

Synthesis and Se–Se Bond Breaking of Polyselenides Containing Pendant Diphosphine Complexes of Manganese(I)[†]

Javier Ruiz,^{*,†} René Araúz,[†] Mario Ceroni,[†] Marilín Vivanco,[†] Juan F. Van der Maelen,[‡] and Santiago García-Granda[‡]

[†]Departamento de Química Orgánica e Inorgánica and, [‡]Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33006 Oviedo, Spain

Received March 25, 2010

Summary: Reaction of $[Mn(CO)_4(PPh_2)_2CH_3]$ (1) with half an equivalent of dipiperidinotetraselane affords the tetraselenide compound $[(CO)_4Mn\{(PPh_2)_2C\text{-}Se_4\text{-}C(PPh_2)_2\}Mn(CO)_4]$ (2-Se₄), which, upon treatment with KOH, is transformed into the corresponding triselenide and diselenide derivatives 2-Se₃ and 2-Se₂. Full or partial protonation of the methanide carbon atoms can be accomplished by reaction of the above compounds with HBF₄, whereas treatment of 2-Se₂ with I_2 gives rise to the formation of the selenelyl iodide derivative $[Mn(CO)_4](PPh_2)_2C\text{-}Se-I_3]$ (5).

Introduction

Organoselenium compounds have attracted attention from the scientific community owing to their versatile reactivity¹ and their unique role in biochemical systems.² In the specific field of organoselenophosphorus chemistry, phosphine and diphosphine selenides are well known, as their synthesis, reactivity, and coordination chemistry have been reported,³ but diphosphines containing selenium in the backbone are only episodically encountered in the literature.⁴ This paper deals with the metal-assisted formation of bridging tetraphosphine ligands containing polyselenide chains of different lengths in manganese(I) carbonyl complexes of general formula $[(CO)_4Mn\{(PPh_2)_2\}$ C-Se_n-C(PPh₂)₂ $\}Mn(CO)_4]$, their controlled protonation reactions, and the reversible selenium–selenium bond breaking and formation therein. The experimental approach involves

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regioselective selenation reaction at the central carbon atom of the bis(diphenylphosphino)methanide ligand in the neutral complex [Mn(CO)₄{(PPh₂)₂CH}].⁵ The dinuclear complexes formed are closely related to those containing polysulfide chains previously described by our group.⁶ Apart from elemental selenium,^{4b,7} a few selenating reagents have been developed in organoselenophosphorus chemistry.8 Thus, Woollins' reagent,8a which contains a phosphorus-selenium ring, has proven to be very useful for the synthesis of P-Se heterocycles and for introducing selenium into organic compounds. Also it is worth mentioning the role of phosphine selenides, which have been used as selenium-transferring reagents for the conversion of phosphite triesters and H-phosphonate diesters into phosphoroselenoates under mild conditions.^{8b} In relation with this, here we have found that dipiperidinotetraselane⁹ can be conveniently employed as a selective selenating reagent to introduce a tetraselenium chain as bridging backbone in manganese(I) diphosphine complexes, as we will show throughout this paper.

Results and Discussion

We first explored the reactivity of the diphosphinomethanide complex $[Mn(CO)_4](PPh_2)_2CH]$ (1) with commercial gray selenium, but no reaction was found even under forcing conditions. By contrast, the molecular form of selenium Se_8^{10} readily reacted with 1 in dichloromethane at room temperature, affording a mixture of polyselenide derivatives of general formula $[(CO)_4Mn\{(PPh_2)_2C-Se_n-C(PPh_2)_2\}Mn(CO)_4]$ (2-Se_n), containing selenium chains of variable length, together with the dppm (bis(diphenylphosphino)methane) parent complex [Mn(CO)₄-(dppm)]⁺. The last was removed from the reaction mixture by column chromatography, but separation of the different polyselane compounds was not feasible owing to their similar solubility in organic solvents. Fortunately, the treatment of 2-Se_n with PPh₃ or KOH acting as selenium abstractors yielded 2-Se₂ as the sole product. The above results can be compared with those found in the reaction of Li[HC(PPh₂)₂] with elemental selenium, leading to selenation of the phosphorus atoms to

