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Polynuclear selenido–carbonyl manganese complexes derived from tertiary phosphine selenides

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Dedicated to Professor João J.R. Fraústo da Silva's career on the occasion of his retirement

Abstract

The reactions of some phosphine selenides with mononuclear and dinuclear manganese complexes have been investigated. The reactions of $Cp'Mn(CO)_2(THF)$ (**1**) with bis(diphenylphosphino)ethane diselenide ($dppeSe_2$) affords $[(Cp'Mn)_2(\mu\text{-}Se)_2(CO)_2(dppe)]$ (**4**), identified by spectroscopic techniques. Complex $CpMn(CO)_2(THF)$ (**2**), by reacting with bis(diphenylphsphino)methane monoselenide (dppmSe) gives a variety of products, $[(CpMn)_2(\mu\text{-}Se)_2(CO)_3(dppm)]$ (**5**), $[CpMn(CO)_2(dppm)]$ (**6**), $[(CpMn)_2(CO)_4(\mu\text{-}dppm)]$ (**7**), $[CpMn(CO)_2(dppmSe)]$ (**8**) have been identified ($Cp = \eta^5\text{-}C_5H_5$, $Cp' = \eta^5\text{-}C_5H_4Me$, THF = tetrahydrofuran). Finally the reactions of $[Mn_2(CO)_8(MeCN)_2]$ (**3**) with diphenylmethylphosphine selenide (dpmpSe) and triphenylphosphine selenide (tppSe) afford clusters with molecular formula $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(dpmp)_2]$ (**9**) and $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(tpp)_2]$ (**10**), respectively. The structure of **9** has been determined by X-ray diffraction methods.

Keywords: Selenido complexes; Manganese complexes; Crystal structures; Cluster complexes

1. Introduction

Tertiary phosphine chalcogenides R_3PE (E = S, Se or Te) have served as useful starting compounds for the synthesis of transition metal clusters containing bridging chalcogenido ligands by reaction with metal carbonyl complexes [1]. This simple preparative method takes advantage of the reactivity of the P=E bond which makes easy the formation of phosphine-substituted chalcogenide clusters through oxidative transfer of chalcogen atoms to low-valent metal species.

In recent years, this synthetic procedure has been intensively used by our group obtaining a variety of selenido–carbonyl, transition metal clusters of different nuclearity starting from $[M_3(CO)_{12}]$ (M = Fe or Ru) [2]. More recently, we have synthesized by this method bimetallic selenido clusters, starting from bimetallic carbonyl clusters [3]. Furthermore, we have found that the use of heterocyclic phosphine selenides in these processes affords selenido clusters containing coordinated heterocyclic fragments derived from P–C bond cleavages [4].

We have now reacted different phosphine selenides with three manganese carbonyl complexes, namely $[Cp'Mn(CO)_2(THF)]$ (**1**), $[CpMn(CO)_2(THF)]$ (**2**) ($Cp = \eta^5\text{-}C_5H_5$, $Cp' = \eta^5\text{-}C_5H_4Me$, THF = tetrahydrofuran) and $[Mn_2(CO)_8(NCMe)_2]$ (**3**) with the aim to produce new phosphine-substituted selenido–carbonyl manganese derivatives.

As regards manganese molecular clusters and complexes containing selenido ligands, there has been little work previously reported, mainly regarding reactions starting from polyselenide anions [5], diorganyl diselenides [6] and elemental selenium [7].

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2. Results and discussion

The reactions between manganese carbonyls and tertiary phosphine chalcogenides were carried out at moderate temperatures by using the labile intermediates $Cp'Mn(CO)_2(THF)$ (**1**), $CpMn(CO)_2(THF)$ (**2**), generated by photochemical activation, and $Mn_2(CO)_8(MeCN)_2$ (**3**) produced by decarbonylation with Me_3NO, respectively, from the parent carbonyls.

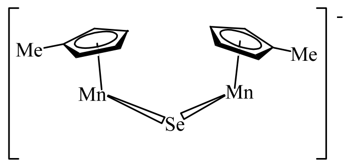
*2.1. Reactions of **1** and **2** with diphosphines selenides*

The reaction between **1** and bis(diphenylphosphino)ethane diselenide ($dppeSe_2$) affords, as the main product, a green compound identified as the 36 electron dinuclear species $[(Cp'Mn)_2(\mu\text{-}Se)_2(CO)_2(dppe)]$ (**4**), formulated on the basis of elemental and mass-spectroscopic data.

