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Synthesis and structural studies of phosphorus carbonyl manganacycles containing the tetraphenyldiselenoimidodiphosphinato ligand

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Dedicated to Professor Víctor Riera on the occassion of his 70th birthday.

Abstract

The $[Mn(CO)_{4-x}(L)\{Ph_2P(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$ complexes, where $x = 1$ for $L = PPh_3$ and $PMePh_2$, and $x = 2$ for $L = Ph_2PCH_2CH_2PPh_2$ (diphos), were synthesized by two routes. The complexes were characterized by IR, mass spectrometry (FAB+), NMR (^1H, ^{13}C, ^{31}P, ^{77}Se) spectroscopy and/or single crystal X-ray diffraction. The X-ray diffraction analysis for $[Mn(CO)_3PMePh_2\{Ph_2P(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$ showed that the unit cell contains two independent mononuclear molecules with different MnSePNPSe rings' conformations.

Keywords: Manganese(I) complexes; ^{77}Se NMR; Carbonyl substitution reactions; Tetraphenyldiselenoimidodiphosphinato complexes; Tertiary phosphines

1. Introduction

There are many reasons that have been invoked to study the synthesis and structural behavior of the complexes involving the tetraphenylimidodichalcogenodiphosphinate ligands $[N(EPPh_2)_2]^-$ (E = O, S, Se); some of the principal ones are as follows: their potential applications in several fields (e.g. catalysis, metal extraction studies, optoelectronics, NMR shift reagents, to mention a few); their capability of joining the metal center in different fashions and, at the same time, adopting several ring conformations in inorganic metallacycles [1]. The fact is that coordination of the $[N(EPPh_2)_2]^-$ (E = O, S, Se) anions has been extensively studied over the last years. It has been found that the ligand $N(SePPh_2)_2$ binds a wide range of atoms varying from main group elements (K [2], group 12 [3]; Al and Ga [4], In [5], Sn [3,6], Pb [3], Sb [7], Bi [5,7], Se [8] and Te [9]), transition metals (V and Cr [10], Mn [11a] and Re [11], Ru [12], Os [13a,13b], Co [14], Rh [2,12b,12c], Ir [12b,15], group 10: Ni [16], Pd [2,12c,16,17], Pt [2,16,17], and group 11: Cu [14,18a] Ag [18a,18b,18c] Au [18b,18d,18e]) to rare-earth metals: Y [19], La, Gd, Er, Yb [20], and Sm [21]. Although the list of $N(SePPh_2)_2$ [22] complexes is certainly long, it is noteworthy the scarcity of metal carbonyl complexes with the $N(SePPh_2)_2$ fragment (or $[N(EPPh_2)_2]^-$; E = O, S for that matter). In order to fill in this gap we have undertaken a systematic study of reactivity of group 7 metal carbonyls towards the $[N(EPR_2)_2]^-$ (E = O, S, Se; R = Me, Ph) ligands [11a,23]. The realization that formation of the $[Mn(CO)_4\{Ph_2P\text{-}(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$ complex was effected in good yield under mild reaction conditions [11a] opened up the possibility of studying its reactivity towards Lewis bases. This led us to the synthesis of the $[Mn(CO)_{4-x}(L)\{Ph_2P(Se)NP\text{-}(Se)Ph_2\text{-}\kappa^2Se\}]$ complexes, where $x = 1$ for $L = PPh_3$, **1**, and $PMePh_2$, **2**; and $x = 2$, for $L = Ph_2PCH_2CH_2PPh_2$ (diphos), **3**, by two routes; consequently, we wish to report in this paper on the details and assessment of Routes **A** and **B** for the preparation of new carbonylphosphinotetraphenylimidodiselenodiphosphinatomanganese(I)

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metallacycles and their characterization in solution and solid state as well.

2. Experimental

All preparative work was conducted in an atmosphere of dry oxygen free nitrogen, using conventional Schlenk techniques. Solvents were carefully dried; tetrahydrofuran, ethyl ether, toluene, and hexane were dried and deoxygenated by distillation from sodium benzophenone ketyl. $[MnBr(CO)_5]$, chlorodiphenylphosphine, hexamethyldisilazane, and potassium *tert*-butoxide were acquired from Strem Chemicals, Co. and used with no further purification except for the chlorodiphenylphosphine, which was distilled under vacuum (102 °C, 1 mm Hg). Methyldiphenylphosphine, triphenylphospine and diphos (1,2-bis(diphenylphosphino)ethane) were from Aldrich, Co. Gray selenium was from Fisher Reagents Scientific Company. $HN(PPh_2)_2$ [24], $HN(SePPh_2)_2$ [17], $[K\{(SePPh_2)_2N\}]$ [2], $[Mn(CO)_4\{Ph_2P(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$ [11a], $[MnBr(CO)_4\{PPh_3\}]$ [25], and $[MnBr(CO)_3\{Ph_2PCH_2CH_2PPh_2\text{-}\kappa^2P\}]$ [26] were prepared according to literature procedures. IR spectra were obtained in solution (4000–580 cm^{-1}) using a Nicolet FT-IR 55X spectrometer and in KBr disk (4000–200 cm^{-1}) using a Perkin–Elmer 283B spectrometer. ^1H(300 MHz), ^{13}C(75.57 MHz), ^{31}P(121.67 MHz), and ^{77}Se(57.34 MHz) NMR spectra were recorded in chloroform-d solutions at room temperature using a Jeol GX300 instrument. The chemical shifts are reported in ppm relative to TMS (for ^1H and ^{13}C), H_3PO_4 (85% aqueous solution for ^{31}P), and $Ph_2Se_2/CDCl_3$ (set to 463.5 ppm for ^{77}Se), respectively. FAB+ mass spectra were recorded using a JEOL SX-102A instrument. The melting points were determined on a Fisher–Johns apparatus and are uncorrected.