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Scheme 1. Reaction of Complex 1 with Dipiperidinotetraselane to Afford Complex 2-Se₄ and Subsequent Selenium Abstraction to Give 2-Se₃ and 2-Se₂



Table 1. Selected Spectroscopic Data for Compounds 2–5

compd	$IR^{a} \nu(CO), cm^{-1}$	$^{31}P{^{1}H} NMR,^{b} (\delta ppm)$	¹ H NMR, ^b (δ ppm, J Hz)	77 Se NMR ^b (δ ppm)	$^{13}C{^{1}H} NMR^{b,c}$ (δ ppm, J Hz)	
2-Se ₄	2072 (s), 1999 (sh)	17.6 (br)		726.8, 817.0	32.7 (t, ${}^{1}J_{\rm PC} = 42$)	
2-Se ₃	1991 (vs), 1966 (s) 2071 (s), 1997 (sh) 1991 (vs), 1963 (s) d	17.1 (br)		663.6 (2Se) 888.6 (1Se)	31.1 (t, ${}^{1}J_{\rm PC} = 42$)	
2-Se ₂	2070 (s), 1997 (sh) 1991 (vs), 1962 (s)	14.0 (br)		635.2	31.9 (t, ${}^{1}J_{\rm PC} = 41$)	
3-Se ₄	2094 (s), 2035 (m) 2012 (vs)	40.2 (br)	6.29 (t ² I _{DH} = 11.4)	558.3, 825.6	50.7 (t, ${}^{1}J_{\rm PC} = 10$)	
3-Se ₃	2094 (s), 2035 (m) 2011 (vs) ^d	41.2 (br)	6.44 (t. ² <i>I</i> _{PH} = 11.1)	581.7 (2Se) 769 8 (1Se)	51.1 (t, ${}^{1}J_{\rm PC} = 10$)	
3-Se ₂	2093 (s), 2035 (m) 2009 (vs)	33.1 (br)	7.27 (t ² $I_{\rm PH} = 7.9$)	462.8	47.8 (t, ${}^{1}J_{\rm PC} = 11$)	
4-Se ₂	2092 (s), 2076 (s) 2032 (m), 2009 (vs)	21.5 (br) 36.4 (br)	$\begin{array}{l} 6.05 \\ (t, {}^{2}J_{\rm PH} = 11.1) \end{array}$	607.7, 718.4	37.3 (t, ${}^{1}J_{PC} = 39$) 45.7 (t, ${}^{1}J_{PC} = 14$)	
5	1994 (s), 1975 (m) 2077 (s), 2006 (sh) 1996 (vs), 1973 (s) ^e	26.2 $(br)^{f}$		1209.9 ^{<i>f</i>}	58.8 (t, ${}^{1}J_{\rm PC} = 34)^{J}$	

^{*a*} CH₂Cl₂ unless noted otherwise. ^{*b*} CD₂Cl₂ unless noted otherwise. ^{*c*} P₂C signal. ^{*d*} Sample enriched in the complex. ^{*e*} THF. ^{*f*} D₂O capillary/THF.

afford the anion $[HC(PPh_2Se)_2]^{-.11}$ In our case, coordination of the diphosphinomethanide ligand [HC(PPh₂)₂]⁻ through the phosphorus atoms to manganese prevents selenation from taking place on these atoms, allowing regioselective selenation at the central carbon atoms of the diphosphinomethanide moiety. A more convenient and clean procedure to prepare these kinds of polyselenide derivatives in a controlled manner is by using dipiperidinotetraselane as selenating reagent. Thus, when complex 1 was treated with half an equivalent of $C_5H_{10}N$ -Se₄-NC₅H₁₀, the tetraselenide compound $[(CO)_4Mn\{(PPh_2)_2-$ C-Se₄-C(PPh₂)₂}Mn(CO)₄] (2-Se₄) was formed after 20 min of stirring at room temperature in dichloromethane, with simultaneous generation of two equivalents of piperidine as a byproduct, as detected by ¹H NMR spectroscopy (Scheme 1). As shown in Scheme 1, the reaction pathway should involve formation of the intermediate adduct I and further proton transfer from the $P_2C(H)$ Se- group to the amide moiety to eliminate piperidine. The tetraselenium chain in 2-Se₄ slowly loses a selenium atom by treatment with KOH in CH₂Cl₂, giving the triselenide compound 2-Se3, but formation of a small amount of the diselenide derivative 2-Se₂ begins before the starting complex 2-Se₄ has been consumed, thus precluding isolation of 2-Se₃ as a pure sample. This is made evident by the ⁷⁷Se NMR spectrum of the reaction mixture, which showed signals corresponding to the three complexes (see below). The prolonged treatment

