

[D001]



Synthesis and Structure of Transition Metal Bisalkynylselenolato Complexes

Rudolf Pietschnig*,¹ Carmen Moser,¹ Stefan Spirk,¹ and Sven Schäfer²

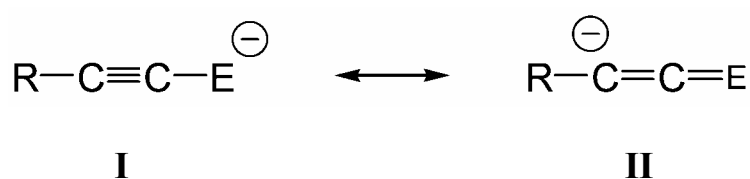
¹ *Institut für Chemie, Karl-Franzens-Universität Graz, Schubertstraße 1, A-8010 Graz, Austria, email: rudolf.pietschnig@uni-graz.at*

² *Fakultät für Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, D-44780 Bochum, Germany*

Introduction

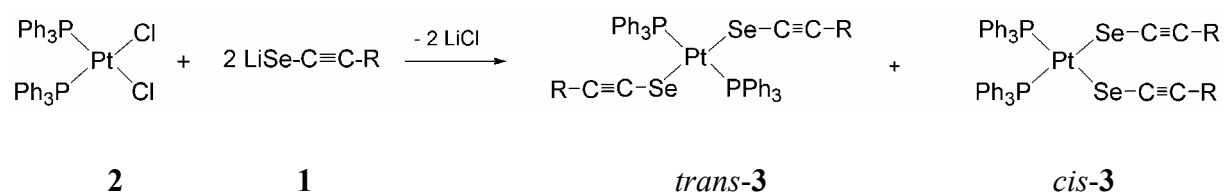
Alkynylchalcogenolates (**I**) can be described as chalcogeno ketene anions (**II**) and are capable of showing unique ambident reactivity.¹ This ambident behavior has been mainly explored towards organic or main group based electrophiles in the case of alkynylthiolates, mostly aiming at thioketenes. In contrast, much less information is available about the reactivity and coordination chemistry of alkynylthiolates towards transition metals, which started to develop only recently.² Even less information is available for their selenium analogues, i.e. the alkynylselenolates, despite the favorable nmr properties of the ⁷⁷Se nucleus. The first examples exploring the coordination behavior of these unusual ligands have been described by Tatsumi and coworkers.^{3,4} Recently we reported some alkynylselenolates carrying substituents with different electronic and steric properties.^{5,6} as well as their complexation behavior towards platinum(II) centers.⁷ The growing interest into the chemistry and coordination behavior of alkynylselenolates stems from their structural flexibility, unique

electronic situation and the antioxidative activity of biomimetic models based on structurally related organoselenium compounds.^{8,9}



Results and Discussion

To minimize electronic interaction of the substituent with the adjacent CCSe unit we have chosen an alkyl derivative, i.e. heptynylselenolate as designated ligand for complexation. Thus, the reaction of lithium heptynylselenolate (**1**) with *cis*-dichlorobis(triphenylphosphane)-platinum(II) (*cis*-(Ph₃P)₂PtCl₂) (**2**) at -78°C furnishes the desired bisalkynylselenato platinum complex **3** as an orange solid ($\lambda_{\text{max}} = 212 \text{ nm}$). Starting from *cis*-**2** results in the formation of a mixture of *cis*-**3** and *trans*-**3**, whereof *trans*-**3** is the dominant form (ratio 4:1) (Scheme 1).



Scheme 1: Synthesis of **3** (R = pentyl).

In the ³¹P nmr spectra *trans*-**3** shows a resonance at 28.0 ppm with a ¹J_{Pt}-coupling constant of 2858 Hz and a ²J_{PSe}-coupling constant of 26 Hz. The *cis* isomer of **3** has a chemical shift of 23.6 ppm with larger coupling constants than found for *trans*-**3** (i.e., *cis*-**3**: ¹J_{Pt} = 3220 Hz and ²J_{PSe} = 42 Hz).

