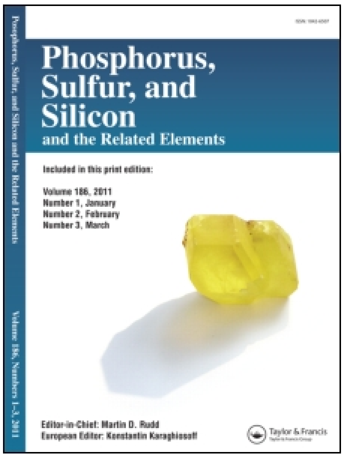

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

From Organometallic Selenolates to Organoselenolato Complexes of Mo, W and Mn

Carsten Thöne

To cite this Article Thöne, Carsten(1998) 'From Organometallic Selenolates to Organoselenolato Complexes of Mo, W and Mn', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 645 — 648

To link to this Article: DOI: 10.1080/10426509808546016

URL: http://dx.doi.org/10.1080/10426509808546016

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 645-648
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint
Printed in Malaysia

FROM ORGANOMETALLIC SELENOLATES TO ORGANOSELENOLATO COMPLEXES OF Mo, W AND Mn

CARSTEN THÖNE
Institut für Analytische und Anorganische Chemie der Technischen
Universität, Hagenring 30, D-38106 Braunschweig, Germany

Organometallic selenolates of Mo, W and Mn can be easily obtained via insertion of selenium into the alkali-metal transition-metal bonds of appropriate carbonylates. Subsequent reactions with various organic electrophiles lead to the corresponding organoselenolato complexes. X-ray structure analyses afforded M - Se bond lengths consistent with the presence of single bonds. ^{77}Se NMR studies were performed to determine electronic influences of the organoselenolato function.

Keywords: Selenolato complexes; ^{77}Se NMR; Crystal structure

INTRODUCTION

In the last few decades, transition-metal organoselenolato complexes have attracted increasing attention, associated with unusual structural aspects and novel applications [1]. Syntheses require the accessibility of the Se-containing organic precursors (*e.g.* diselenides, selenolates). However, the straightforward transformation of organo-halides into the corresponding selenolates is not always possible and in any case involves malodorous reaction intermediates. Additionally, some synthetical problems arise from the redox behaviour of the organic selenolates.

Recent studies in our laboratory have shown that many of these difficulties can be avoided by using selenium as starting material in reactions with appropriate transition-metal complexes [2-4].

SYNTHESES

Grey selenium readily inserts into the alkali-metal transition-metal bonds of appropriate carbonylates producing organometallic selenolates:

$$\mathrm{M[Mo(W)cp(CO)_3]} \xrightarrow[20^\circ\mathrm{C},\ 15\ \mathrm{min}]{\mathrm{Se,\ THF}} \mathrm{M[SeMo(W)cp(CO)_3]}$$

$$2\ \mathrm{MMn(CO)_5} \xrightarrow[15\ \mathrm{min},\ -2\ \mathrm{CO}]{2\ \mathrm{Se,\ THF},\ 20^\circ\mathrm{C}} \mathrm{M_2[SeMn(CO)_4]_2}$$

Subsequent reactions with organic electrophiles lead directly to the corresponding organoselenolato complexes under mild conditions (Fig. 1).

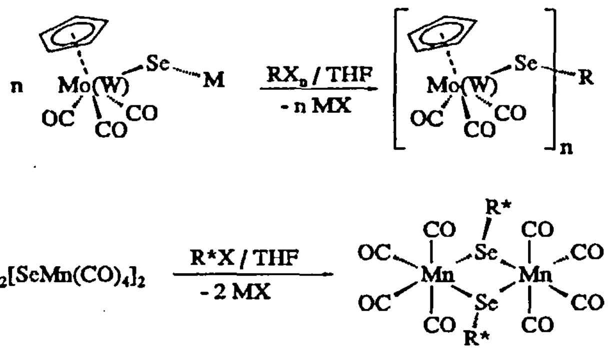

FIGURE 1 Organoselenolato complexes of Mo, W and Mn from organometallic selenolates

The transformations can be performed advantageously as one pot syntheses and lead to crystalline, air-stable products in moderate to good yields. Some selected examples are presented in Table 1 together with their ^{77}Se NMR data.