of this mixture with KOH afforded **2-Se₂**, which was isolated in good yield. The IR spectra of compounds **2-Se₄**, **2-Se₃**, and **2-Se₂** in the ν (CO) region are almost identical; also the broad singlet signal observed in the ³¹P{¹H} NMR spectra, corresponding to the diphosphino groups, appears at very similar chemical shifts for the three complexes (Table 1). This means that the shortening of the selenium chain has little electronic effect on the two pendant octahedral manganese(I) complexes. However, the ⁷⁷Se NMR chemical shifts were found to be quite sensitive to the selenium atom environment, and hence to the selenium chain length. Thus, a singlet at 635.2 ppm was observed for the diselenide compound **2-Se₂**, two singlets at 663.5 and 888.6 ppm in a 2:1 ratio, respectively, for the triselenide **2-Se₃**, and two singlets of equal intensity at 726.8 and 817.0 ppm for the tetraselenide derivative **2-Se₄**.¹²

Reaction of **2-Se₂** or **2-Se₄** with an excess of an strong acid (HBF₄ or HClO₄) immediately afforded the cationic complexes [(CO)₄Mn{(PPh₂)₂C(H)-Se_n-C(H)(PPh₂)₂}Mn(CO)₄]²⁺ (**3-Se₂**, n = 2; **3-Se₄**, n = 4) (Scheme 2), as a result of the protonation of both methanide carbon atoms, which were isolated as yellow solids and fully spectroscopically characterized. Protonation of the above-mentioned mixtures of complexes **2-Se₂**, **2-Se₃**,

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ĊC 2-Sen 00 n = 2-4 00 and 2-Se4 also allowed spectroscopic characterization of the triselenide complex [(CO)₄Mn{(PPh₂)₂C(H)-Se₃-C(H)- $(PPh_2)_2$ $Mn(CO)_4$ ²⁺ (**3-Se**₃). Naturally, the ν CO bands in the IR spectra undergo a substantial change to high frequencies on going from the neutral to the cationic complexes (Table 1). The most characteristic signal in the ¹H NMR spectra is that corresponding to the P₂CH proton, which appears as a triplet at 7.27, 6.44, and 6.29 ppm for complexes 3-Se₂, 3-Se₃, and 3-Se₄, respectively. Note that this signal is significantly shifted downfield in complex $3-Se_2$ compared with that in the other two polyselenide derivatives, **3-Se₃** and **3-Se₄**. Furthermore, the ${}^{2}J_{PH}$ coupling constant is appreciably lower for 3-Se₂ (7.9 Hz) than for 3-Se₃ (11.1 Hz) and 3-Se₄ (11.4 Hz). Also of note is the chemical shift of the signal corresponding to the phosphorus atoms of the diphosphine in the ${}^{31}P{}^{1}H$ NMR spectra, which is notably lower for complex 3-Se₂ (33.1 ppm) than for complexes 3-Se₃ (41.2 ppm) and 3-Se₄ (40.2 ppm). These data suggest that in the diselenide complex 3-Se2 there is a unique electronic interaction between the diselenide chain and the P₂CH groups that is not present, or at least not to the same extent, in the other two polyselenide complexes, 3-Se3 and 3-Se4. A similar situation was observed in the polysulfide counterparts previously reported by our group.⁶ In order to gain insight into the structural disposition of the tetraphosphine ligand (PPh₂)₂C(H)-Se₂-

C(H)(PPh₂)₂ in the cationic complex **3-Se**₂, an X-ray analysis of the corresponding perchlorate salt was carried out. Crystals of [**3-Se**₂](ClO₄)₂ suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution of the compound. A view of the complex cation is shown in Figure 1 together with a selection of bond distances and angles. The molecular cation contains two almost identical halves, which are twisted around the Se–Se segment (C9–Se1–Se2–C10 torsion angle 104.2(3)°). The Se–Se and C–Se bond lengths are similar to those found in dimethylselane (2.326(4) and 1.954(5) Å, respectively).¹³ The C–H10···Se1 (3.27(5) Å) and C–H9···Se2 (3.12(5) Å) distances are similar to the sum of van der Waals radii of hydrogen and selenium atoms (3.25 Å), which could allow a weak hydrogen bond interaction,¹⁴ although the C–H···Se angle is too close (94° in average). Compounds