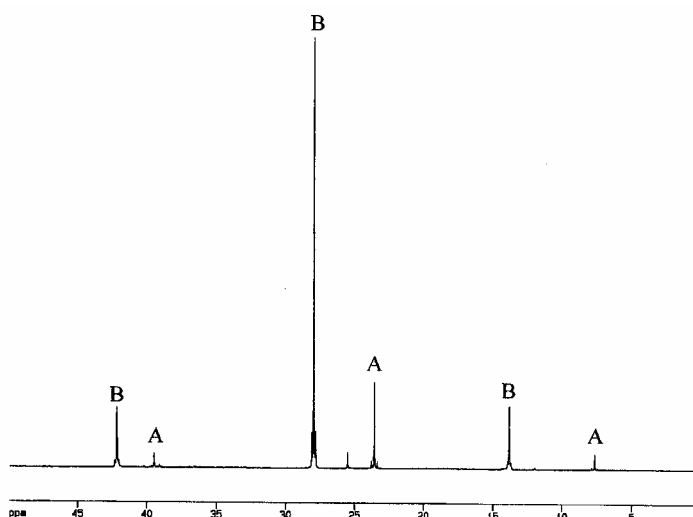


Figure 1: ^{31}P -NMR of a mixture of *trans*-3 (designated B) and *cis*-3 (designated A).

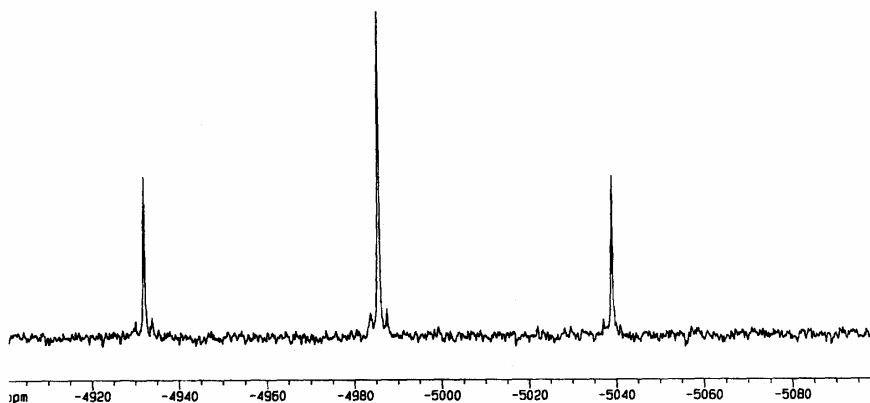
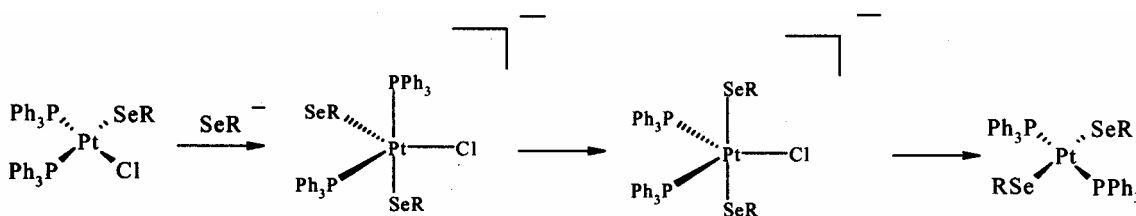


Figure 2: ^{195}Pt -NMR of *trans*-3.

The isomerization process is likely to proceed through pseudorotation of a pentacoordinate intermediate as depicted below:



Scheme 2: Possible mechanism for the *cis/trans* isomerization in the formation of **3**.

Recrystallization from dry methylene chloride affords pure crystalline *trans*-**3** for which we were able to obtain a crystal structure. The asymmetric unit of *trans*-**3** contains a planar coordinated Pt (II) center, which is also an inversion center, and two molecules of methylene chloride. As already derived from the nmr spectra the alkynylselenolato ligands adopt a *trans* configuration in the approximately square planar coordination environment around platinum (Figure 3). The phosphane and the alkynylselenolato units in *trans*-**3** show Pt(1)-P(1) (2.348(2) Å) and Pt(1)-Se(2) (2.4902(9) Å) distances which are slightly longer than the values reported for the related *trans*-[Pt(PPh₃)₂(SePh)₂] and even more so compared to *cis*-[Pt(PPh₃)₂(SePh)₂].

