Preparation, Properties, and Reactions of Metal-Containing Heterocycles, XCV[◇]

Transition-Metal-Mediated Cyclocotrimerization of Selenophosphinites with Activated Alkynes☆

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Selenophosphinito complexes $(OC)_4Mn(\eta^2\text{-}Se{=}PR^1_2)$ (**2a, b**) [R^1 = *cyc*-Hex (**a**), *t*Bu (**b**)] are formed by the reaction of $BrMn(CO)_5$ with the phosphane selenides R^1_2HPSe (**1a, b**) in the presence of the auxiliary base $Et(iPr)_2N$. According to an X-ray structural analysis, **2a** crystallizes in the space group $P\bar{1}$ with $Z = 2$. The dimeric complex $[(OC)_4Mn(\mu\text{-}Se{=}PMe_2)]_2$ (**4c**) is not obtained in a straightforward way. Compound **4c** is only obtained via the intermediate $Br(OC)_4Mn{-}Se{=}P(H)Me_2$ (**3c**) by HBr elimination with *n*BuLi. Complex **3c** is formed by replacement of carbon monoxide in $BrMn(CO)_5$ by Me_2HPSe (**1c**). A dissociative equilibrium between $[(OC)_4Mn(\mu\text{-}Se{=}PMe_2)]_2$ (**4c**) and the monomeric species $(OC)_4Mn(\eta^2\text{-}Se{=}PMe_2)$ was not observed. The cyclocotrimerization of the >P=Se function with the activated alkynes ZC≡CZ [Z = CO_2R^2; R^2 = Me (**d**), Et (**e**), *i*Pr (**f**), *cyc*-Hex (**g**)] was successful only in the case of the cyclohexyl derivative **2a** to give the selenaphosphamanganabicycloheptadienes **5d–g**. An X-ray structural analysis proved that **5d** crystallizes in the space group $P\bar{1}$ with $Z = 2$. Under CO pressure **5d** was degraded to the selenophene **6**.

The transition metal-catalyzed or -mediated cyclotrimerization of alkynes and cyclocotrimerization of alkynes with nitriles represent important synthetic methods for the synthesis of highly substituted benzenes[2–6] and pyridines[7]. Recently, the cyclooligomerization of phosphaalkynes which takes place in the coordination sphere of certain transition metal fragments was also reported[8,9]. With the exception of phosphaacetylenes these reactions proceed via metallacyclopropenes and metallacyclopentadienes as intermediates. Depending on the electronic nature of the alkyne, either metallacycloheptatrienes or metallabicycloheptadienes are formed with an additional alkyne[10,11]. The final products are obtained by reductive elimination of the transition metal moiety. Analogous cyclocotrimerizations are possible by the employment of the >P=S group which stems from deprotonated diorganylphosphane sulfides[12]. Its alkyne-like character is explained by similar covalent radii and electronegativities of the phosphorus and sulfur atoms. The observed intermediates in the cyclocotrimerization of the >P=S group with electron-poor alkynes – thiaphosphametallacyclopentadienes and thiaphosphametallabicycloheptadienes – are comparable to those of the cyclotrimerization of alkynes[13]. Oxidative and hydrolytic degradation of thiaphosphamanganabicycloheptadienes lead to regiosepecifically substituted thiophenes[14] and furans[15], respectively.

Although selenium is somewhat bigger than sulfur we wanted to examine whether the >P=Se group in selenophosphinites shows a reactive behavior comparable to that of the >P=S function. In the first part of this article we describe the preparation of three- and six-membered heterocycles containing the >P=Se unit. These heterocycles serve as starting compounds for the cyclocotrimerization of the >P=Se function with activated alkynes which is described in the second part of this paper. Finally, we were interested in finding out whether selenophenes are accessible by means of this new method.

Results and Discussion

1) Three- and Six-Membered Heterocycles 2a, b, 4c Containing the >P=Se Unit

In recent investigations we observed that the formation of three- and six-membered heterocycles of the type $(OC)_4Mn(\eta^2\text{-}S{=}PR^1_2)$ and $[(OC)_4Mn(\mu\text{-}S{=}PR^1_2)]_2$ depends on the steric encumbrance of the substituent R^1[16]. Therefore three different secondary phosphane selenides **1a–c** (Scheme 1) were selected and allowed to react with the starting compound $BrMn(CO)_5$. Although the phosphane selenides **1a–c** are mentioned in a patent[17,18], no spectroscopic and other analytical data were available. Compounds **1a–c** are colorless and thermodynamically unstable. They dissolve readily in polar organic solvents. In the FD mass spectra the molecular peaks are in agreement with the expected composition of **1a–c**. The $^{31}P\{^1H\}$-NMR spectra of **1a–c** reveal a singlet the chemical shift of which is located in the same region as that of the corresponding phosphane sulfides[19]. The ^{77}Se satellites in the $^{31}P\{^1H\}$-NMR spectra enable the determination of the $^1J_{SeP}$ coupling constants (about 700 Hz), which were also confirmed by the

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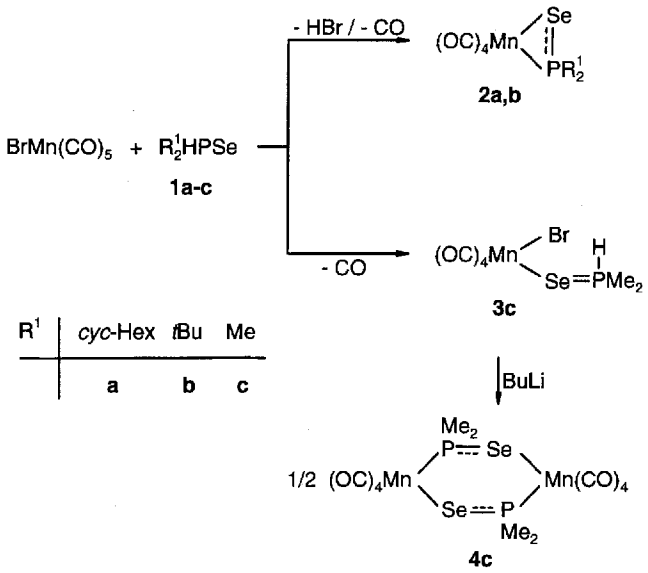
$^{77}Se\{^1H\}$-NMR spectra of **1a–c**. In the latter a high-field doublet between $\delta = -300$ and -500 is ascertained.