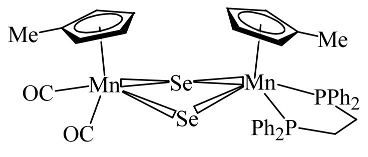
The IR spectrum of **4** exhibits two bands at 1999 and 1944 cm^{-1}, due to the stretching modes of geminal carbonyls; they are at higher frequencies with respect to parent derivative **1** (1927, 1851 cm^{-1}), in agreement with the higher formal oxidation state of the metal in **4**. The ^{31}P NMR spectrum of **4**, shows a singlet at δ 88 ppm, indicating that the two phosphorous atoms are equivalent; no satellites (which would be due to the presence of the selenium on the phosphine) are present, so the phosphine is directly coordinated on the metal and having lost the selenium atoms. The presence of the selenium in the molecule has been evidenced by mass spectrometry, as the isotopic pattern of this element is characteristic and has been compared with calculated data.

The most important fragments in the NICI spectrum are: $[(Cp'Mn)_2Se]^-$ (*m/z* 348), $[\{(Cp')_2Mn_2(CO)_2Se]^-$ (*m/z* 404) and $[(Cp'Mn)_2Se_2]^-$ (*m/z* 427) which indicate the presence of a dimeric species with selenium atoms bridging the two metals (see Scheme 1).

The existence of the *m/z* 348 and *m/z* 404 fragments is also supported by data reported in the literature: in fact the X-ray crystal structure of $[\{Cp^*Mn(CO)_2\}_2Te]$, ($Cp^* = \eta^5\text{-}C_5Me_5$) in which tellurium bridges two manganese atoms, has already been reported by Herrmann et al. [8]. On the basis of these data we propose for compound **4** the structure shown in Scheme 1.



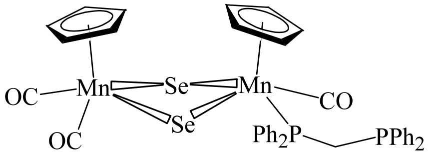
$[(Cp')_2Mn_2Se]^-$ (m/z 348)



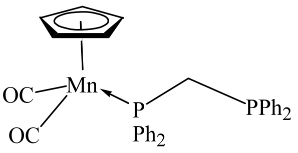
Scheme 1.

From the reactions of **2** with dppmSe, one green and three yellow products were obtained, namely $[(CpMn)_2(\mu\text{-}Se)_2(CO)_3(dppm)]$ (**5**), $[CpMn(CO)_2(dppm)]$ (**6**), $[(CpMn)_2(CO)_4(\mu\text{-}dppm)]$ (**7**), $[CpMn(CO)_2(dppmSe)]$ (**8**), respectively. Their structures have been proposed on the basis of their characterization data and by comparison with those observed for compound **5** and for literature [9] (see Scheme 2).

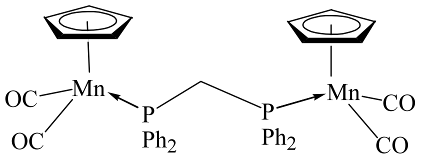
In all the IR spectra of the different products it possible to recognize in the 2000–1850 cm^{-1} region the signals due to the stretching of the carbonyl groups. In particular for compound **5** the three main bands are at 2004 and 1946 cm^{-1}, values quite similar to those of compound **4**. The ^{31}P NMR spectrum shows two doublets with no satellites at δ 85.3 and δ –25.9, indicating that the phosphine acts as a monodentate ligand coordinating the metal through one P atom (positive chemical shift value) while the latter P atom remains free. Considering these experimental evidences and the number of electrons necessary for the manganese to reach the total count of 18 electrons, also in this



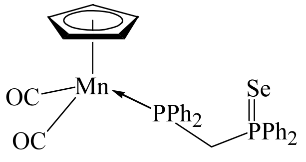
$[(CpMn)_2(\mu\text{-}Se)_2(CO)_3(dppm)]$ (**5**)



$[CpMn(CO)_2(dppm)]$ (**6**)



$[(CpMn)_2(CO)_4(\mu\text{-}dppm)]$ (**7**)



$[CpMn(CO)_2(dppmSe)]$ (**8**)

Scheme 2.

case a dimeric structure with two bridging selenium atoms can be proposed.