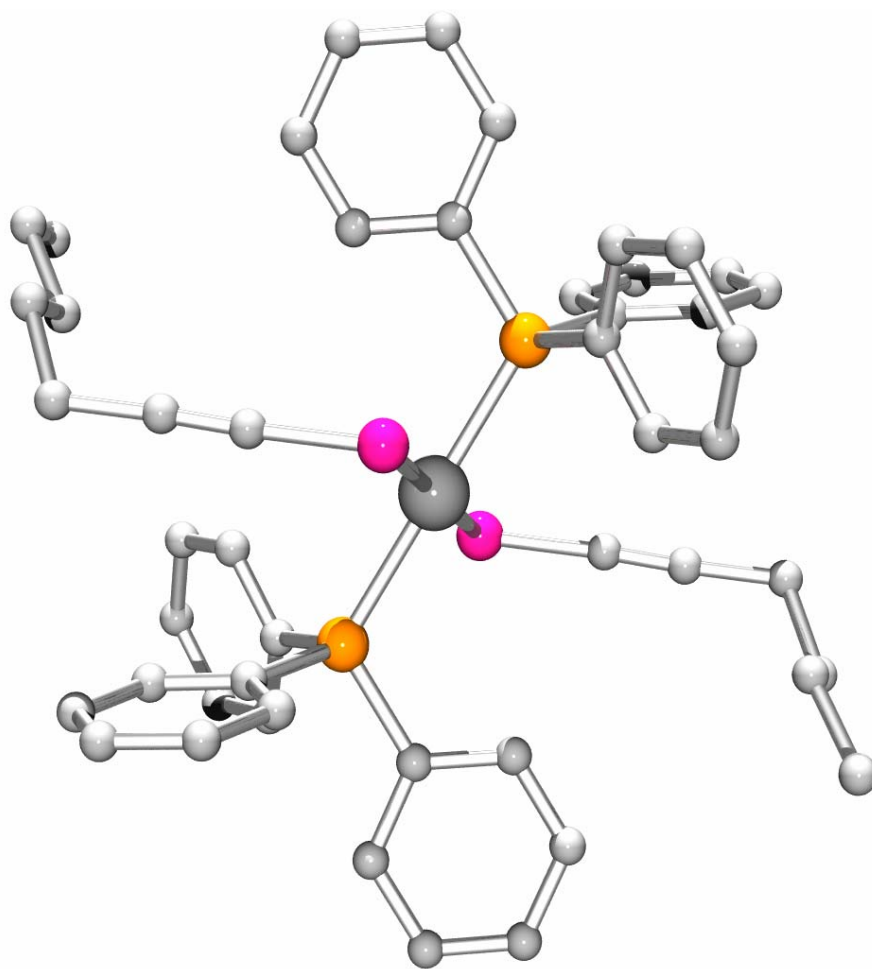
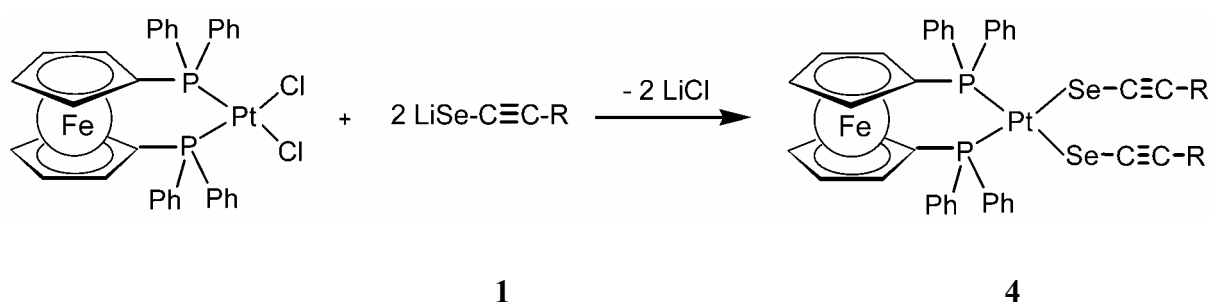


Figure 3: Molecular structure of *trans*-**3**.