Scheme 1

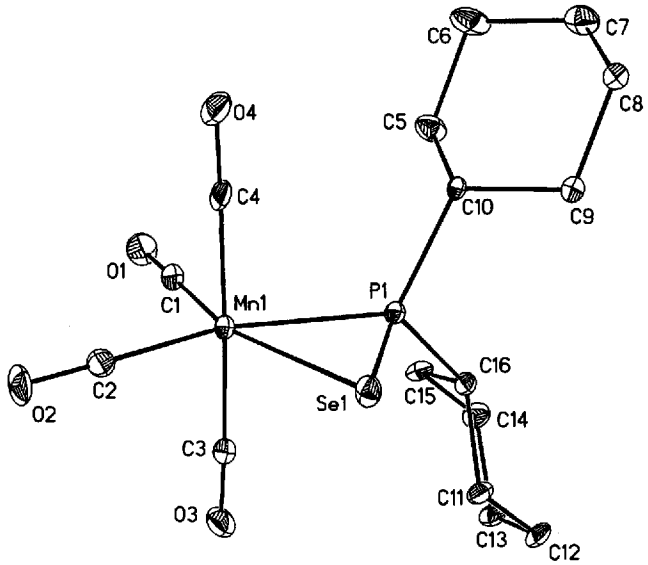


Only in the case of **1a**, **b** could the corresponding complexes $(OC)_4Mn(\eta^2\text{-}Se{=}PR^1_2)$ (**2a**, **b**) be obtained (Scheme 1) when $BrMn(CO)_5$ was treated with the phosphane selenides R^1_2HPSe (**1a–c**) in THF in the presence of the auxiliary base $Et(iPr)_2N$. The yellow kinetically stabilized compounds **2a**, **b** are soluble in all common organic solvents. A dimerization to the six-membered species $[(OC)_4Mn(\mu\text{-}Se{=}PR^1_2)]_2$ does not take place. In a side reaction the diselenophosphinato complexes $R_2PSe_2Mn(CO)_4$ (R = *cyc*-Hex, *t*Bu) could also be isolated. The latter were separated from **2a**, **b** by medium-pressure liquid chromatography (MPLC). The ring size of **2a**, **b** was confirmed by FD mass spectra showing the corresponding molecular mass. Both compounds **2a**, **b** exhibit a broad ^{31}P singlet in their $^{31}P\{^1H\}$-NMR spectra which is typical of a Mn–P bond. In contrast to this finding, the diselenophosphinato complex $(cyc\text{-Hex})_2PSe_2Mn(CO)_4$ shows a sharp singlet with ^{77}Se satellites at nearly the same field as the signal in the spectrum of **2a**.

The structure of **2a** was confirmed by an X-ray structural analysis (Figure 1); it is comparable to that of the corresponding compound $(OC)_4Mn(\eta^2\text{-}S{=}PR^1_2)$ (R^1 = *cyc*-Hex)[20]. The P1–Mn1 distances in both three-membered rings have similar dimensions. The Mn1–Se1 contact corresponds to a common single bond[21], whereas the P1–Se1 interaction is shorter than a typical single bond[22]. Due to the small P1–Mn1–Se1 angle, the octahedral geometry of the complex is slightly distorted.

Interestingly, the phosphane selenide Me_2HPSe (**1c**) does not react with $BrMn(CO)_5$ in THF to give either a three- or a six-membered heterocycle. Instead, the diselenophosphinato complex $Me_2PSe_2Mn(CO)_4$ was formed in high yields. Therefore, the reaction of **1c** with $BrMn(CO)_5$ was performed in absence of the auxiliary base $Et(iPr)_2N$ in diisopropyl ether (Scheme 1). In this case the unstable Se isomer $Br(OC)_4Mn{-}Se{=}P(H)Me_2$ (**3c**) was formed which decomposes rapidly in chlorinated hydrocarbons. The FD spectrum of **3c** is consistent with this formula. ^{31}P- and ^1H-NMR spectra of **3c** prove the absence of a Mn–P bond, while the P–H bond is still intact. Both spectra display a characteristic doublet of septets. In the proton-decoupled ^{31}P-NMR spectrum only a singlet with ^{77}Se satellites appears. A rearrangement of **3c** to the isomer $Br(OC)_4Mn{-}PMe_2SeH$ as in the case of the sulfur analogue does not take place[23].

Figure 1. ORTEP plot of the molecular structure of the three-membered heterocycle **2a**. – Selected bond lengths [Å] and angles [°]: Mn(1)–P(1) 2.268(2), Se(1)–P(1) 2.164(2), Mn(1)–Se(1) 2.5629(11); P(1)–Mn(1)–Se(1) 52.81(4), P(1)–Se(1)–Mn(1) 56.58(4), Se(1)–P(1)–Mn(1) 70.61(5)



Such an isomerization is anyway not necessary, because HBr could be abstracted by treatment of **3c** with *n*BuLi in THF at −65 °C. The chromatographically purified product was recognized as the yellow thermodynamically stable six-membered heterocycle $[(OC)_4Mn(\mu\text{-}Se{=}PMe_2)]_2$ (**4c**). The same compound was synthesized by Vahrenkamp et al. several years ago in a completely different way[24]. A broad signal in the $^{31}P\{^1H\}$-NMR spectrum of **4c** points to a direct Mn–P bond. In contrast to the corresponding sulfur-containing heterocycle $[(OC)_4Mn(\mu\text{-}S{=}PMe_2)]_2$[16], the ^1H-NMR spectrum of **4c** displays a virtual triplet of an $A_6A'_6$-XX′ pattern which indicates that the PP coupling constant is large. This triplet was only detected above 40 °C, below this temperature the multiplet collapses into a broad singlet. The conservation of the PP coupling constant is in agreement with an intramolecular exchange process. This dynamic behavior can be explained by a fast ring inversion which equilibrates the six equatorial with the six axial CH_3 protons. If the ^1H-NMR spectrum is measured ^{31}P-decoupled only one singlet appears at 40 °C. In the $^{13}C\{^1H\}$-NMR spectrum of **4c** the corresponding AXX′ pattern for the CH_3 carbon atoms is noticed.