In the case of the three yellow compounds, as already indicated by the colour, the manganese has not been oxidated by the selenium atom; in particular in compound **6** the ^{31}P NMR shows a spectrum with two signal at δ 85.5 and δ -25.9, with no satellites: also in this case the coordination of the phosphine is through one P atom while the latter remains non-coordinated, giving a monomeric compound in which the metal atom is surrounded by two carbonyl groups and the dppm ligand.

In compound **7** the situation is different; in this case ^{31}P NMR shows a sharp singlet with no satellites at δ 87.6: the two P atoms are equivalent and both are bound to the metal. These data, together with the IR spectrum which shows two bands at 1928 and 1862 cm^{-1}, the same absorptions of the intermediate compound **2**, suggest that the manganese atom coordinates two carbonyl groups. The structure is likely to be that of a dimer in which the dppm bridges two metals. This hypothesis is also supported by the comparison of these spectroscopic data with those of another compound reported in the literature, namely the tetracarbonyl-(μ_2-dppm)-(μ_2-η^5-fulvalene)dimanganese [10]. The IR spectrum for this compound recorded at the solid state shows two bands at 1927 and 1863 cm^{-1}. The ^{31}P NMR presents a singlet at δ 87.26; the slight differences between the two compounds are due to the rigidity given by the fulvalene to the system.

The ^{31}P NMR spectrum of compound **8** shows two signals both at positive values of chemical shift, one of them is accompanied by two satellites due to the coupling with ^{77}Se. This suggests a η^1 coordination of the phosphine through the P atom, which is at higher chemical shift values, while the P=Se group remains non-coordinated.

2.2. Reaction of 3 with phosphine selenides

Recently, the synthesis and the structure of the simplest chalcogenido manganese cluster, $[Mn_2(\mu_2\text{-}S)_2(CO)_7]$, have been reported [11]. The same paper describes also the synthesis and the structure of the tetranuclear cluster $[Mn_4(\mu_3\text{-}S)_2(\mu\text{-}CO)(CO)_{14}(dmpp)_2]$, obtained as a product of the reaction of $Mn_2(\mu_2\text{-}S)_2(CO)_7$ with dimethylmethylphenylphosphine (dmpp). The reactions of **3** with diphenylmethylphosphine selenide (dpmpSe) and triphenylphosphine selenide (tppSe) afford analogous tetranuclear clusters of formula $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(dpmp)_2]$ (**9**) and $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(tpp)_2]$ (**10**), respectively. The ^{31}P NMR spectra of **9** and **10** show broad singlets at δ 29.0 and δ 45 ppm, respectively. The bridging carbonyl stretching band is clearly distinguishable at 1867 cm^{-1} in the FTIR spectrum in the solid state. FTIR spectrum of **10** is quite similar to that of **9**. All the reactions are strongly selective, the products being air stable and obtainable in high yields (80–90%). The reaction mechanism could involve the formation of $[\{Mn_2(\mu\text{-}Se)(CO)_8(PR_3)]$ as intermediate product, resulting from of the primary attack of the phosphine selenide. This dinuclear intermediate could then undergo a self-condesation that leads to the formation of the final product with loss of a carbonyl molecule.

The same reactions, carried out under the same conditions with R_3PS replacing R_3PSe, proceed with the progressive decomposition of **3**, without the formation of observable sulfido carbonylic molecular species. This behaviour could be explained considering that tertiary phosphine sulfides are less reactive than the correspondent selenides, a higher temperature is requested to activate the P=S bond.

The crystal structure of the dichloromethane solvate of **9** has been determined by X-ray diffraction. A view of the structure of **9** is shown in Fig. 1. Selected bond distances and angles are given in Table 1.