2.1. General procedures

2.1.1. Route *A*

Synthesis of $[Mn(CO)_{4-x}(L)\{Ph_2P(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$ complexes, where $x = 1$ for L = PPh_3, **1**, and $PMePh_2$, **2**; and $x = 2$, for L = $Ph_2PCH_2CH_2PPh_2$ (diphos), **3**.

0.1 g (0.14 mmol) of $[Mn(CO)_4\{Ph_2(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$ were added to a 100 mL round bottom flask with stirring containing 30 mL of dry toluene. An equimolar amount of the corresponding phosphine (PPh_3 0.037 g, $PMePh_2$ 0.028 g, and diphos 0.044 g) was dissolved in 40 mL of toluene and transferred via cannula to the reaction flask. After some minutes under reflux (10 min for **1**, 5 for **2**, and 30 min for **3**) the solvent was eliminated under reduced pressure leaving an oil (**1**) or a solid (**2** and **3**). Crystallization was effected in hexane at 4 °C for several days yielding crystalline powders in the three cases.

2.1.2. *[Mn(CO)$_3$(PPh$_3$){Ph$_2$P(Se)NP(Se)Ph$_2$-κ^{2}Se}]*, **1**

0.09 g, 69% yield; m.p. 157–159 °C. IR (KBr): ν(CO) 2005 vs, 1902 vs cm^{-1}; $\nu(P_2N)$ 1177 m, 780 vw cm^{-1}; ν(PSe) 540 m cm^{-1}. IR ($CHCl_3$): ν(CO) 2010 vs, 1938 m, 1908 m cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.96 [dd, H_o(PNP), $^3J_{Ho-P} = 14$ Hz], 7.8–7.0 [m, aromatic protons: PNP and PPh_3]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 134.05 [d, C_o (PNP), $^2J_{Co-P} = 10$ Hz]; 132.49 [d, C_o (PPh_3), $^2J_{Co-P} = 11$ Hz], 130.97 [d, C_i (PNP), $J_{Ci-P} = 22$ Hz], 130.82 [d, C_i (PPh_3), $J_{Ci-P} = 22$ Hz], 130.19 [s, C_p (PNP)], 129.67 [s, C_p (PPh_3)], 127.9 [d, C_m (PNP), $^3J_{Cm-P} = 10$ Hz], 127.36 [d, C_m (PPh_3), $^3J_{Cm-P} = 7$ Hz]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 48.45 [s(broad), PPh_3], 28.3 [d, (PNP), $^3J_{PNP-PPh3} = 21$ Hz, $\{^2J_{Se-PPh3} = 22$ Hz $^1J_{PNP-Se} = 573$ Hz (satellites)}]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 57.34 MHz): δ/ppm: −281.7 [dd, $^1J_{PNP-Se} = 573$ Hz, $^2J_{PPh3-Se} = 22$ Hz]. MS (*m*/*e*): 888, $[M-2CO]^+$; 598, $[M-(CO)-(PPh_3)]^+$.

2.1.3. *[Mn(CO)$_3$(PMePh$_2$){Ph$_2$P(Se)NP(Se)-Ph$_2$-κ^{2}Se}]*, **2**

0.11 g, 89% yield; m.p. 162–164 °C. IR (KBr): ν(CO) 2003 vs, 1923 vs, 1904 vs cm^{-1}; $\nu(P_2N)$ 1177 m, 780 vw cm^{-1}; ν(PSe) 539 m cm^{-1}. IR ($CHCl_3$): ν(CO) 2012 vs, 1938 s, 1906 s cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ/ppm: 8.06 [d, broad, H_o(PNP), $^3J_{Ho-P} = 11$ Hz], 7.43 [m, $H_{m/p}$ (PNP)], 7.92–7.13 [m, aromatic protons: PNP and PPh_2Me], 2.26 [d, H_{Me}, $PMePh_2$, $^2J_{PH} = 8$ Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 138.87 [s, broad, C_p, $PMePh_2$], 138.1 [d, broad, C_i (PNP), $J_{Ci-P} = 96$ Hz], 134.53 [d, broad, C_i ($PMePh_2$), $J_{Ci-P} = 36$ Hz], 132.27 [s, C_p (PNP)], 132.0 [d, C_o (PNP), $J_{Co-P} = 9$ Hz], 130.67 [s, broad, C_o ($PMePh_2$)], 127.82 [s, broad, C_m ($PMePh_2$)], 15.46 [d, C_{Me}, $PMePh_2$, $J_{C-P} = 26$ Hz], 220.88 [s, broad, *C*O], 217.12 [s, broad, *C*O]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 31.6 [s, broad, $PMePh_2$], 28.02 [dd, (PNP), $^3J_{PNP-PPh2Me} = 22$ Hz, $\{^2J_{Se-PPh2Me} = 23$ Hz $^1J_{PNP-Se} = 578$ Hz (satellites)}]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 57.34 MHz): δ/ppm: −285.0 [dd, $^1J_{PNP-Se} = 578$ Hz, $^2J_{PPh2MeSe} = 23$ Hz]. MS (*m*/*e*): 797, $[M-2CO]^+$; 597, $[M-(PPh_2Me)]^+$.

