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Six-membered tetracarbonylmanganese(I) and -rhenium(I) metalacycles containing the $[Ph_2P(Se)NP(Se)Ph_2]$ ligand: solution and solid state characterization

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Abstract

The halocarbonyls $BrM(CO)_5$, M = Mn and Re, were reacted with the $KN(SePPh_2)_2$ salt in equimolar amounts; the reactions were thermally carried out and resulted in the generation of the hexacoordinated isostructural complexes $[M(CO)_4\{Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se'\}]$ with a twist MSePNPSe ring conformation. Complexes' characterizations were achieved by IR, mass, NMR (^1H, ^{13}C, ^{31}P, ^{77}Se) spectroscopies, and by single-crystal X-ray diffraction.

Keywords: Manganese; Rhenium; Halocarbonyls; Diselenoimidodiphosphinato complexes; ^{77}Se NMR

1. Introduction

The report by Fluck and Goldmann on the preparation of $HN(OPPh_2)_2$ 40 years ago [1] opened up an area of research that has proven fruitful to this very day: the coordination chemistry of the imidodiphosphinic acids and their salts. Schmidpeter et al. explored the coordination chemistry of $HN(OPPh_2)_2$ [2b,c,e] and consequently the synthesis of the $HN(SPPh_2)_2$ [2d] analog along with its coordination chemistry with some metals [2e]; it was soon found out that the alkali metal salts of the imidodiphosphinic acids (basically Li, Na, and K) were to play an important role in this kind of chemistry [2a]. It was not until 1978, when the $HN(SePPh_2)_2$ acid and its K salt syntheses were first reported, that the coordination capacity of the $N(SePPh_2)_2$ moiety began to be tested [3]; during the course of these studies an easy, expeditious way of preparing the $HN(SePPh_2)_2$ acid and its K salt was developed [4b,c]. The metal cores to which the $N(SePPh_2)_2$ ligand has been attached range from main group elements (K [4b], groups 11 [5] and 12 [6]; Al and Ga [7], In [8], Sn [6,9a,b], Pb [6], Sb [9,10], Bi [8,10], Se [11] and Te [12]), transition metals (V [13], Cr [13], Re [14a,b], Ru [15a,b,c,d], Os [16a,b], Co [5d], Rh [4b,15b,c], Ir [15b,17], group 10: Ni [4a], Pd [4a,b,c,15c] and Pt [4a,b,c]) to rare-earth metals: Y [18a,b], La, Gd, Er, Yb [19], and Sm [20].

The ligation modes of the $N(SePPh_2)_2$ [21] moiety, detected by X-ray single crystal diffraction analysis, include the η^2- and η^3-fashions (Fig. 1(a) and (b), respectively), biconnective binuclear bridging (Fig. 1(c)), and tetraconnective trinuclear bridging (Fig. 1(d)).

The $N(SePPh_2)_2$ fragment can stabilize high and low oxidation states transition metal complexes (see for example [16a] for Os(II) and [16b] for Os(VI)). The oxo, nitrido, and imido Re(V) complexes are the only

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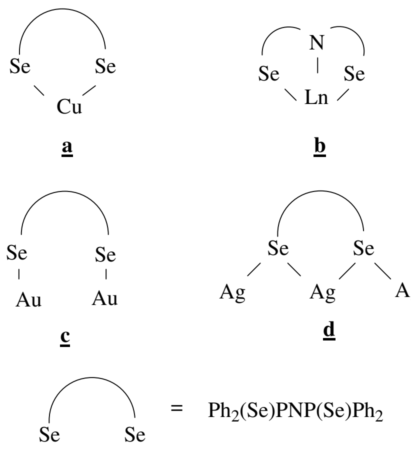

Fig. 1. Coordination modes of the $Ph_2(Se)PNP(Se)Ph_2$ ligand. (a) [5d]; (b) Ln = La, Gd, Er [19]; (c) [5c]; (d) [5a].

examples of rhenium complexes containing the $N(SePPh_2)_2$ ligand described in the literature [14]; to our knowledge, neither low oxidation state $N(SePPh_2)_2$ complexes of rhenium nor manganese have been reported. Herein we wish to report the synthesis and characterization, in solution and in the solid state, of two new complexes, $\{M(CO)_4[Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se']\}$, M = Re and Mn.