We were interested to compare the structural results obtained for *trans*-**3** with its *cis* isomer. As in the case of the related phenylselenolate platinum complexes, slow isomerization of *cis*-**3** to *trans*-**3** in solution precluded the growth of crystals of *cis*-**3** suitable for X-ray diffraction, however. To circumvent this issue, we replaced the triphenylphosphane ligands with a chelating diphosphane to enforce *cis* geometry. We have chosen bisdiphenylphosphino ferrocene (dppf) rather than bisdiphenylphosphino ethylene (dppe) which has been used in previous investigations,² because from its electronic and steric properties the ferrocenylene unit is closer to a phenyl group than alkylidene units.¹⁰ To synthesize an analogous complex with *cis*- geometry, we started from (dppf)PtCl₂ which we reacted with lithium heptynl-selenolate (**1**) to give the *cis* bisalkynylselenato platinum complex **4** (Scheme 3).



Scheme 3: Synthesis of **4** (R = pentyl).

We determined the structure of **4** in the solid state by X-ray diffraction which confirms the *cis* arrangement of the alkynylselenolate ligands (Figure 4). The Pt-P distances (2.2819(13)-2.2882(12) Å) and the Pt-Se bond lengths (2.4608(6)-2.4639(5) Å) in **4** are both shorter than the respective ones in *trans*-**3**. In contrast, the bond lengths associated with the alkynylselenolate unit appear slightly elongated in the *cis* complex compared to the *trans* complex as for instance the C≡C triple bonds in **4** are 1.199(7) to 1.205(8) Å relative to 1.177(5) Å in *trans*-**3**. As is evident from the C≡C-C angles (175.6(10)-178.1(10)°) the

alkynyl groups show an arrangement close to linearity. Somewhat larger are the deviations from ideal linearity for the corresponding Se-C≡C angles which range from 170.3(6)° to 175.5(7)°. Within the approximately square planar coordination environment around platinum the neighboring atoms show angles in the range between 85.07(2) and 97.98(4)° where the largest value corresponds to the P1-Pt1-P1 angle involving the bisphosphane ligand. To adjust the bite angle of the dppf ligand, the Cp rings of the ferrocenyl unit are twisted by 34.5° (P(1)-Cp(1)-Cp(2)-P(2)). The Cp-Fe-Cp system is almost linear with an angle of 178.8(3)°. The Pt-Fe distance of 4.299 Å significantly exceeds the sum of the van-der-Waals radii, therefore any direct interaction between these atoms appears unlikely.

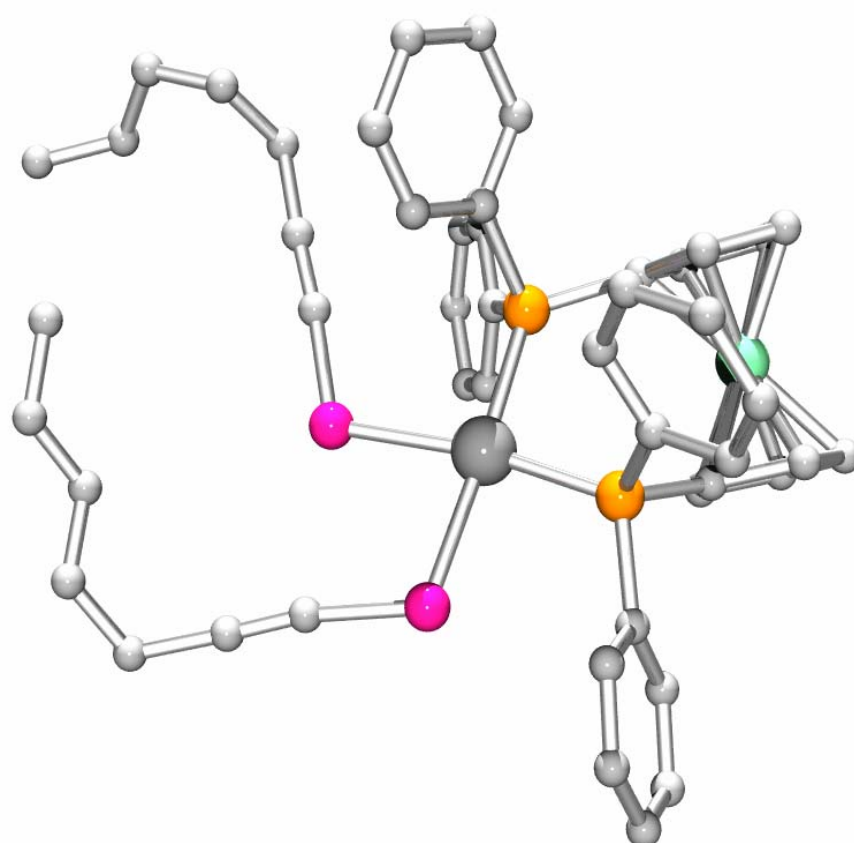


Figure 4: Molecular structure of **4**.