2.1.4. *[Mn(CO)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$-κ^{2}P){Ph$_2$P(Se)-NP(Se)Ph$_2$-κ^{2}Se}]*, **3**

0.087 g, 74% yield; mp 195–196 °C. IR (KBr): ν(CO) 2003 vs, 1925 s, 1859 s cm^{-1}; $\nu(P_2N)$ 1175 m, 738 m cm^{-1}; ν(PSe) 538 m, 511 m cm^{-1}. IR ($CHCl_3$): ν(CO) 1930 vs, 1863 s cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ/ppm: 8.25 [dd, broad, H_o(PNP), diphos, $^3J_{HH} = 6$ Hz, $^3J_{Ho-P} = 11$ Hz], 7.83–6.84 [m, $H_{m/p}$ PNP, diphos], 2.9 [dd, CH_2CH_2 (diphos), $^3J_{PH} = 59$ Hz, $^3J_{PH} = 26$ Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 139.67–133.63 [m, C_i, PNP, diphos], 133.21–127.0 [m, $C_{o,m,p}$ PNP, diphos], 28.04 [s, broad, CH_2–CH_2, diphos]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 94.37 [s, diphos], 66.01 [d, diphos, $^2J_{PP} = 20$ Hz], 27.33 [t, PNP, $J_{PSe} = 604$ Hz, $^2J_{PP} = 20$ Hz, $^3J_{PSe} = 21$ Hz, $^3J_{PNP\text{-}diphos} = 20$ Hz], 26.35 [d, PNP, $J_{PSe} = 605$ Hz, $^3J_{PP} = 25$ Hz, $^3J_{PSe} = 26$ Hz]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 57.34 MHz): δ/ppm: −227.0 [dtd, Se(PN) *trans* to P(diphos), $J_{PSe} = 604$ Hz, $^2J_{PSe} = 44$ Hz, $^2J_{PSe} = 44$ Hz, $^3J_{PSe} = 6$ Hz], −328.17 [dddd, Se(PNP) *trans* to CO, $J_{PSe} = 576$ Hz, $^2J_{PSe(cis)}z = 16$ Hz, $^2J_{PSe(trans)} = 40$ Hz, $^3J_{PSe} = 8$ Hz]. MS (*m*/*e*): 996, $[M-2CO]^+$; 597, $[M-(diphos)]^+$.

2.1.5. Route **B**

Complexes **1**, **2**, and **3** were synthesized by Route **B** in a similar way: in a 100 mL round bottom flask the phosphine complex was added (0.164 g, 0.32 mmol of $[MnBr(CO)_4(PPh_3)]$; 0.2 g, 0.32 mmol of $[MnBr(CO)_3(PMePh_2)_2]$; and 0.2 g, 0.32 mmol of $[MnBr(CO)_3(diphos)]$) to approximately 30 mL of dry toluene. 0.187 g, 0.32 mmol of $K[N(Se(PPh_2)_2]$ in 30 mL of toluene were added via cannula and set under reflux. Reaction times were determined by IR spectroscopy (1 h for complex **1**, 2 h for **2**, and 4.5 h for **3**). After the reaction was completed the KBr was filtered off leaving a colored solution (orange for **1**, yellow for **2**, and dark orange for **3**). Evaporation under vacuum afforded solid materials. The yields were as follows: 76.0% for **1** (0.23 g, 0.25 mmol); 49.6% for **2** (0.141 g, 0.16 mmol); and 62% for **3** (0.211 g, 0.20 mmol).

2.1.6. Synthesis of $[MnBr(CO)_3\{PMePh_2\}_2]$, **b**

$[MnBr(CO)_5]$ (2.0 g; 7.27 mmol) was dissolved in 25 mL of $CHCl_3$ in a 50 mL round bottom flask giving a yellow–orange solution; after stirring for 10 min a solution of methyldiphenylphosphine (1.45 g, 7.27 mmol) in 25 mL of chloroform was added under a stream of dinitrogen. Stirring for 22 h at room temperature and evaporation under reduced pressure afforded a reddish oil. Extraction with hexane (3×15 mL) and evaporation gave a yellow solid (1.46 g, 65% yield). IR (KBr): ν(CO) 2091 m, 2009 vs, 1960 s cm^{-1}. IR (nujol): ν(CO) 2022 s, 1950 vs, 1904 s cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ/ppm: 2.26 [d, 6H, $^2J(PH) = 9$ Hz]; 7.48–7.64 [m, 10H]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6): δ/ppm: 128.7 [s, C_m]; 130.7 [s, C_p]; 131.5 [s, C_o]; 133.8 [d, C_i, $^1J(PC) = 42$ Hz]; 210.6, 216.3 [bs, *C*O]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7): δ/ppm: 21.7 [s]. MS (*m*/*e*): 535 $[M-3CO]^+$, 455 $[M-Br]^+$.

2.2. Crystal data

See Tables 1 and 2.