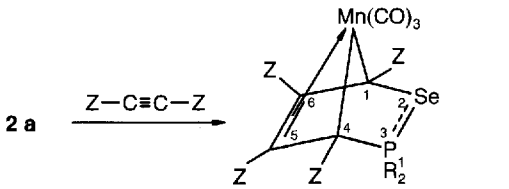
If six-membered heterocycles of the type $[(OC)_4Mn(\mu\text{-}S{=}PR_2)]_2$ are employed for the cyclocotrimerization of the

>P=S function with activated alkynes, the existence of an equilibrium in solution between the six-membered species and the monomeric complexes $(OC)_4Mn(\eta^2\text{-}S{=}PR_2)$ is a precondition[25]. However, the selenium analogue **4c** does not display a peak at $[M^+]/2$ like the corresponding sulfur-containing ring. Additionally, an osmometric molecular mass determination of **4c** verified the dimer.

2) Behavior of the Selenaphosphamanganacyclopropenes 2a, b and the Six-Membered Heterocycle 4c Toward Activated Alkynes

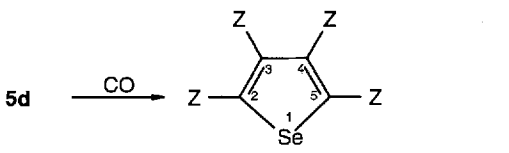
In contrast to **2b** and **4c**, only the >P=Se group in the heterocycle **2a** is able to undergo a cyclocotrimerization with the electron-poor acetylenes Z−C≡C−Z (Z = CO_2R^2; R^2 = Me, Et, *i*Pr, *cyc*-Hex) to the selenaphosphamanganabicycloheptadienes **5d−g**. These reactions were carried out in *n*-hexane and do not proceed in polar organic solvents like THF. The yellow novel cyclocotrimerization products are rather stable and were purified chromatographically. Their solubility depends on the size of the substituents R^2. **5f, g** dissolve readily in all common organic solvents, whereas **5d, e** are only soluble in more polar solvents. The molecular peaks in the FD mass spectra of **5d−g** are in agreement with the expected composition of these compounds. In their $^{31}P\{^1H\}$-NMR spectra a singlet with ^{77}Se satellites appears which has nearly the same chemical shift as the sulfur analogues[25]. In the case of **5d** the $^{77}Se\{^1H\}$-NMR spectrum reveals a doublet due to the SeP coupling.

Scheme 2



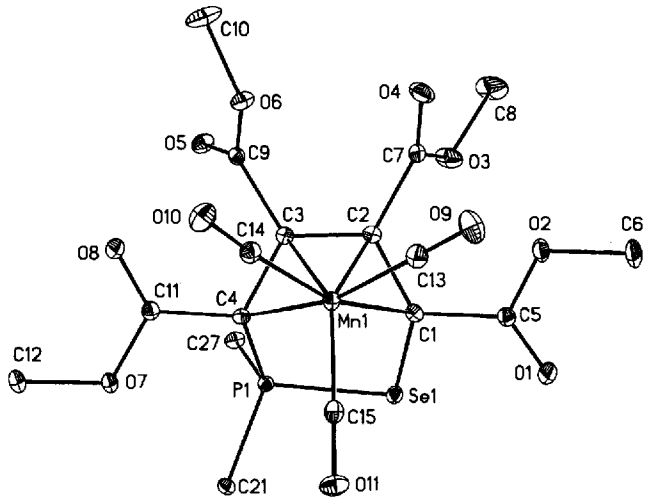
R^1 \ R^2	Me	Et	*i*Pr	*cyc*-Hex
cyc-Hex	**d**	**e**	**f**	**g**

Z = CO_2R^2



The structure of **5d** was confirmed by an X-ray structure analysis. The ORTEP diagram with atom labelling is depicted in Figure 2. As expected the structural features of **5d** do not differ much from those of the sulfur analogue[26]. The P1−Se1 distance is shorter than a single bond[22] and is similar to that in **2a**. The C−C bonds in the ring skeleton are alternating long (C1−C2), short (C2−C3), and long (C3−C4) (Figure 2). In contrast to Mn1−C1 and Mn1−C4, the distances between Mn1−C2 and Mn1−C3 are slightly shorter. This is consistent with a limiting structure in which the manganese atom is linked by two σ bonds and one π bond to C1 and C4 and to C2 and C3, respectively[27].

Figure 2. ORTEP plot of the molecular structure of the bicyclic compound **5d**. The cyclohexyl groups at the phosphorus atom are omitted for clarity. − Selected bond lengths [A] and angles [°]: Mn(1)−C(1) 2.124(2), Mn(1)−C(2) 2.079(2), Mn(1)−C(3) 2.068(2), Mn(1)−C(4) 2.174(2), Se(1)−P(1) 2.1881(7), Se(1)−C(1) 1.967(2), P(1)−C(4) 1.807(2), C(1)−C(2) 1.448(3), C(2)−C(3) 1.408(3), C(3)−C(4) 1.474(3); C(1)−Mn(1)−C(4) 81.20(9), C(3)−C(2)−C(1) 117.6(2), C(2)−C(3)−C(4) 119.1(2), C(1)−Se(1)−P(1) 93.44(7), C(4)−P(1)−Se(1) 105.24(8), C(2)−C(1)−Se(1) 122.4(2), C(3)−C(4)−P(1) 117.0(2)



Divergent from the cyclocotrimerizations of thiophosphinites with alkynes[25], in the present investigations no intermediates could be detected. Even when the reactions were monitored $^{31}P\{^1H\}$-NMR spectroscopically no peaks occurred which point to the appearance of such species. Another feature distinguishing both reactions is the fact, that with selenophosphinites no cyclocotrimerization was observed with partially activated alkynes, e.g. $CH_3C{\equiv}C{-}Z$ or $HC{\equiv}C{-}Z$ (Z = CO_2R^2)[28]. Also attempts to initiate reactions of selenophosphinites with phosphaalkynes failed. It is not surprising that $(OC)_4Mn(\eta^2\text{-}Se{=}P(t\text{Bu})_2)$ (**2b**) was not able to react with alkynes, because the phosphorus atom is sterically hindered by two bulky *t*Bu substituents. Hence, an attack of the alkyne at this P atom is impossible.