TABLE 1 Selected physical data of some organoselenolato complexes of Mo and W

Metal center	R	Yield [%]	^{77}Se NMR[a]
Mo	CH_2SiMe_3	56	- 479.3
Mo	$CH_2C(CH_3)=CH_2$	69	- 363.5
W	CH_2-$CH=CH_2$	42	- 401.8
W	C(O)Ph	41	+ 12.0
W	CH-Ph	41	- 160.3

[a] in $CDCl_3$, rel. to $Me_2Se_{ext.}$

The observed chemical shifts are typical of simple two-coordinate organoselenolato Mo and W complexes and can be explained by different electronic effects of the organoselenolato groups. Only in the case of the benzoyl derivative $cp(CO)_3WSeC(O)Ph$ were ^{183}W satellites observed, with a corresponding coupling constant $^1J(^{77}Se$-$^{183}W)$ of 35 Hz (*cf.* 49 Hz in $[(CO)_5WSe(Me)(\sigma$-$C_5Me_5)]$, 112 Hz in $[W_3Se_9]^{2-}$) [5,6]

CRYSTAL STRUCTURES

Several crystal structures of the new complexes were determined and as examples, the structures of $C_6H_5CH[SeW(CO)_3cp]_2$ **1** and $[(CO)_4MnSeCH_2Ph]_2$ **2** are shown in Fig. 2. In **1**, a W-Se bond length of 2.655(1) Å is observed, which is consistent with the formulation as a W-Se single bond and typical of tungsten complexes with terminal organoselenolato ligands (*cf.* 2.623(1) Å in cp(CO)$_3$WSeCH$_2$Ph), 2.588(2) Å in (η^7-C$_7$H$_7$)(CO)$_2$WSePh)[2,7].

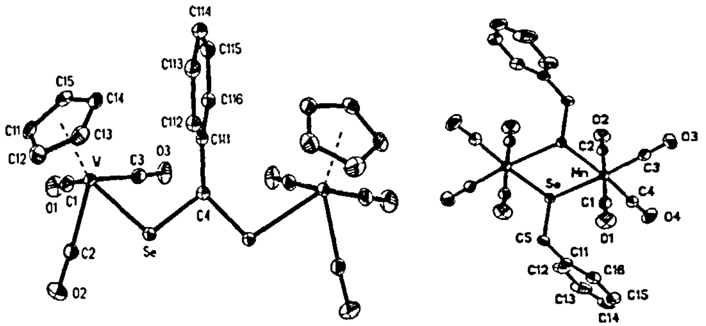

FIGURE 2 Molecular structures of C$_6$H$_5$[SeW(CO)$_3$cp]$_2$ **1**and [(CO)$_4$MnSeCH$_2$Ph]$_2$ **2**

The central moiety in the structure of **2** is a planar Mn$_2$Se$_2$ core, which forms a parallelogram with Mn-Se bond lengths of 2.499(1) and 2.493(1) Å and corresponding angles of 82.55(1)° at Mn and 97.45(1)° at Se (*cf.* 2.505(6), 2.490(6) Å in [(CO)$_4$MnSeCF$_3$]$_2$)[8].

References

[1.] J. Arnold, *Progr. Inorg. Chem.*, **43**, 353 (1995).

[2.] W. Eikens, C. Kienitz, P. G. Jones, C. Thöne, *J. Chem. Soc., Dalton Trans.*, **1994**, 3329.

[3.] W. Eikens, S. Jäger, P. G. Jones, C. Thöne, *J. Organomet. Chem.*, **511**, 67 (1996).

[4.] P. G. Jones, J. Laube, C. Thöne, *Inorg. Chem.*, **36**, 2097 (1997).

[5.] C. M. Bates, C. P. Morley, *J. Organomet. Chem.*, **533**, 197 (1997).

[6.] R. W. M. Wardle, S. Bhaduri, C.-N. Chau, J. A. Ibers, *Inorg. Chem.*, **27**, 1747 (1988).

[7.] A. Rettenmaier, K. Weidenhammer, M. L. Ziegler, *Z. Anorg. Allg. Chem.*, **473**, 91 (1981).

[8.] C. J. Marsden, G. M. Sheldrick, *J. Organomet. Chem.*, **40**, 175 (1972).