Table 2
Crystal data for *cis*-$[MnBr(CO)_3\{PMePh_2\}_2]$, **b**

Molecular formula	$C_{29}H_{26}BrMnO_3P_2 + 0.25\ CH_2Cl_2$
Molecular weight	640.52
Temperature (°C)	20
Crystal size (mm)	$0.462 \times 0.142 \times 0.114$
Crystal system	Tetragonal
Space group	$I\bar{4}$
a (Å)	26.574(1)
b (Å)	26.574(1)
c (Å)	8.583(1)
V (Å^3)	6061.1(8)
Z	8
θ Range for data collection (°)	1.53–27.57
Reflections collected	30,548
Independent reflections	7011 ($R_{int} = 0.1404$)
Maximum and minimum transmission	0.8176 and 0.5295
Final R indices $[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0590$, $wR_2 = 0.0997$
R indices (all data)	$R_1 = 0.1110$, $wR_2 = 0.1072$

2.3. Structures determination

2.3.1. Complexes **2** and **3**

Suitable crystals of **2** and **3** were obtained from a CH_2Cl_2/hexane 1:1 solution at 4 °C for several days. Data were collected at 20 °C on a Bruker Smart Apex CCD diffractometer for 62,131 (for **2**) and 69,413 (for **3**) reflections of which 13,492 (**2**) and 18,395 (**3**) ($F > 4.0\sigma(F)$) were independent ($R_{int} = 11.19\%$ for **2** and 12.12% for **3**) and used in the full-matrix least-squares refinement. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The residual electron densities from a final difference Fourier synthesis were in the ranges of 0.992, −0.504 for **2** and 1.149 (0.06 Å from Se(2)), −0.381 eÅ^{-3} for **3**.

2.3.2. Complex cis-$[MnBr(CO)_3\{PMePh_2\}_2]$, **b**

Suitable crystals of *cis*-$[MnBr(CO)_3\{PCH_3Ph_2\}_2]$ were obtained from a CH_2Cl_2/hexane (1:1) solution at 4 °C for

Table 1
Crystal data for **2** and **3**

	2	**3**
Molecular formula	$C_{40}H_{33}MnNO_3P_3Se_2$	$C_{52}H_{44}MnNO_2P_4Se_2{+}CH_2Cl_2$
Molecular weight	881.44	1136.55
Temperature (°C)	20	20
Crystal size (mm)	$0.326 \times 0.298 \times 0.058$	$0.320 \times 0.252 \times 0.168$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	22.821(1)	17.147(1)
b (Å)	17.255(1)	16.456(1)
c (Å)	20.776(1)	18.686(1)
β (°)	110.518(1)	105.087(1)
V (Å^3)	7662.1(7)	5090.9(5)
Z	8	4
θ Range for data collection (°)	1.58–25.00	1.67–32.57
Reflections collected	62,131	69,413
Independent reflections	13,492 ($R_{int} = 0.1119$)	18,395 ($R_{int} = 0.1212$)
Maximum and minimum transmission	0.8723 and 0.4752	0.76 and 0.5504
Final R indices $[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0576$, $wR_2 = 0.0664$	$R_1 = 0.0576$, $wR_2 = 0.0641$
R indices (all data)	$R_1 = 0.1400$, $wR_2 = 0.0766$	$R_1 = 0.1246$, $wR_2 = 0.0803$

several days. Data were collected at 20 °C on a Bruker Smart Apex CCD diffractometer for 30,548 reflections ($\theta/2\theta$ scan mode) of which 7011 ($F > 4.0\sigma(F)$) were independent ($R_{int} = 14.04\%$) and used in the full-matrix least-squares refinement. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The residual electron density from a final difference Fourier synthesis was in the range of 0.738, -0.543 eÅ^{-3}.

3. Results and discussion

3.1. Syntheses

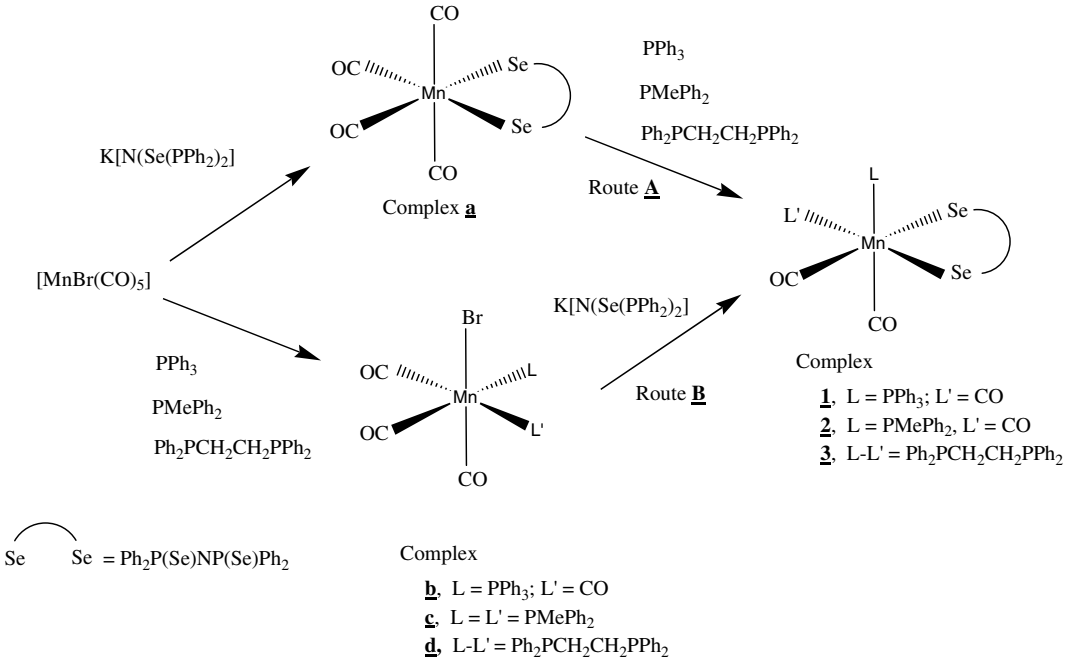
The complexes $[Mn(CO)_{4-x}(L)\{Ph_2P(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$, where $x = 1$ for $L = PPh_3$, **1**, and $PMePh_2$, **2**; and $x = 2$, for $L = Ph_2PCH_2CH_2PPh_2$ (diphos), **3**, were prepared by two routes: Route **A** consisted in the formation of complexes **1**, **2**, and **3** by reaction of $[Mn(CO)_4\{Ph_2P(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$ **a** [11a], with the corresponding phosphine under toluene reflux (Scheme 1). In Route **B** the three complexes were obtained by reaction of the phosphine precursors $[MnBr(CO)_4\{PPh_3\}]$ **b**, *cis*-$[MnBr(CO)_3\{PMePh_2\}_2]$ **c**, and $[MnBr(CO)_3\{diphos\}]$ **d**, with $K[N(Se(PPh_2)_2]$ to afford **1**, **2**, and **3**, respectively.