The complex, having an approximate C_2 symmetry, consists of a Mn_4Se_2 core with two Mn and two Se atoms in a butterfly configuration, the two Mn atoms occupying the hinge sites [Mn3–Mn4 = 2.7029(8) Å] and the two Se atoms the wings sites [Mn–Se bond lengths in the range 2.4510 (12)–2.4784(7) Å]. Both Mn3 and Mn4 are bound to three terminal carbonyl groups, while a fourth carbonyl asymmetrically bridges them [Mn3–C5 and Mn4–C5 = 2.159(4) and 2.015(4) Å, respectively]. Each of two Se atoms is also attached to another Mn atom of an octahedral $Mn(CO)_4(dpmp)$ group in which a P atom from the phosphine is coordinated to the Mn atom [Mn1–P1 and Mn2–P2 = 2.3808(12) and 2.3697(12) Å, respectively], in such a way that the Se atoms triply bridge three Mn atoms. It is to note that the Se–Mn bond lengths

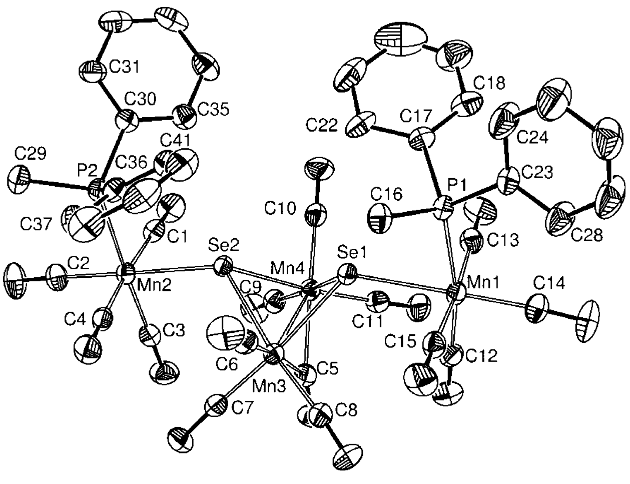


Fig. 1. View of the molecular structure of $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(dpmp)_2]$ (**9**) together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

Table 1
List of selected bond lengths (Å) and bond angles (°) for **9**

Bond lengths			
Mn(1)–P(1)	2.3808(12)	Mn(3)–Se(1)	2.4572(10)
Mn(1)–Se(1)	2.5339(12)	Mn(3)–Mn(4)	2.7029(8)
Mn(2)–P(2)	2.3697(12)	Mn(4)–Se(2)	2.4735(10)
Mn(2)–Se(2)	2.5189(10)	Mn(4)–Se(1)	2.4784(7)
Mn(3)–Se(2)	2.4510(12)		
Bond angles			
P(1)–Mn(1)–Se(1)	82.94(3)	Mn(3)–Se(1)–Mn(4)	66.41(2)
P(2)–Mn(2)–Se(2)	86.80(4)	Mn(3)–Se(1)–Mn(1)	122.25(2)
Se(2)–Mn(3)–Se(1)	75.47(2)	Mn(4)–Se(1)–Mn(1)	122.94(4)
Se(2)–Mn(3)–Mn(4)	57.11(3)	Mn(3)–Se(2)–Mn(4)	66.58(3)
Se(1)–Mn(3)–Mn(4)	57.17(2)	Mn(3)–Se(2)–Mn(2)	120.92(4)
Se(2)–Mn(4)–Se(1)	74.69(4)	Mn(4)–Se(2)–Mn(2)	122.12(3)
Se(2)–Mn(4)–Mn(3)	56.31(4)	Mn(4)–C(5)–Mn(3)	80.63(13)
Se(1)–Mn(4)–Mn(3)	56.42(2)		

involving the external Mn atoms are much longer than those involving the Mn atoms of the hinge [Mn1–Se1 and Mn2–Se2 = 2.5339(12) and 2.5189(10) Å, respectively].

The structure of **9**, as pointed out above, is strictly comparable to that of $[Mn_4(\mu_3\text{-}S)_2(\mu\text{-}CO)(CO)_{14}(dmpp)_2]$, in which the Mn–Mn hinge is shorter [2.6356(16) Å] and the bridging carbonyl is symmetric [11].