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 and hexane were dried and deoxygenated by distillation from sodium benzophenone ketyl. $[BrM(CO)_5]$, M = Mn [22a] and Re [22b], $[K\{(SePPh_2)_2N\}]$ [4b,c] 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 (300.0 MHz), ^{13}C (75.6 MHz), ^{31}P (121.7 MHz), and ^{77}Se (57.3 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), and $Ph_2Se_2/CDCl_3$, respectively. FAB(+) mass spectra were recorded using a JEOL SX-102A instrument. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The melting points were determined on a Fisher-Johns apparatus and are uncorrected.

2.1. General procedure

2.1.1. Synthesis of $[M(CO)_4\{Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se'\}]$

*2.1.1.1. M = Mn, **1**.* $[K\{N(SePPh_2)_2\}]$ (0.422 g; 0.727 mmol) was dissolved in 50 mL of dry THF in a 100 mL round bottom flask previously purged with nitrogen; then, a solution of $[BrMn(CO)_5]$ (0.200 g; 0.727 mmol) in 20 mL of anhydrous THF was added via cannula. The changes in the reaction were monitored by IR spectroscopy in the characteristic region for carbonyl stretching vibrations. The reaction mixture was stirred under THF reflux for 1 h. An off-white powder (KBr) was filtered off remaining a yellow solution. Removal of the solvent under reduced pressure resulted in a yellow material (0.402 g, 78% yield) which was recrystallized from a 4:1 mixture of CH_2Cl_2/hexane at 4 °C for several days; m.p. 223–225 °C. Anal. Calc. for $C_{28}H_{20}O_4NP_2MnSe_2$: C, 47.42; H, 2.84; N, 1.98%; Found: C, 46.9; H, 3.1; N, 1.56%. IR (KBr): ν(CO) 2076m, 2003vs, 1985s, 1932s; $\nu(P_2N)$ 1188m; ν(PSe) 540m cm^{-1}. IR ($CHCl_3$): ν(CO) 2080m, 2009vs, 1991s, 1950s cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ/ppm: 7.9 {dd, 8H, H_o [$^3J(PCCH) = 14$ Hz, $^3J(H_oH_m) = 7$ Hz]}; 7.4 (m, 12H, H_m/H_p). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 27.0 [$^1J(PSe) = 562$ Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 136.2 [dd, C_i, $^1J(PC) = 100$ Hz, $^3J(PNC) = 4$ Hz]; 127.2 [d, C_o, $^2J(PCC) = 14$ Hz]; 129.9 [d, C_m, $^3J(PCCC) = 12$ Hz]; 130.3 (s, C_p); 214.9, 209.9 (s, CO). $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 57.34 MHz): δ/ppm: −352.2 (d, $^1J(PSe) = 562$ Hz). MS (*m*/*e*): P_B 597, $[M-4CO]^+$.