Complexes **1**, **2**, and **3** are unstable in solution: after 1 h at room temperature in dichloromethane complex **1** decomposed into a dark precipitate (presumably MnO_2) leaving in solution $Ph_3P{=}Se$, detected by ^{31}P NMR among other unidentified phosphine materials. A similar behavior was detected for complexes **2** and **3** (in the case of complex **3** the monoselenophosphine compound $Ph_2PCH_2CH_2PPh_2(Se)$ was identified).

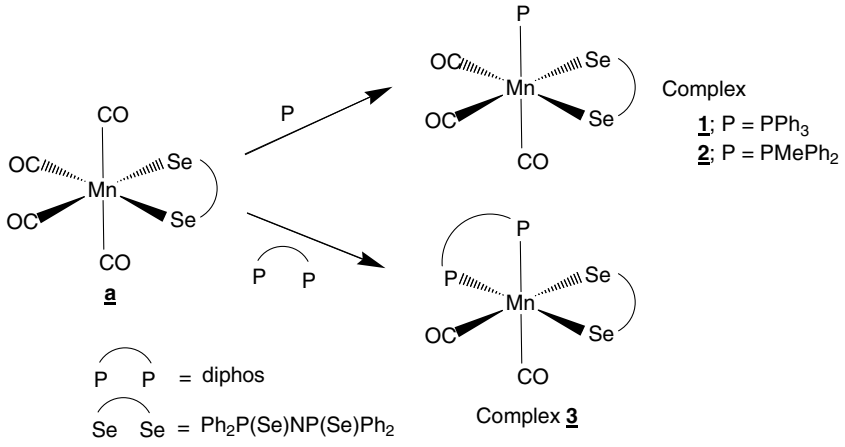
The reaction times were established by monitoring with IR spectroscopy in the ν(CO) region. The reactions, in both routes, were carried out at toluene reflux temperature; so, it can be assumed that reaction times reflect the degree of reactivity of the phosphines towards **a**. The longer reaction time for formation of **3** can be accounted for by a second CO substitution to permit diphos chelation as depicted in Scheme 2. Variation of the phosphine concentration did not exert any detectable effect on the reaction yields and/or reaction times. The stereochemistry of complexes **1** and **2** was dictated by the mutually *trans* effect of two carbonyl groups: no product of labilization of the Mn–Se bond *trans* to a carbonyl group was detected. For the dicarbonylspiro complex **3** diphos chelation was accomplished by elimination of a CO group *trans* to an Mn–Se bond.

Route **B** (Scheme 3) involves complexes **b**, **c**, and **d**. Complexes **b** [25] and **d** [26] were prepared according to literature procedures. Complex **c** was synthesized by mixing equimolar amounts of $[MnBr(CO)_5]$ with $PMePh_2$ in $CHCl_3$ at room temperature (see Section 2): shorter reaction times led to a poor yield of **c**. When the reaction was carried out with two equivalents of phosphine a mixture of products resulted whose work-up turned out to be extremely laborious rendering exiguous amounts of phosphine di- and trisubstitution complexes among other unidentified products.

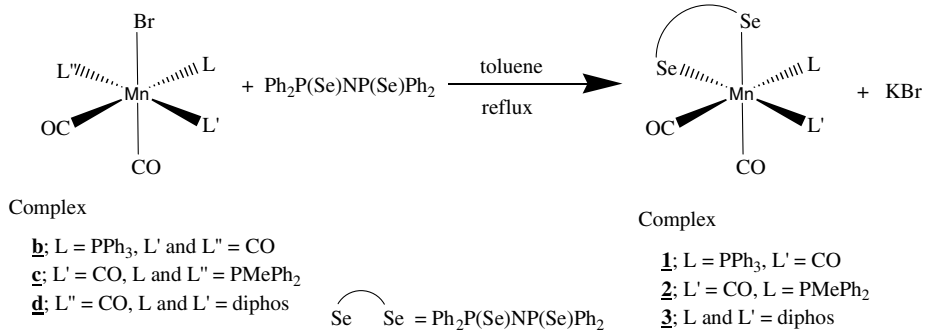
Route **B** can be broken down into two steps: initial attack of the tetraphenylimidodiselenophosphinate to the metal center followed by coordination of the selenium atom with elimination of a neutral ligand (CO or $PMePh_2$). The reaction times for this route are longer than those for Route **A**; if nucleophilic attack of the selenium ligand to



Scheme 1.