A special peculiarity of the dimer **4c** is its missing ability to react with activated alkynes. As mentioned above we suppose that the lack of an equilibrium between **4c** and a possible monomeric species $(OC)_4Mn(\eta^2\text{-}Se{=}PMe_2)$ is the reason for this behavior. This is a supporting evidence that cyclocotrimerizations of >P=S and >P=Se functions with alkynes take place only with the above-mentioned three-membered moieties.

3) Formation of the Selenophene 6

In former studies we demonstrated that thiophenes and furans are obtained by oxidative and hydrolytic degradation of thiaphosphamanganabicycloheptadienes, respectively[14,15,25]. However, if, for example, **5d** was oxidized with $(NH_4)_2[Ce(NO_3)_6]$ only traces of the selenophene **6** could

be detected. Much more successful was the treatment of a THF solution of **5d** with carbon monoxide under a pressure of 150 bar at 100°C[26]. In rather good yields the colorless, stable selenophene **6** was formed which is soluble in more polar organic solvents. The $^{13}C\{^1H\}$-NMR spectrum displays two low-field singlets for the two sets of carbon atoms. Due to the electron-donating property of selenium, the signal at higher field was assigned to the selenium atom adjacent to the carbon atoms[29]. Recently, the selenophene **6** was mentioned in the literature. It was observed as a byproduct in the reaction of the cobalt complex $(\eta^5\text{-}C_5H_2)Co(CO)_2$ with selenium and the alkyne Z−C≡C−Z (Z = CO_2Me)[30].

Conclusion

In accordance with the >P⩵S chemistry the formation of the monomeric complexes $(OC)_4Mn(\eta^2\text{-}Se{=}PR^1_2)$ (**2a, b**) is preferred, if bulky substituents are attached to the phosphorus atom[16]. In the case of R^1 = Me only the dimeric species $[(OC)_4Mn(\mu\text{-}Se{=}PMe_2)]_2$ (**4c**) occurs. The latter complex was obtained in a way different from that of the already known sulfur analogous compound[16]. The reactive behavior of both types of selenophosphinito complexes differs from that of the thiophosphinites[25]. Only $(OC)_4Mn(\eta^2\text{-}Se{=}P(cyc\text{-}Hex)_2)$ (**2a**) is able to undergo a cyclocotrimerization with activated alkynes to give the selenaphosphamanganabicycloheptadienes **5d−g**, whereas **2b** is kinetically too stable to react with acetylenes. The dimer $[(OC)_4Mn(\mu\text{-}Se{=}PR^1_2)]_2$ (**4c**) reveals no equilibrium with the monomeric species $(OC)_4Mn(\eta^2\text{-}Se{=}PR^1_2)$ in solution which is a basic requirement for the cyclocotrimerization of the >P⩵Se group with electron-poor alkynes. Comparable to the corresponding thiaphosphamanganabicycloheptadienes[26] the selenium homologues can be degraded to selenophenes.

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Experimental

All manipulations were carried out under argon by using standard Schlenk techniques. Solvents were dried with appropriate reagents and stored under argon. The starting compounds like the secondary phosphanes[31,32], $BrMn(CO)_5$[33], and the alkynes[34] were prepared as described.

MS (FD): Finnigan MAT 711A modified by AMD (8 kV, 60°C). − Osmometric molar mass determination: Knauer Dampfdruck-Osmometer. − IR: Bruker IFS 48. − ^1H NMR: Bruker AC 250, DRX 250 at 250.13 MHz, and AC 80 at 80.13 MHz. − $^{13}C\{^1H\}$ NMR: Bruker AC 250, DRX 250 at 62.90 MHz, and AC 80 at 20.15 MHz. ^1H and $^{13}C\{^1H\}$ chemical shifts are reported relative to TMS. − $^{31}P\{^1H\}$ NMR: Bruker AC 80 at 32.44 MHz and Bruker DRX 250 at 101.25 MHz, external standard 1% H_3PO_4 in [D_6]acetone. − $^{77}Se\{^1H\}$ NMR: Bruker DRX 250 at 47.69 MHz, the chemical shifts are reported relative to Me_2Se. − Medium-Pressure Liquid Chromatography (MPLC): Knauer HPLC pump 64, UV/Vis photometer, Merck Lobar® Column B (310-25), LiChroprep® Si 60 (40−63). − Microanalyses: Carlo Erba, model 1106 and AAS Perkin-Elmer, model 4000. The Br analysis was carried out according to Schöniger[35] and evaluated as described by Dirschel and Erne[36].

1. *General Procedure for the Synthesis of the Phosphane Selenides* **1a, b**: The corresponding secondary phosphane R^1_2HP was added dropwise to a stirred suspension of red selenium in 50 ml of toluene. The reaction was slightly exothermic. After heating at 70°C for 10 min, the yellow solution contained only traces of red selenium which were filtered off (P4). After removal of the solvent in vacuo the phosphane selenides **1a, b** were recrystallized from ethanol.

1.1. *Dicyclohexylphosphane Selenide* (**1a**): A suspension of red selenium (1.12 g, 14.18 mmol) was allowed to react with dicyclohexylphosphane (2.81 g, 14.17 mmol) to give 3.14 g (79.9%) of **1a**, m.p. 115−116°C (dec.). − MS (FD), *m/z*: 278.0 [M^+]. − ^1H-NMR (80.13 MHz, $CDCl_3$, −30°C): δ = 0.8−2.2 (m, 22H, C_6H_{11}), 5.56 (dt, $^1J_{PH}$ = 417.5, $^3J_{HH}$ = 3.7 Hz, PH). − $^{13}C\{^1H\}$ NMR (20.15 MHz, $CDCl_3$, −30°C): δ = 25.32−28.24 (m, C_6H_{11}), 33.80 (d, $^1J_{PC}$ = 41.8 Hz, PCH). − $^{31}P\{^1H\}$ NMR (32.44 MHz, $CDCl_3$, −30°C): δ = 32.2 (s, $^1J_{SeP}$ = 668 Hz, PH). − $^{77}Se\{^1H\}$ NMR (47.69 MHz, $CDCl_3$): δ = −499 (d, $^1J_{SeP}$ = 668 Hz, PSe). − $C_{12}H_{23}PSe$ (277.3): calcd. C 51.99, H 8.36; found C 52.41, H 8.57.