*2.1.1.2. M = Re, **2**.* $[BrRe(CO)_5]$ (0.500 g; 1.23 mmol) was dissolved in 90 mL of dry toluene in a previously nitrogen purged device. $[K\{N(SePPh_2)_2\}]$ (0.715 g; 1.23 mmol) was added and the solution was refluxed for 30 min (the changes in the reaction were monitored by IR spectroscopy in the characteristic region for carbonyl stretching vibrations) after which the solution was filtered through diatomaceous earth to remove KBr. The toluene was eliminated under reduced pressure remaining a light-yellow product (0.750 g, 73% yield). Adequate crystals for X-ray analysis were grown from a hexane solution left overnight at room temperature; m.p. 155 °C (dec.). Anal. Calc. for $C_{28}H_{20}O_4NP_2ReSe_2$: C, 40.01; H, 2.40; N, 1.67%; Found: C, 39.55; H,2.47; N,1.55%. IR (KBr): ν(CO) 2096m, 2002vs, 1979s, 1919s; $\nu(P_2N)$ 1191m; ν(PSe) 535m cm^{-1}. IR ($CHCl_3$): ν(CO) 2099m, 2007vs, 1985s, 1939s cm^{-1}. ^1H NMR ($CDCl_3$, 300.0 MHz): δ/ppm: 7.9 {ddd, 8H, H_o [$^3J(PCCH) = 14$ Hz, $^3J(H_oH_m) = 8$ Hz, $^4J(H_oH_p) = 2$ Hz]}; 7.4–7.5 (m, 12H, H_m/H_p). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ/ppm: 24.3 [$^1J(PSe) = 546$ Hz, $^1J(PC) = 100$ Hz, $^3J(PSe) = 6$ Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz): δ/ppm: 136.7 [dd, C_i, $^1J(PC) = 100$ Hz, $^3J(PNPC) = 5$ Hz]; 128.4 [d, C_o, $^2J(PCC) = 14$ Hz]; 131.0 [d, C_m, $^3J(PCCC) = 11$ Hz]; 131.5 (s, C_p); 184.4 (t, CO), 183.3 (d, CO). $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 57.3 MHz): δ/ppm: −340.1 (dd, $^1J(PSe) = 546$ Hz, $^3J(PSe) = 6$ Hz). MS (*m*/*e*): 841, $[M]^+$; 813, $[M-CO]^+$; 785, $[M-2CO]^+$; 729, $[M-4CO]^+$.

2.2. Structure determination

2.2.1. $Mn(CO)_4\{Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se'\}$, 1

Suitable crystals of **1** were obtained from a CH_2Cl_2/hexane 4:1 solution at 4 °C for several days. Data were collected at 25 °C on a Bruker Smart Apex CCD diffractometer for 16884 reflections of which 4186 ($F > 4.0\sigma(F)$) were independent ($R_{int} = 9.96\%$) and used in the full matrix least squares refinement. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The final R values are $R = \sum|F_o - F_c|/\sum|F_o| = 3.38\%$ and $wR = [\sum w(|F_o - F_c|)^2/\sum|F_o|_2]^{1/2} = 6.59\%$ ($R = 6.05\%$ and $wR = 7.08\%$ for all data) with weights $w^{-1} = \sigma^2(F) + 0.0015F_2$; goodness-of-fit 0.976. The residual electron density from a final difference Fourier synthesis was in the range of 0.542, −0.498 e Å^{-3}.

2.2.2. $Re(CO)_4\{Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se'\}]$, 2

Suitable crystals of **2** were obtained from a hexane solution at room temperature left overnight. Data were collected at 25 °C on a Bruker Smart Apex CCD diffractometer for 20,403 reflections ($\theta/2\theta$ scan mode) of which 3308 ($F > 4.0\sigma(F)$) were independent ($R_{int} = 6.12\%$) and used in the full matrix least squares refinement. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The final R values are $R = \sum|F_o - F_c|/\sum|F_o| = 2.98\%$ and $wR = [\sum w(|F_o - F_c|)^2/\sum|F_o|^2]^{1/2} = 6.82\%$ ($R = 3.54\%$ and $wR = 6.95\%$ for all data) with weights $w^{-1} = \sigma^2(F) + 0.0015F_2$; goodness-of-fit 0.981. The residual electron density from a final difference Fourier synthesis was in the range of 0.73, −0.953 e Å^{-3}. Crystal data and experimental details for **1** and **2** are given in Table 1.