Scheme 2. Route **A** for formation of **1**, **2**, and **3**.

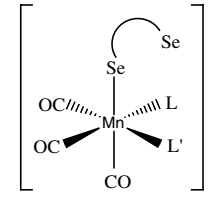


Scheme 3. Route **B** for formation of **1**, **2**, and **3**.

the metal center is governed by charge [27]; then, it can be proposed that formation of intermediates **A**, **B**, and **C** (shown in Fig. 1) will depend on the electron density at the metal center. Formation of **1** (from intermediate **A**) will be more favored with only one coordinated phosphine.

The second step involves displacement of a neutral two electron donor ligand (CO or $PMePh_2$). The stereochemistry of the resulting complex is governed by the *trans* effect (except for complex **3** arising from intermediate **C**, see below). In complex **2** the *trans* effect is exerted on $PMePh_2$ leaving one phosphine in the coordination sphere; while for complex **3** phosphine decoordination does not take place due to stabilization of the chelated diphos. The reaction times of Route **B** reflect the difficulty with which both steps, charged and neutral nucleophilic attacks, take place, being the longest time for the formation of complex **3** (4.5 h). In this respect it is worth mentioning that formation of complex $[Mn(CO)_4\{Ph_2P(Se)NP(Se)Ph_2\text{-}\kappa^2 Se\}]$ **a** starting from $[MnBr(CO)_5]$ (with a proposed intermediate similar to the ones shown in Fig. 1 with $L = L' = CO$) requires softer reaction conditions (1 h under THF reflux) [11a].

A comparison of the routes herein reported (both starting from $[MnBr(CO)_5]$) cannot straightforwardly be made as preparation times of the phosphine precursors ($[MnBr(CO)_4\{PPh_3\}]$ **b**, 24 h, *cis*-$[MnBr(CO)_3\{PMePh_2\}_2]$ **c**, 22 h, and $[MnBr(CO)_3\{diphos\}]$ **d**, 10 min under toluene reflux) drastically vary; however, it can be stated that Route **A** is more efficient for the synthesis of **1**, **2**, and **3**.



Intermediate

A	L = PPh_3, L' = CO
B	L = L' = $PMePh_2$
C	L and L' = $Ph_2PCH_2CH_2PPh_2$

Fig. 1. Proposed intermediates for the formation of **1**, **2**, and **3** by Route **B** starting from **b**, **c**, and **d** respectively.

3.2. Infrared spectroscopy

Complexes **1** and **2** present three bands (in $CHCl_3$) in the ν(CO) carbonyl region corresponding to the $2A' + A''$ vibration modes [28] arising from the carbonyl groups' local symmetry with a C_s point group. The carbonyl group

IR pattern is assigned to mononuclear complexes with *fac* disposition, where the selenium PNP ligand is bound through its two chalcogen atoms. The IR spectrum of complex **3** shows two carbonyl bands derived from a C_s point group symmetry with vibration modes $A' + A''$ due to a mononuclear complex where both the PNP and the diphos ligands are attached to the metal center in a chelate fashion directing the carbonyl groups to a *cis* arrangement in the complex. The ν(PSe) vibration in the starting material ($K[N(SePPh_2)_2]$) appears at 545 cm^{-1} in KBr [2]; in the case of complexes **1**–**3** the corresponding bands appear around this value (540, 539, and 538 cm^{-1} for **1**, **2** and **3**, respectively).

3.3. NMR spectroscopy

Complexes **1** and **2** show a symmetrical coordination of the $Ph_2P(Se)NP(Se)Ph_2$ ligand in solution as evidenced by the appearance of one signal in ^{31}P- and ^{77}Se NMR spectra. In complex **3** the coordination of diphos and $Ph_2P(Se)NP(Se)Ph_2$ ligand in a chelate fashion originate a spiro compound with four signals: one for each phosphorus atom. The ^{77}Se NMR chemical shifts do not show any trend which can be straightforwardly accounted for; it would be desirable to count on more data in order to explore the governing effects on the ^{77}Se NMR chemical shifts in these systems; however, ^{77}Se NMR not only reflects the symmetry in complexes **1**, **2**, and **3**, but also gives insight into the interaction of the P–Se atoms through the $^1J_{P-Se}$ coupling constants (Table 3).

Table 3
^{77}Se NMR shifts and coupling constants

Compound	δ (ppm)	$^1J_{P-Se}$ (Hz)	Reference
a	−352.2	562	[11a]
1	−281.7	573	This work
2	−285.0	578	This work
3	−227.0	604	This work
$KN(SePPh_2)_2$	−125.4	687	[2]
$HN(SePPh_2)_2$	−156.6	786	[17]

It is readily seen from Table 3 that the P–Se coupling constant values increase in the order **a** < **1** < **2** < **3** < $KN(SePPh_2)_2$ < $HN(SePPh_2)_2$. The assumption that a higher P–Se coupling constant value reflects a stronger interaction between both atoms makes evident, for complexes **a**, **1**, **2**, and **3**, that higher electron density at the metal center renders a stronger interaction of the P–Se atoms of the $Ph_2P(Se)NP(Se)Ph_2$ ligand. Extrapolation of this reasoning to compounds $KN(SePPh_2)_2$ and $HN(SePPh_2)_2$ indicates that the P–Se strongest interaction shown in Table 3 takes place when the selenium atom is not involved in any other bonding apart from its interaction with the phosphorus atom.