1.2. *Di-tert-butylphosphane Selenide* (**1b**): A suspension of red selenium (1.10 g, 13.93 mmol) was allowed to react with di-*tert*-butylphosphane (2.00 g, 13.68 mmol) to give 1.83 g (59%) of **1b**, m.p. 129−131°C (dec.). − MS (FD), *m/z*: 226.2 [M^+]. − ^1H NMR (250.13 MHz, $CDCl_3$): δ = 1.27 [d, $^3J_{PH}$ = 16.9 Hz, 18H, $C(CH_3)_3$], 5.41 (d, $^1J_{PH}$ = 409.7 Hz, PH). − $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 27.92 [d, $^2J_{PC}$ = 2.1 Hz, $C(CH_3)_3$], 35.07 [d, $^1J_{PC}$ = 34.1 Hz, $PC(CH_3)_3$]. − $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = 67.8 (s, $^1J_{SeP}$ = 704 Hz, PH). − $^{77}Se\{^1H\}$ NMR (47.69 MHz, $CDCl_3$): δ = −446 (d, $^1J_{SeP}$ = 704 Hz, PSe). − $C_8H_{19}PSe$ (225.2): calcd.C 42.67, H 8.51; found C 42.57, H 8.70.

2. *Dimethylphosphane Selenide* (**1c**): The dimethylphosphane generated as described in ref.[33] was distilled from the reaction mixture and directly passed into a stirred suspension of red selenium (4.00 g, 50.65 mmol) in 50 ml of benzene. After the complete addition of Me_2PH the solution was stirred for 15 min at ambient temp. Traces of selenium were filtered off (P4), and the solvent was removed in vacuo. The remaining liquid was dissolved in 10 ml of ethanol, and the solution was cooled to −30°C. While cooling a colorless precipitate formed which was collected by filtration with a cooled frit (−30°C) (P4) and dried in vacuo to give 4.60 g (64%) of **1c**, m.p. 11−13°C. − MS (FD), *m/z*: 142.1 [M^+]. − ^1H NMR (250.13 MHz, $CDCl_3$): δ = 1.92 [dd, $^2J_{PH}$ = 14.4, $^3J_{HH}$ = 5.0 Hz, 6H, $HP(CH_3)_2$], 6.36 (dsept, $^1J_{PH}$ = 441.8, $^3J_{HH}$ = 5.0 Hz, PH). − $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 18.15 [d, $^1J_{PC}$ = 48.4 Hz, $P(CH_3)_2$]. − $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = −19.1 (s, $^1J_{SeP}$ = 701 Hz, PSe). − $^{77}Se\{^1H\}$ NMR (47.69 MHz, $CDCl_3$): δ = −309 (d, $^1J_{SeP}$ = 701 Hz, PSe). − C_2H_7PSe (141.0): calcd. C 17.03, H 5.00; found C 16.62, H 5.15.

3. *General Procedure for the Synthesis of* $(OC)_4Mn(\eta^2\text{-}Se{=}PR^1_2)$ (**2a, b**) *and of* $(cyc\text{-}Hex)_2PSe_2Mn(CO)_4$: A solution of **1a, b** in 50 ml of THF was added dropwise to a stirred solution of $BrMn(CO)_5$ in 50 ml of THF. Subsequently, one equivalent of $Et(iPr)_2N$ was added. The solution was heated to 60°C and stirred at this temp. for 1 h. After removal of the solvent in vacuo, the residue was redissolved in ice-cold methanol. The insoluble material was filtered off (P4) and dried in vacuo. The crude product contained the three-membered rings **2a** and **2b**, respectively and $(cyc\text{-}Hex)_2PSe_2Mn(CO)_4$.

3.1. *Tetracarbonyl(η²-dicyclohexylselenophosphinito)manganese* (**2a**): A solution of $BrMn(CO)_5$ (1.40 g, 5.09 mmol) was allowed to react with **1a** (1.46 g, 5.27 mmol) and $Et(iPr)_2N$ (0.9 ml, 5.29 mmol) to give a crude product which was dissolved in 5 ml of *n*-hexane and chromatographed on a silica gel column [(10 × 2.5 cm), silica gel (32–63 μm), *n*-hexane]. The main purification was carried out by employing MPLC, and the product was eluted with *n*-hexane (silica gel column, 1. fraction). The solvent was removed and the residue dried vacuo to yield 710 mg (31.5%) of **2a**, m.p. 118°C (dec.). – MS (FD), *m/z*: 443.9 [M^+]. – IR (*n*-hexane): $\tilde{\nu}$ = 2069, 1996, 1981, 1953 cm^{-1} (C≡O). – ^{1}H-NMR (250.13 MHz, $CDCl_3$): δ = 1.12–2.02 (m, C_6H_{11}). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 25.66–32.87 (m, C_6H_{11}), 41.40 (d, $^1J_{PC}$ = 13.7 Hz, PCH). – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = 93.1 (br. s, PSe). – $^{77}Se\{^1H\}$ NMR (47.69 MHz, $CDCl_3$): δ = −400 (br. s, PSe). – $C_{16}H_{22}MnO_4PSe$ (443.2): calcd. C 43.36, H 5.00, Mn 12.40; found C 43.33, H 5.14, Mn 12.75.