3. Experimental

3.1. General remarks

The starting reagents, elemental selenium and sulfur, KSeCN, $[CpMn(CO)_3]$, $[Cp'Mn(CO)_3]$, $Mn_2(CO)_{10}$, Me_3NO, and all the phosphines were pure commercial products (Aldrich and Fluka) and were used as received. Selenido phosphines tppSe [12], $dppmSe_2$ [13] dppmSe [14] were synthesized according to the literature procedure using KSeCN, dpmpSe was synthesized by reaction of diphenylmethyl phosphine with elemental selenium at 70 °C under nitrogen atmosphere for 5 h (yield 95%). $Cp'Mn(CO)_2(THF)$ (**1**), $CpMn(CO)_2(THF)$ (**2**) [15] and $[Mn_2(CO)_8(MeCN)_2]$ (**3**) [16] were prepared from the parent carbonyls according to the literature.

The solvents (C. Erba) were dried and distilled by standard techniques before use. All manipulations (prior to the TLC separations) were carried out under dry nitrogen by means of standard Schlenk-tube techniques. Elemental (C, H, N) analyses were performed with a Carlo Erba EA 1108 automated analyzer. IR spectra (KBr discs or CH_2Cl_2 solutions) were recorded on a Nicolet 5PC FT and a Nicolet 'Nexus' spectrometers. Mass spectra were recorded 'flow injection' on a LC-MS integrated system equipped with Particle Beam Hewlett–Packard 59980B and H. P. 5989A MS engine ^1H (300 MHz), ^{31}P (81.0 MHz, 85%-H_3PO_4 as external reference) NMR spectra ($CDCl_3$ solutions) were recorded on Bruker instruments, AC 300 (^1H) and CXP 200 (^{31}P).

3.2. Reaction of **1** with $dppeSe_2$

$dppeSe_2$ (511 mg, 0.92 mmol) dissolved in 50 ml of THF was added to a concentrated solution of **1** (50 ml, 0.92 mmol). The mixture was stirred for 3 h till the change of the colour from red to green, and then the solution was evaporated to dryness. The green rough solid product was separated and purified by TLC on silica, using CH_2Cl_2–hexane (1:1) as eluent. The green compound $[(Cp'Mn)_2(\mu\text{-}Se)_2(CO)_2(dppe)]$ (**4**) was separated in modest yield (20%). FTIR (CH_2Cl_2, cm^{-1}): 1999s, 1944vs. MS-NICI, *m/z* (%): 839 (28), $[(Cp'(-Me))(Cp')Mn_2Se_2(dppe)\ (CO)]^-$; 427 (88), $[(Cp')_2Mn_2Se_2]^-$; 404 (62), $[(Cp')_2Mn_2Se(CO)_2]^-$; 348 (48), $[(Cp')_2Mn_2Se]^-$ *Anal*. Found: C, 54.68; H, 4.10. Calc. for $Mn_2Se_2P_2C_{40}O_2H_{36}$: C, 54.8; H, 4.3%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 88s.

3.3. Reaction of **2** with dppmSe

dppmSe (454 mg, 0.98 mmol) dissolved in THF was added to a concentrated solution of **2** (50 ml, 0.98 mmol). The solution was then stirred for 3 h, till the complete change of the colour from red to green, and then evaporated to dryness. The green product was separated and purified by TLC on silica, using CH_2Cl_2–hexane (1:1) as eluent. Four main compounds (one green and three yellow) were separated and recognized to be $[(CpMn)_2(\mu\text{-}Se)_2(CO)_3(dppm)]$ (**5**), $[CpMn(CO)_2(dppm)]$ (**6**), $[(CpMn)_2(CO)_4(\mu\text{-}dppm)]$ (**7**), $[CpMn(CO)_2(dppmSe)]$ (**8**), respectively, through IR spectroscopy and $^{31}P\{^1H\}$ NMR.

5: FTIR (CH_2Cl_2, $\nu(CO)$, cm^{-1}): 2004w, 1946w. *Anal*. Found: C, 51.5; H, 3.6. Calc. for $Mn_2Se_2P_2C_{38}O_3H_{30}$: C, 52.79; H, 3.47%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 85.3d, −25.9d, *J*(P,P) 68 Hz.

6: FTIR (CH_2Cl_2, $\nu(CO)$, cm^{-1}): 1929m, 1861m. *Anal*. Found: C, 61.5; H, 4.3. Calc. for $MnSeP_2C_{32}O_2H_{26}$: C, 60.20; H, 4.08%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 85.5d, −25.85d, *J*(P,P) 72 Hz.