Figure 1. Structure of the dication $3-Se_2$ (50% thermal ellipsoids). Phenyl groups have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mn1–P1 2.298(2), Mn1–P2 2.331(2), P1–C9 1.853(6), P2–C9 1.851(7), C9–Sel 1.982(6), Se1–Se2 2.318(1), Se2–C10 1.977(6), C10–P3 1.853(6), C10–P4 1.860(6), Mn2–P3 2.305(2), Mn2–P4 2.329(2), H9···Se2 3.12(5), H10···Se1 3.27(5); P2–Mn1–P1 71.54(7), P1–C9–P2 93.9(3), Se1–C9–P1 108.9(3), Se1–C9–P2 113.2(3), C9–Se1–Se2 99.0(2), Se1–Se2–C10 99.1(2), Se2–C10–P3 108.5(3), Se2–C10–P4 113.2(3), P3–C10–P4 94.2(3), P3–Mn2–P4 71.87(7), C9–H9···Se2 88(3), C10–H10···Se1 99(3).

containing C–H···Se hydrogen bonds are very rare;¹⁵ for a comparison, values such as 2.92 Å and 101.7° for intramolecular C–H···Se interactions have been reported.^{15a} In our case, an additional cooperative effect could exist as the two proposed hydrogen bonds are interconnected.¹⁶ Despite this, HMQC measurements showed that the J_{SeH} value in complex 3-Se₂ is low (7.2 Hz), which seems to rule out the existence of typical C–H···Se hydrogen bonds in this complex.^{15a}

In order to clarify the existence of an apparently special electronic interaction in the C(H)-Se-Se-C(H) core, theoretical electron density calculations within the framework of the quantum theory of atoms in molecules $(QTAIM)^{17}$ were performed for complex **3-Se**₂ as well as for the disulfide counterpart [(CO)₄-Mn{(PPh₂)₂C(H)-S₂-C(H)(PPh₂)₂}Mn(CO)₄]²⁺ (**3-S**₂).⁶ Delocalization indices for the nonbonding interactions of the central C(H)-S-S-C(H) and C(H)-Se-Se-C(H) cores are listed in Table 2. No critical points or bond paths were found for these weak interactions from the QTAIM calculations, which is consistent with the rather low values obtained for each $\delta(A \cdots B)$ index. Nevertheless, $\delta(Se \cdots H)$, $\delta(Se \cdots C)$, $\delta(S \cdots H)$, and $\delta(S \cdots C)$ indices are not negligible at all but comparable to other values for nonbonding interactions.¹⁸

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Table 2. Delocalization Indices for Nonbonded Interactions in 3-S₂ and 3-Se₂

		$\begin{array}{c} Se\cdots H\\ S\cdots H\end{array}$	$\begin{array}{c} S \cdots C \\ S e \cdots C \end{array}$	С…н	н∙∙∙н	С…С	total
3-S ₂	$ \begin{array}{c} \delta \left(\mathbf{A} \cdots \mathbf{B} \right) \\ \delta \left(\mathbf{A} \cdots \mathbf{B} \right) \end{array} $	0.061	0.091	0.002	0.001	0.006	0.31
3-Se ₂		0.058	0.085	0.001	0.001	0.005	0.29