3.2. *Tetracarbonyl(η²-di-tert-butylselenophosphinito)manganese* (**2b**): A solution of $BrMn(CO)_5$ (1.40 g, 5.09 mmol) was allowed to react with **1b** (1.17 g, 5.20 mmol) and $Et(iPr)_2N$ (0.9 ml, 5.29 mmol) to give the crude product which was dissolved in 5 ml of *n*-hexane/ethyl acetate (10:1) and chromatographed on a silica gel column [(14 × 3 cm), silica gel (32–63 μm), *n*-hexane/ethyl acetate (10:1)]. The main purification was carried out by employing MPLC, and the product was eluted with *n*-hexane/ethyl acetate (10:1) (silica gel column, 2. fraction). The solvent was removed and the residue dried in vacuo to yield 480 mg (24%) of **2b**, dec. 89°C. – MS (FD), *m/z*: 391.9 [M^+]. – IR (*n*-hexane): $\tilde{\nu}$ = 2086, 2018, 2005, 1950 cm^{-1} (C≡O). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.36 [d, $^3J_{PH}$ = 13.3 Hz, $PC(CH_3)_3$]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 31.85 [s, $C(CH_3)_3$], 36.52 [d, $^1J_{PC}$ = 13.7 Hz, $PC(CH_3)_3$]. – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = 75.4 (br. s, PSe). – $C_{12}H_{18}MnO_4PSe$ (391.1): calcd. C 36.85, H 4.64, Mn 14.05; found C 36.84, H 4.98, Mn 14.14.

3.3. *Tetracarbonyl(dicyclohexyldiselenophosphinato-Se,Se')manganese:* A solution of $BrMn(CO)_5$ (1.40 g, 5.09 mmol) was allowed to react with **1a** (1.46 g, 5.27 mmol) and $Et(iPr)_2N$ (0.9 ml, 5.29 mmol) to give the crude product which was dissolved in 5 ml of *n*-hexane and chromatographed on a silica gel column [(10 × 2.5 cm), silica gel (32–63 μm), *n*-hexane]. The main purification was carried out by employing MPLC, and the product was eluted with *n*-hexane (silica gel column, 2. fraction). The solvent was removed and the residue dried in vacuo to yield 920 mg (34%) of the diselenophosphinato complex, dec. 137°C. – MS (FD), *m/z*: 523.6 [M^+]. – IR (*n*-hexane): $\tilde{\nu}$ = 2079, 2002, 1990, 1953 cm^{-1} (C≡O). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.14–2.08 (m, C_6H_{11}). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 25.34–26.14 (m, C_6H_{11}), 41.29 (d, $^1J_{PC}$ = 21.0 Hz, PCH). – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = 92.6 (s, $^1J_{SeP}$ = 451.6 Hz, SePSe). – $C_{16}H_{22}MnO_4PSe_2$ (522.2): calcd. C 36.80, H 4.25, Mn 10.52; found C 36.95, H 4.36, Mn 10.09.

4. *Bromotetracarbonyl(dimethylphosphane selenide-Se)manganese* (**3c**): A solution of **1c** (420 mg, 2.98 mmol) in 10 ml of diisopropyl ether was added dropwise to a stirred suspension of $BrMn(CO)_5$ (830 mg, 3.02 mmol) in 30 ml of diisopropyl ether. The suspension was heated to 50°C. On maintaining this temp. the solution became clear after 20 min. While cooling to ambient temp. a yellow precipitate formed. The precipitate was collected by filtration (P4) and dried in vacuo to give 820 mg (70%) of **3c**, dec. 91°C. – MS (FD), *m/z*: 388.1 [M^+]. – IR (CCl_4): $\tilde{\nu}$ = 2091, 2017, 2001, 1957 cm^{-1} (C≡O). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 2.02 [dd, $^2J_{PH}$ = 14.2, $^3J_{HH}$ = 4.3 Hz, 6H, $P(CH_3)_2$], 6.51 (dsept, $^1J_{PH}$ = 490.6, $^3J_{HH}$ = 4.3 Hz, PH). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 13.85 [d, $^1J_{PC}$ = 47.4, $P(CH_3)_2$], 210.3 (m_c, C≡O). – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = −11.0 (s, $^1J_{SeP}$ = 599.2 Hz, PSe). – ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −11.0 (dsept, $^1J_{PH}$ = 490.6, $^2J_{PH}$ = 14.2 Hz, PH). – $C_6H_7BrMnO_4PSe$ (387.9): calcd. C 18.58, H 1.82, Br 20.60, Mn 14.16; found C 18.84, H 2.26, Br 20.91, Mn 13.99.

5. *Octacarbonylbis(μ-dimethylselenophosphinito-S,P)dimanganese* (**4c**): To a stirred solution of **3c** (400 mg, 1.03 mmol) in 20 ml of THF at −65°C *n*BuLi [0.7 ml (1.6 mol/l solution in *n*-hexane), 1.2 mmol)] was added dropwise. The solution was stirred for 2 h at this temp. After removal of the solvent in vacuo the crude product was chromatographed on a silica gel column [(10 × 2 cm), silica gel (32–63 μm), *n*-hexane] (1. fraction). The solvent was removed and the residue dried in vacuo to give 110 mg (35%) of **4c**, m.p. 125°C (dec.). – MS (FD), *m/z*: 615.7 [M^+]. – MS (osmometrically determined): *M* = 607.5. – IR (*n*-hexane): $\tilde{\nu}$ = 2081, 2070, 2014, 1999, 1992, 1976, 1959 cm^{-1} (C≡O). – ^{1}H NMR (250.13 MHz, $CDCl_3$, 22°C): δ = 2.14 [br. s, $P(CH_3)_2$]. – ^{1}H NMR (250.13 MHz, $CDCl_3$, 40°C): δ = 2.14 [virtual t, $P(CH_3)_2$]. – $^1H\{^{31}P\}$ NMR (250.13 MHz, $CDCl_3$, 40°C): δ = 2.14 [s, $P(CH_3)_2$]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, 40°C): δ = 26.26 [virtual t, $P(CH_3)_2$], 215.0 (m_c, C≡O). – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = 12.8 (br. s, MnPSe). – $C_{12}H_{12}Mn_2O_8P_2Se_2$ (614.0): calcd. C 23.48, H 1.97, Mn 17.90; found C 23.82, H 2.13, Mn 17.65.