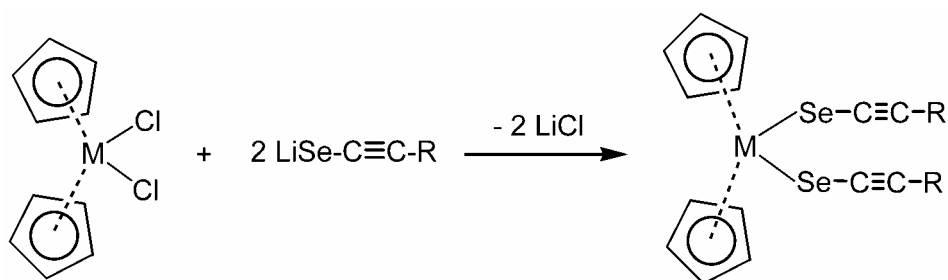
In addition to the structural changes that can be observed for *cis*-**3** and **4**, the heteronuclear nmr spectra reveal valuable information related to the bonding situation in alkynylselenolate platinum complexes. Relevant nmr spectroscopic data for *cis/trans*-**3** and **4** are summarized in table 3. It can be noted that the ^{31}P resonance of the phosphane unit in the *trans* form appears at lower field than in the *cis* form. In contrast the ^{195}Pt resonances show the opposite trend with the ^{195}Pt nucleus in the *cis* form being more shielded than in the *trans* form. Significant changes are observed for the coupling constants $^1J_{\text{PPt}}$ and $^1J_{\text{PtSe}}$ which reflect the metal ligand interactions. Thus, going from *trans* to *cis* these coupling constants increase by 15% ($^1J_{\text{PPt}}$) and 21% ($^1J_{\text{PtSe}}$) indicating an increased bond order.¹¹ This correlates clearly with the structural findings for compounds *trans*-**3** and **4** for which both the Pt-P and the Pt-Se distances decrease from *trans* to *cis*.

Table 3: Relevant nmr spectroscopic data for *cis/trans*-**3** and **4**.

| | <i>trans</i> - 3 | <i>cis</i> - 3 | <i>cis</i> - 4 |
|---------------------------------|-------------------------|-----------------------|-----------------------|
| $\delta(^{31}\text{P})$ [ppm] | 28.0 | 23.6 | 19.4 |
| $\delta(^{77}\text{Se})$ [ppm] | - | - | 330 |
| $\delta(^{195}\text{Pt})$ [ppm] | -4985 | - | -5009 |
| $^1J_{\text{PPt}}$ [Hz] | 2858 | 3220 | 3287 |
| $^1J_{\text{PtSe}}$ [Hz] | 198 | - | 240 |
| $^2J_{\text{PSe}}$ [Hz] | 26 | 42 | - |

To probe the coordination behavior of alkyl substituted alkynylselenolates towards hard metal centers, we reacted (**1**) with the metallocenedichlorides Cp_2MCl_2 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) (Scheme 4). In all these cases exclusive coordination at the selenium atom is observed based on our preliminary spectroscopic data. However, somewhat surprising the ^{77}Se -NMR shift values for these compounds appear at unusually low field compared with their Pt(II)

analogues. As an example the ^{77}Se -NMR spectrum of $\text{Cp}_2\text{Ti}(\text{Se-C}\equiv\text{C-Pen})_2$ is depicted in Figure 5.



Scheme 4: Synthesis of $\text{Cp}_2\text{M}(\text{Se-C}\equiv\text{C-Pen})_2$ ($\text{M} = \text{Ti, Zr, Hf}$; $\text{R} = \text{pentyl}$).