7: FTIR (CH_2Cl_2, $\nu(CO)$, cm^{-1}): 1928m, 1862m. *Anal*. Found: C, 60.1; H, 3.6. Calc. for $Mn_2P_2C_{39}O_4H_{30}$: C, 63.77; 4.08%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 87.6s

8: FTIR (CH_2Cl_2, $\nu(CO)$, cm^{-1}): 1928m, 1859m. *Anal*. Found: C, 68.4; H, 4.3. Calc. for $MnP_2C_{32}O_2H_{26}$: C, 68.71; H, 4.65%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 87.8d, 23.8d, *J*(P,P) 20 Hz, *J*(P,Se) 736 Hz.

3.4. Synthesis of [$Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(dpmp)_2$] (**9**)

A toluene solution of [$Mn_2(CO)_8(MeCN)_2$] (**3**) (300 mg, 0.72 mmol) and dpmpSe (201 mg, 0.72 mmol) was stirred at 50 °C for 1 h under a nitrogen atmosphere. The brown solution was evaporated to dryness yielding a brown residue which was redissolved in a small amount of dichloromethane. TLC separation on silica, using a CH_2Cl_2–petroleum ether (1:1) mixture as eluent, yielded a brown band containing [$Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(dpmp)_2$] (**9**) (yield 80%). Purification by crystallization (from a CH_2Cl_2–MeOH mixture at 5 °C for some days) gave crystals suitable for X-ray analysis. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2078m, 2064s 2014vs, 1985sh, 1962m, 1932s. FTIR (KBr, ν(CO), cm^{-1}): 2078s, 2066s, 2007vs, 1959s, 1931vs, 1911s, 1867w. *Anal.* Found: C, 42.5; H, 2.0. Calc. for $Mn_4Se_2P_2C_{41}O_{15}H_{26}$: C, 41.08; H, 2.17%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.0 br, ^1H NMR ($CDCl_3$): δ 2.28 (t, 6 H, CH_3, ^1J(H,P) = 7.8 Hz), δ 7.3–7.8 (m, 20 H, Ph).

3.5. Synthesis of [$Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(tpp)_2$] (**10**)

Using the method described previously, [$Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(tpp)_2$] was prepared (yield 90%) from 300 mg (0.72 mmol) of **3** and 247 mg of tppSe. The product was recognized by comparison of its spectroscopical data with those observed for [$Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(dpmp)_2$] (**10**). FTIR ($CH_2Cl_2$, δ(CO), cm^{-1}): 2078m, 2064s 2014vs, 1985sh, 1962m, 1932s. *Anal.* Found: C, 45.5; H, 2.1. Calc. for $Mn_4Se_2P_2C_{51}O_{15}H_{30}$: C, 46.30; H 2.26% $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 45.05.

3.6. Crystal structure determination of complex **9**·CH_2Cl_2

In the crystals of **9** dichloromethane molecules of solvation were found. The intensity data of **9**·CH_2Cl_2 were collected at room temperature on a Bruker AXS Smart 1000 single crystal diffractometer equipped with an area detector using a graphite monochromated Mo Kα radiation. Crystallographic and experimental details for the structure are summarized in Table 2. A correction for absorption was made using the Bruker software packing. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) (SHELX-97) [17] first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms excepting for the hydrogen atoms of the solvent. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2 F_o^2 + (0.0304P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, was used.

Table 2
Crystal data and structure refinement for compound **9**·CH_2Cl_2

Formula	$Mn_4Se_2P_2O_{15}C_{41}H_{26}\cdot CH_2Cl_2$
Formula weight	1283.16
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	19.697(3)
b (Å)	15.057(5)
c (Å)	16.667(5)
β (°)	94.81(5)
V (Å^3)	4926(2)
Z	4
D_{calc} (g cm^{-3})	1.730
F(000)	220
μ (cm^{-1})	27.18
Reflections collected and unique	37750, 13630 [$R_{int} = 0.0494$]
Observed reflections [$I > 2\sigma(I)$]	6751
Parameters	606
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0365$, $wR_2 = 0.0662$
R indices (all data) [a]	$R_1 = 0.1051$, $wR_2 = 0.0782$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

4. Supplementary material

The supplementary material for the structures includes the lists of atomic coordinates for the non-H atoms, of calculated coordinates for the hydrogen atoms, of anisotropic thermal parameters and complete lists of bond lengths and angles. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 205586. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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