6. Tetramethyl 7,7,7-Tricarbonyl-3,3-dicyclohexyl-2λ³-*selena*-3λ⁵-*phospha*-7-*mangana*-η²-*bicyclo*[2.2.1]*hepta*-2,5-*diene*-1,4,5,6-*tetracarboxylate* (**5d**): To a stirred solution of **2a** (640 mg, 1.44 mmol) in 50 ml of *n*-hexane 4 equivalents of the alkyne RC≡CR (R = CO_2CH_3) (821 mg, 5.78 mmol) was added. The reaction mixture was stirred for 20 h. During that time a yellow precipitate formed which was collected by filtration (P4), washed with 3 × 5 ml of *n*-hexane and dried in vacuo to give 460 mg (66%) of **6a**, dec. 154°C. – MS (FD), *m/z*: 700.0 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2011, 1923 cm^{-1} (C≡O), 1749, 1716 (C=O). – IR (*n*-hexane): $\tilde{\nu}$ = 2021, 1949, 1944 cm^{-1} (C≡O). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.79–2.79 (m, 22H, C_6H_{11}), 3.63, 3.67, 3.75, 3.76 (s, 12H, OCH_3). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 25.3–29.4 (m, C_6H_{11}), 37.40, 37.70 (d, $^1J_{PC}$ = 29.0, $^1J_{PC}$ = 33.6 Hz, PCH), 46.43 (d, $^1J_{PC}$ = 42.7, C-4), 50.60 (s, C-1), 51.84, 52.57, 52.84, 52.89 (s, OCH_3), 100.82, 103.13 (s, C-5,6), 166.96–172.13 (m, CO_2CH_3), 221.0 (m_c, C≡O). – $^{31}P\{^1H\}$ NMR (32.44 MHz, CH_2Cl_2, −30°C): δ = 89.9 (s, $^1J_{SeP}$ = 409 Hz, PSe). – $^{77}Se\{^1H\}$ NMR (47.69 MHz, $CDCl_3$): δ = 171 (d, $^1J_{SeP}$ = 409 Hz, PSe). – $C_{27}H_{34}MnO_{11}PSe$ (699.4): calcd. C 46.37, H 4.90, Mn 7.86; found C 45.93, H 4.93, Mn 7.76.

7. *Tetraethyl 7,7,7-Tricarbonyl-3,3-dicyclohexyl-2λ³-selena-3λ⁵-phospha-7-mangana-η²-bicyclo[2.2.1]hepta-2,5-diene-1,4,5,6-tetracarboxylate* (**5e**): To a stirred solution of **2a** (310 mg, 0.70 mmol) in 30 ml of *n*-hexane 4 equivalents of the alkyne RC≡CR (R = CO_2Et) (580 mg, 341 mmol) was added at ambient temp. After stirring for 20 h the solvent was removed. The residue was dissolved in 5 ml of diisopropyl ether and chromatographed on a silica gel column [(11 × 3 cm), silica gel (32–63 μm), diisopropyl ether] (1. fraction). After removal of the solvent the residue was dried in vacuo to yield 180 mg (34%) of **5e**, dec. 106°C. – MS (FD), *m/z*: 755.9 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2012, 1936, 1925 cm^{-1} (C≡O), 1750, 1710 (C=O). – IR (*n*-hexane): $\tilde{\nu}$ = 2019, 1947, 1942 cm^{-1} (C≡O). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.18–2.83 (m, Et, C_6H_{11}), 4.00–4.33 (m, 4H, OCH_2CH_3). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 13.83, 13.86, 14.06 (s, OCH_2CH_3), 25.37–29.31 (m, C_6H_{11}), 37.45, 37.85 (d, $^1J_{PC}$ = 29.0, $^1J_{PC}$ = 34.6 Hz, PCH), 46.72

(d, $^1J_{PC}$ = 42.0 Hz, C-4), 51.42 (s, C-1), 61.26, 61.90, 61.93 (s, OCH_2CH_3), 100.88, 103.17 (s, C-5,6), 166.37–171.98 (m, CO_2Et). – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = 91.8 (s, $^1J_{SeP}$ = 411 Hz, PSe). – $C_{31}H_{42}MnO_{11}PSe$ (755.5): calcd. C 49.28, H 5.60, Mn 7.20; found C 48.86, H 5.68, Mn 7.12.

8. *Tetraisopropyl 7,7,7-Tricarbonyl-3,3-dicyclohexyl-2λ³-selena-3λ⁵-phospha-7-mangana-η²-bicyclo[2.2.1]hepta-2,5-diene-1,4,5,6-tetracarboxylate* (**5f**): To a stirred solution of **2a** (300 mg, 0.68 mmol) in 30 ml of *n*-hexane 4 equivalents of the alkyne RC≡CR (R = CO_2*i*Pr) (540 mg, 2.72 mmol) was added at ambient temp. After stirring for 36 h the solvent was removed. The residue was dissolved in 3 ml of *n*-hexane/ethyl acetate (10:1) and chromatographed on a silica gel column [(10 × 2.5 cm), silica gel (32–63 μm), *n*-hexane/ethyl acetate (10:1)] (3. fraction). After removal of the solvent the residue was dried in vacuo to give 160 mg (29%) of **5f**, m.p. 124°C (dec.). – MS (FD), *m/z*: 812.1 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2012, 1930 cm^{-1} (C≡O), 1748, 1706, (C=O). – IR (*n*-hexane): $\tilde{\nu}$ = 2019, 1946, 1940 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.81–2.69 (m, *i*Pr, C_6H_{11}), 4.98 [m_c, 4H, $OC(H)(CH_3)_2$]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 21.61, 21.65, 21.68, 21.72 [s, $CO_2C(H)(CH_3)_2$], 25.40–29.04 (m, C_6H_{11}), 37.28, 37.82 (d, $^1J_{PC}$ = 32.3, $^1J_{PC}$ = 38.4 Hz, PCH), 46.60 (d, $^1J_{PC}$ = 39.6 Hz, C-4), 51.82 (s, C-1), 69.79, 69.95, 70.02, 70.07 [s, $OC(H)(CH_3)_2$], 101.37, 103.26 (s, C-5,6), 165.11–171.43 (m, CO_2-*i*Pr), 221.87 (m_c, C≡O). – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = 90.2 (s, $^1J_{SeP}$ = 415 Hz, PSe). – $C_{35}H_{50}MnO_{11}PSe$ (811.6): calcd. C 51.79, H 6.21, Mn 6.77; found C 51.86, H 6.59, Mn 6.35.