It is worth noting the almost equal results obtained for the same interactions in the two different complexes. The only reason for not finding critical points for these weak interactions is the Poincaré-Hopf relationship applied to the QTAIM theory, which restricts the number of bonds to the strongest interactions, while the weakest ones may be recognized only by their non-negligible $\delta(A \cdots B)$ values. Moreover, by adding up $\delta(A \cdots B)$ indices for all the Se \cdots H, Se \cdots C, C \cdots C, and H \cdots H interactions in the central part of $3-Se_2$ (and the corresponding interactions for $3-S_2$) a value of 0.3 is found (Table 2), which is comparable to, and even larger than, the ones found in bonding interactions such as Zn-C in $Zn_2(\eta^5-C_5Me_5)_2$ (0.23), Na-F in NaF (0.27), Co-Co in Co₂(CO)₈ (0.46), and B-C in H₃BCO (0.50).¹⁹ A correlation between spin-spin coupling and electron delocalization measured by these delocalization indices is well known.²⁰ Then, it is fair to conclude that there exists a collaborative multicenter delocalized interaction in the central part of complexes 3-S₂ and 3-Se₂, which could well be responsible for the NMR data observed.²¹

Protonation of just one methanide carbon atom of 2-Se2 can be accomplished by controlled treatment of a dichloromethane solution of this compound with an equivalent of HBF₄, affording the cationic complex $[(CO)_4Mn\{(PPh_2)_2C(H)-Se_2-C(PPh_2)_2\}$ - $Mn(CO)_4$ ⁺ (4-Se₂) (Scheme 2). The IR spectrum of 4-Se₂ in the ν CO region showed two groups of bands corresponding to the two nonequivalent sides of the complex cation. Also two broad resonances were present in the ³¹P{¹H} NMR spectrum at 37 and 32 ppm due to the diphosphinomethane and diphosphinomethanide parts of the bridging ligand, respectively. As expected, two singlet signals were observed in the ⁷⁷Se NMR spectrum (607.7 and 718.4 ppm), whereas the $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum showed two triplets at 45.7 (${}^{1}J_{PC} = 14$ Hz) and 37.3 (${}^{1}J_{PC} = 39$ Hz) ppm corresponding to P₂C(H)Se and P₂CSe carbon atoms, respectively.

Complex 2-Se₂ readily undergoes Se-Se bond breaking by treatment with an equivalent of I₂, yielding the selenenyl iodide compound [Mn(CO)₄{(PPh₂)₂C-Se-I}] (5) (Scheme 3), in a similar way to that found in the disulfide counterpart.²² The appearance of a very low field singlet (1209.9 ppm) in the ⁷⁷Se NMR spectrum of this complex clearly indicates that formal

Scheme 3. Reversible Selenium-Selenium Bond Breaking and Formation in Complex 2-Se₂



oxidative scission of the Se-Se chain with formation of a new Se-I bond has taken place. Consequently, the IR spectrum in the ν CO region shows bands at higher frequencies (8 cm⁻¹ on average, Table 1) than those for the disulfide derivative 2-Se₂, and the signal corresponding to the diphosphino group in the ³¹P{¹H} NMR spectrum is shifted 12 ppm downfield with respect to compound 2-Se2. Selenenyl iodide compounds are scarce in the literature, owing to their very favored disproportionation to the corresponding diselenide and iodine,²³ and they can be isolated in a few cases only by introducing highly demanding alkyl substituents²⁴ or internally chelating groups.² Nevertheless, organoselenenyl iodides are relevant molecules in biochemical systems, as they play a crucial role in thyroid hormone action; in fact an enzyme selenenyl iodide complex is formed in the deiodination of thyroxine by the selenocysteine active site of iodothyronine deiodinase to afford the biologically active hormone triiodothyronine.²⁶ In view of this, formation of new molecules containing Se-I bonds appears to be an interesting goal. In this sense complex 5 is a rare example of an organometallic complex containing a selenenyl iodide functionality. Reduction of 5 with Na in THF readily regenerates the selenium-selenium bond, affording the diselenide derivative 2-Se₂. Curiously, this process is the opposite of that found in the reaction of the carbodiphosphorane selenolate zwitterion PPh₃C(Se)PPh₃ with iodine, which leads to the coupling of two selenolate functions upon oxidation to afford the cation $[(PPh_3)_2C$ -Se-Se-C $(PPh_3)_2]^{2+27}$

Acknowledgment. This work was supported by the Spanish Ministerio de Ciencia e Innovación (PGE and FEDER funding, Project CTQ2009-11457). The authors thank Isabel Merino for valuable help in the NMR measurements.

Supporting Information Available: Experimental details regarding the synthesis and characterization of compounds 2-5 and crystallographic data in CIF format of complex 3-Se2. This material is available free of charge via the Internet at http:// pubs.acs.org.

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