3.4. Structural studies

Complexes **b**, **1**, and **2** were each crystallized in a 1:1 mixture of CH_2Cl_2/hexane at 4 °C giving adequate crystals for single-crystal X-ray diffraction analyses. To the best of our knowledge no crystal structure of complex **b** has ever been reported. The geometry around the manganese center is slightly distorted octahedral with the carbonyl groups in *fac* disposition. The molecular structure of **b** including its

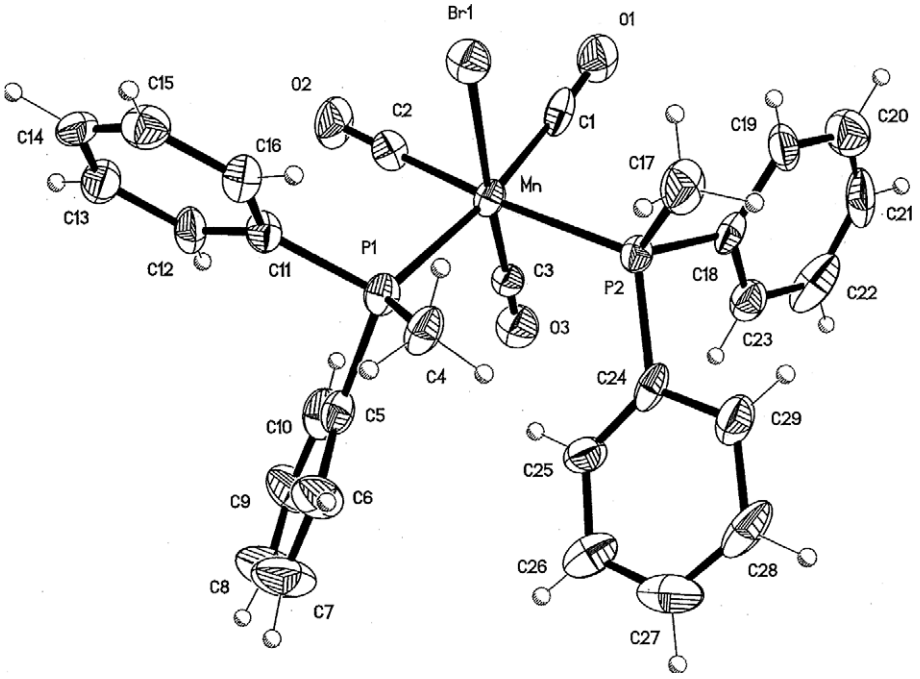


Fig. 2. Molecular structure of **b** including atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Mn–Br(1) 2.527(1), Mn–C(1) 1.810(9), Mn–P(1) 2.387(2); P(1)–Mn–C(1) 169.8(2), P(2)–Mn–C(2) 174.5(2), Br(1)–Mn–C(3) 175.4(3).

atom numbering scheme is shown in Fig. 2 together with some selected bond distances and angles.

The unit cell of complex **2** contains two independent, mononuclear molecules (**2** and **2a**). In Fig. 3 are shown three dimensional representations of both molecules with the corresponding atom numbering scheme and some bond distances and angles germane to the discussion of both complexes' solid state structures.

The diselenoimidodiphosphinato ligand is symmetrically coordinated to Mn through both selenium atoms; the Mn–Se bond lengths are equivalent within experimental error (average 2.5372(1) and 2.5362(1) Å in **2** and **2a**, respectively) indicating a covalent interaction (Σ_{cov} (Mn, Se) = 2.56 Å) [29]. The P–Se and P–N bond distances in the SePNPSe backbone are also equivalent (average P–Se and P–N: 2.170(2) and 1.579(2) Å in **2**, 2.171(2) and 1.584 Å in **2a**). In compound $Ph_2P(Se)NHP(Se)Ph_2$ neither the P–Se nor the P–N bond lengths are symmetrical (P–Se = (2.085(1), 2.101(1) Å and P–N = 1.678(4), 1.686(3) Å [17]; the equivalence and lengthening of both P–Se bond distances as well as the shortening and equivalence of both P–N bond distances in **2** and **2a** are indicative of electron delocalization over the $MnSe_2P_2N$ metallacycle. The difference in value of the PNP angle in **2**, **2a** (139.0(3)° and 138.4(3)°, respectively) compared with the PNP angle in **a** (130.0(2)° [11a]) attests to the flexibility of the SePNPSe backbone (in the gold complex $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$ the PNP angle measures 121.37(12)° [18b]).

The MnSePNPSe ring in **2** displays a half-chair conformation with the Mn(1) atom out of the plane (with a deviation of −1.5369 Å) defined by P(2), P(1), Se(1), S(2), and N(1) (with −0.0147, 0.0147, −0.0120, 0.0120, and 0.0760 Å mean deviations, respectively). The preferred conformations of the MSePNPSe metallacycles are related to the boat conformation (distorted, pseudo, or twisted boat), although a half-chair conformation has been reported [9]. In **2a** the MnSePNPSe ring shows a distorted boat conformation with the N and Mn atoms at the apices. The distance Se(1)–Se(2), known as the bite distance, amounts to 3.615 Å in **2** and 3.637 Å in **2a**.

The coordination geometry around the manganese atoms in **2** and **2a** is distorted octahedral.