9. *Tetracyclohexyl 7,7,7-Tricarbonyl-3,3-dicyclohexyl-2λ³-selena-3λ⁵-phospha-7-mangana-η²-bicyclo[2.2.1]hepta-2,5-diene-1,4,5,6-tetracarboxylate* (**5g**): To a stirred solution of **2a** (400 mg, 0.90 mmol) 4 equivalents of the alkyne RC≡CR (R = CO_2*cyc*-Hex) (1.00 g, 3.60 mmol) was added at ambient temp. After stirring for 70 h the solvent was removed. The residue was dissolved in 5 ml of *n*-hexane/ethyl acetate (100:3) and chromatographed on a silica gel column [(10 × 2.5 cm), silica gel (32–63 μm), *n*-hexane/ethyl acetate (100:3)] (2. fraction). The solvent was removed and the residue dried in vacuo to yield 380 mg (43%) of **5g**, m.p. 116–120°C. – MS (FD), *m/z*: 972.9 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2014, 1931 cm^{-1} (C≡O). – IR (*n*-hexane): $\tilde{\nu}$ = 2019, 1945, 1940 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 1.22–2.68 (m, 62H, C_6H_{11}), 4.69–4.81 (m, 4H, OCH). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 22.3–28.7 (m, C_6H_{11}), 37.25, 37.57 (d, $^1J_{PC}$ = 31.1, $^1J_{PC}$ = 34.7 Hz, PCH), 46.07 (d, $^1J_{PC}$ = 38.4 Hz, C-4), 51.74 (d, $^2J_{PC}$ = 2.9 Hz, C-1), 73.96, 74.61, 75.19, 75.54 (s, OCH), 101.46, 103.48 (s, C-5,6), 164.62–171.08 (m, $CO_2C_6H_{11}$), 222.0 (m_c, C≡O). – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$): δ = 89.8 (s, $^1J_{SeP}$ = 415 Hz, PSe). – $C_{47}H_{66}MnO_{11}PSe$ (971.9): calcd. C 58.08, H 6.85, Mn 5.65; found C 58.52, H 7.20, Mn 5.26.

10. *Tetramethyl 2,3,4,5-Selenophenetetracarboxylate* (**6**): A solution of **5d** (320 mg, 0.46 mmol) in 50 ml THF was treated with 150 bar of CO. Under these conditions the stirred reaction mixture was heated at 100°C and maintained at this temp. for 12 h. The solvent was removed, the residue dissolved in 10 ml of benzene and the solution chromatographed by the aid of a silica gel column [(10 × 2.5 cm), silica gel (32–63 μm), 1. benzene, 2. benzene/ethyl acetate (25:1)]. The $Mn(CO)_x$ compounds were eluted with benzene; compound **6** was eluted with benzene/ethyl acetate (25:1). After removal of the solvent, **6** was dissolved in 5 ml of THF, then 20 ml of *n*-hexane was added to the solution. The obtained precipitate was filtered off (P4) and dried in vacuo to yield 100 mg (61%) of **6**, m.p. 133–135°C. – MS (FD), *m/z*: 364.0 [M^+]. – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 3.84 (s, CO_2CH_3). – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 53.12, 53.30 (s, CO_2CH_3), 139.25 (s, C-2,5), 142.49 (s, C-3,4), 161.65, 163.94 (s, CO_2Me). – $^{77}Se\{^1H\}$ NMR (47.68 MHz, $CDCl_3$): δ = 699 (s, CSeC). – $C_{12}H_{12}O_8Se$ (363.2): calcd. C 39.69, H 3.33; found C 39.83, H 3.49.

Crystal Structure Determinations: Single crystals were obtained from concentrated *n*-hexane solutions of **2a** and **5d**, respectively. Crystals were mounted on a glass fibre and transferred to a P4 Siemens diffractometer by taking rotation photographs to find a suitable reduced cell (graphite-monochromated Mo-K_α radiation). The final cell parameters and specific data collection parameters for **2a** and **5d**, respectively, are compiled in Table 1. All structures were solved by Patterson methods[37] and refined by least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). An absorption correction (ψ scan) was applied to all data. Maximum and minimum peaks in the final difference synthesis were 0.811 and −0.553 (**2a**), 0.284 and −0.358 (**5d**) $eÅ^{-3}$, respectively. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-404914 (**5d**) and -404915 (**2a**), the names of the authors, and the journal citation.

Table 1. Crystal data and refinement details for compounds **2a** and **5d**

	2a	**5d**
formula	$C_{16}H_{22}MnO_4PSe$	$C_{27}H_{34}MnO_{11}PSe$
M_r	443.21	699.41
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	8.315(2)	9.6320(10)
b [Å]	10.561(2)	10.271(2)
c [Å]	12.174(2)	16.292(3)
α [°]	68.89(1)	98.16(1)
β [°]	85.62(2)	93.30(1)
γ [°]	69.27(1)	108.20(1)
V [Å³]	931.1(3)	1506.7(4)
$\rho_{calcd.}$ [g cm^{-3}]	1.581	1.542
Z	2	2
F(000) [e]	448	716
T [°C]	-100	-100
μ (Mo-K_α) [mm^{-1}]	2.764	1.756
scan mode	Wyckoff	ω
hkl range	±9, ±12, ±14	±11, ±12, ±19
2θ limits [°]	4-50	4-50
measured refl.	6550	10618
observed refl. I>2δ(I)	2355	3943
refined parameters	209	371
S	1.630	1.320
R1[a]	0.05	0.025
wR2[b]	0.119	0.052

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$.
[b] $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

☆ Dedicated to Professor *Rudolf Taube* on the occasion of his 65th birthday.

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