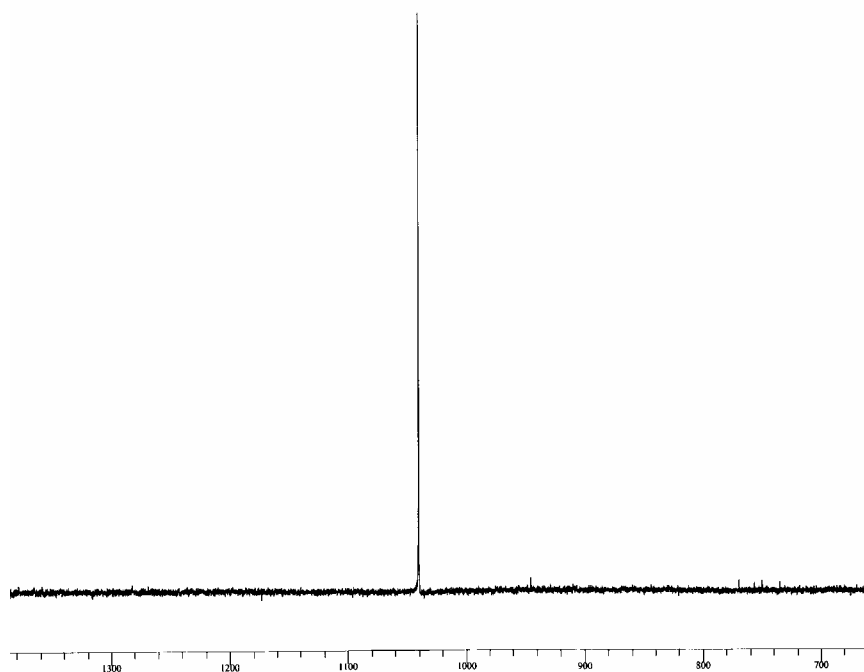


Figure 5: ^{77}Se -NMR of $\text{Cp}_2\text{Ti}(\text{Se-C}\equiv\text{C-Pen})_2$.

Summary

We synthesized closely related cis and trans platinum complexes of $\text{SeCC-n-C}_5\text{H}_{11}$ and elucidated their structures in solution and the crystalline state. In line with previous work we find exclusive coordination of the selenium atom of the ambident alkynylselenolate ligand and a preference for the obviously more stable *trans* isomer. In contrast to previous work we

find a uniform increase of all metal ligand bond lengths in the *cis* vs. the *trans* isomers. Moreover we studied the coordination of alkynylselenolate ligands to group 4 metals.

Acknowledgements

We acknowledge the Austrian Science Fund (FWF) for financial support (project P17882-N11).

References:

- (1) Raubenheimer, H. G.; Kruger, G. J.; Linford, L.; Marais, C. F.; Otte, R.; Hattingh, J. T. Z.; Lombard, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1565-1577.
- (2) Weigand, W.; Weishäupl, M.; Robl, C. *Z. Naturforschung* **1996**, *Teil B*, 501-505.
- (3) Sugiyama, H.; Hayashi, Y.; Kawaguchi, H.; Tatsumi, K. *Inorg. Chem.* **1998**, *37*, 6773-6779.
- (4) Sunada, Y.; Hayashi, Y.; Kawaguchi, H.; Tatsumi, K. *Inorg. Chem.* **2001**, *40*, 7072-7078.
- (5) Pietschnig, R.; Merz, K.; Schäfer, S. *Heteroatom Chem.* **2005**, *16* (2), 169.
- (6) Pietschnig, R.; Schäfer, S.; Merz, K. *Org. Lett.* **2003**, *5*, 1867-1869.
- (7) Schäfer, S.; Moser, C.; Tirrée, J. J.; Nieger, M.; Pietschnig, R. *Inorg. Chem.*, **2005**, *44*, 2798.
- (8) Ma, N. L.; Wong, M. W. *Eur. J. Org. Chem.* **2000**, 1411-1421.
- (9) Mugesh, G.; Panda, A.; Singh, H. B.; Punekar, N. S.; Butcher, R. J. *J. Chem. Soc., Chem. Commun.* **1998**, 2227-2228.
- (10) Pietschnig, R. *Ferrocenylphosphane und -phosphorane*; Tectum Verlag: Marburg, 1997.
- (11) Nixon, J. F.; Pidcock, A. *Ann. Rev. NMR Spectr.* **1969**, *2*, 345-422.