Fig. 4 shows a three dimensional representation with corresponding atom numbering scheme and some selected bond lengths and angles of complex **3**.

The inorganic selenium ligand binds symmetrically rendering a six-membered ring manganacycle. Diphos also coordinates in a chelate fashion to build another ring; this one with five members to form a spiro compound. Bond lengths and angles are similar to those in complex **2**, except for the PNP angle: in complex **3** this angle measures

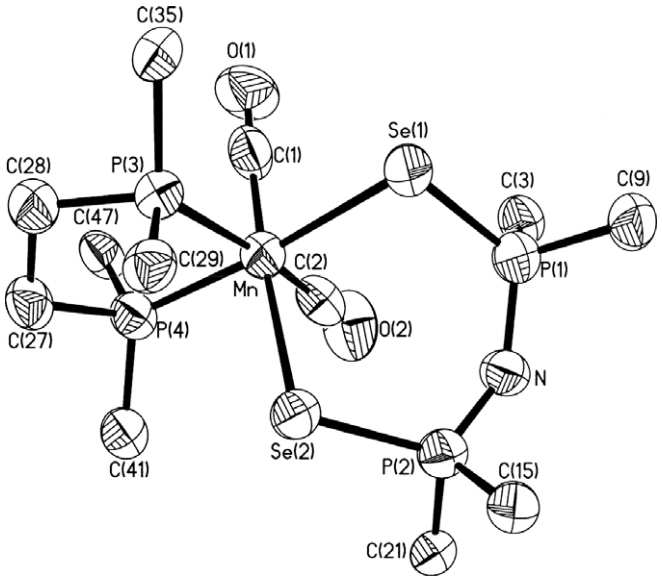


Fig. 4. Molecular structure of **3** with atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]; Mn–Se(1) 2.5514(7), Se(1)–P(1) 2.166(1), P(1)–N 1.593(3); P(1)–N–P(2) 133.5(2), Se(1)–Mn–Se(2) 88.60(2), N–P(1)–Se(1) 117.8(1), P(1)–Se(1)–Mn 99.83(4).

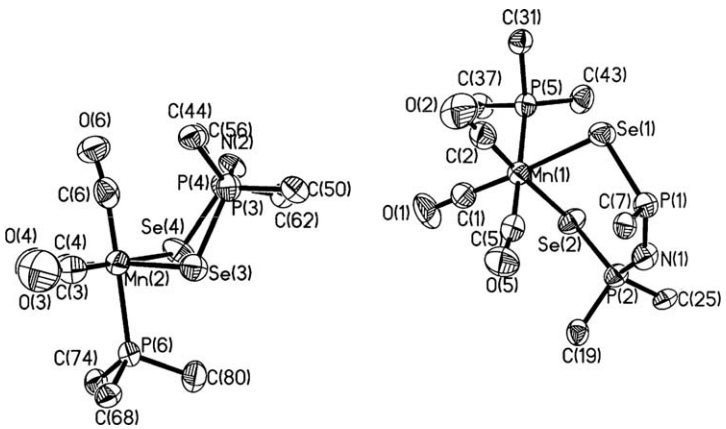


Fig. 3. Molecular structures of **2** and **2a** including atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]; **2**: Mn(1)–Se(1) 2.539(1), Se(1)–P(1) 2.173(2), P(1)–N(1) 1.557(5); P(1)–N(1)–P(2) 139.0(3), Se(1)–Mn(1)–Se(2) 90.87(4), N(1)–P(1)–Se(1) 119.4(2), P(1)–Se(1)–Mn(1) 103.19(6). **2a**: Mn(2)–Se(3) 2.538(1), Se(3)–P(3) 2.168(2), P(3)–N(2) 1.482(5); P(3)–N(2)–P(4) 138.5(3), Se(3)–Mn(2)–Se(4) 91.63(4), N(2)–P(3)–Se(3) 118.4(2), P(3)–Se(3)–Mn(2) 101.66(6).

133.5(2)° which is an intermediate value between **a** and **2**. The MnSePNPSe ring in **3** shows a twisted boat conformation with the Mn and N atoms at the apices and a bite distance of 3.558 Å. The five-membered ring formed by the $MnPCH_2CH_2P$ atoms adopts a pseudo-envelope conformation.

The geometry around the manganese atom in complex **3** is pseudooctahedral. Major causes of distortion arise from the five- and six-membered rings.

4. Conclusions

Two routes for formation of complexes of the type $[Mn(CO)_{4-x}(L)\{Ph_2P(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$, where $x = 1$ for $L = PPh_3$ and $PMePh_2$; and $x = 2$, for $L = Ph_2PCH_2\text{-}CH_2PPh_2$ have been achieved. It has been found Route **A** more efficient for the preparation of the complexes herein reported. For complex **2** the unit cell contains two independent, mononuclear molecules (**2** and **2a**) with different MnSePNPSe ring conformations. ^{31}P–^{77}Se coupling constants, $^1J_{P-Se}$, are promising tools to gain insight into the coordination of PNP ligands. An understanding of the effects governing the ^{77}Se NMR shifts in the imidodiselenodiphosphinato systems, upon coordination, is yet to be found.

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Appendix A. Supplementary data

Crystallographic data have been deposited for compounds **b**, **3**, and **2** in the Cambridge Crystallographic Database, CCDC nos. 299076, 299077, and 299078, respectively, in CIF format. 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; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.027.

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