toluene) to give *trans*-PtCl₂(Se((CH₂)₆CH=CH₂)₂)₂ (**10**, 85%). The reaction of **10** and Grubbs' first generation catalyst yields macrocyclic *trans*-PtCl₂(Se((CH₂)₆CH=CH(CH₂)₆)₂-Se) (**11**, 60%) as a mixture of *syn/anti* isomers with respect to the selenium lone pairs. The reaction of **11** and Ph₂Zn gives the diphenyl complex *trans*-PtPh₂(Se((CH₂)₆CH=CH(CH₂)₆)₂Se) (**12**, 86%; mixture of isomers). When **11** is treated with H₂ under conditions that hydrogenate related diphosphine complexes (5 bar, 50 °C, (Ph₃P)₃RhCl or PtO₂, CH₂Cl₂), no reaction occurs. Under more forcing conditions, (8 bar, 85 °C, Pd/C, C₂H₅OH), **11** and **12** give the demetalated diselenamacrocycle Se(C₁₄H₂₈)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

submitted to *Journal of Organometallic Chemistry*
for the special issue in honor of Richard J. Puddephatt

dedication: "to our colleague Richard Puddephatt in appreciation of his many contributions to the organometallic chemistry of the noble metals"

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