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

	1	**2**
Molecular formula	$C_{28}H_{20}MnNO_4P_2Se_2$	$C_{28}H_{20}NO_4P_2ReSe_2$
M	709.25	840.51
Crystal size (mm)	0.338×0.268×0.218	0.260×0.198×0.178
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	13.960(1)	13.940(1)
b (Å)	16.665(1)	16.812(1)
c (Å)	12.328(1)	12.294(1)
β (°)	90.367(1)	90.771(2)
V (Å^3)	2868.0(4)	2881.1(3)
Z	4	4
θ Range for data collection (°)	1.90–30.03	1.90–27.51
Reflections collected	16,884	20,403
Independent reflections	4186 ($R_{int} = 0.0996$)	3308 ($R_{int} = 0.0612$)
Max. and min. transmission	0.5435 and 0.4011	0.4431 and 0.1578
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0338$, $wR_2 = 0.0659$	$R_1 = 0.0298$, $wR_2 = 0.0682$
R indices (all data)	$R_1 = 0.0605$, $wR_2 = 0.0708$	$R_1 = 0.0354$, $wR_2 = 0.0695$

3. Results and discussion

3.1. Syntheses

Reaction of equimolar amounts of $K[N(SePPh_2)_2]$ and $[BrMn(CO)_5]$, according to Eq. (1), in boiling THF for 1 h, afforded **1**, $\{Mn(CO)_4[Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se']\}$, in 178% yield as a complex stable in air and moisture in the solid state, the stability was maintained in solution at low temperatures; at ambient temperature, slow decomposition took place in solution after several weeks. Complex **1** is mainly soluble in non polar organic solvents

$$BrMn(CO)_5 + K[N(SePPh_2)_2] \xrightarrow[1\ h]{THF\ \ reflux} \{Mn(CO)_4[Ph_2(Se)PNP(Se)Ph_2\text{-}Se,Se']\} + K + CO \quad (1)$$

The reaction time reflects the greater affinity of the selenium ligand compared with its sulfur analog, $K[N(SPPh_2)_2]$, whose reaction with the same halocarbonyl complex, $BrMn(CO)_5$, took 3 h, under THF reflux, to give the corresponding sulfur complex, $\{Mn(CO)_4[Ph_2P(S)NP(S)Ph_2\text{-}S,S']\}$ with a comparable yield (74 %) [23]. This behavior greatly contrasts with that of the reaction of the $Na[Ph_2P(O)NP(O)Ph_2]$ salt with $BrMn(CO)_5$, where the $\{Mn(CO)_4[Ph_2P(O)NP(O)Ph_2\text{-}O,O']\}$ complex readily oxidized to the violet Mn^{3+} complex, $\{Mn[Ph_2P(O)NP(O)Ph_2\text{-}O,O']_3\}$ [24].

The more vigorous reaction conditions (30 min under toluene reflux) for the generation of **2**, $\{Re(CO)_4[Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se']\}$, compared with the conditions for the formation of **1** (THF reflux for 1 h) show the greater stability of the starting material, $BrRe(CO)_5$, over its Mn analog: no reaction took place when boiling THF was used instead of toluene for the formation of **2** from $BrRe(CO)_5$ and $K[Ph_2P(Se)NP(Se)Ph_2]$.

The stability granted by the selenium inorganic ligand to **2** is apparent in its reluctance to decompose, in solid state and in solution, after long periods of time, even at room temperature. Complex **2** is soluble in most organic solvents.

The generation of $\{Mn(CO)_4[Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se']\}$ **1** was irrespective of the molar ratio used, no further substitution of $N(SePPh_2)_2$ took place when an excess of the $K[Ph_2P(Se)NP(Se)Ph_2]$ salt was employed; however, stoichiometric ratios greater than 1 ($K[Ph_2P(Se)NP(Se)Ph_2]/BrRe(CO)_5$) led to the formation of unidentified products and a decrease in the yield of **2**. This was also observed with longer reaction times.

The fact that the green rhenium(V) complex, {ReO(Cl)[N($PPh_2Se)_2]_2$}, was prone to lose one Se atom per ligand to give the brown-orange complex {ReO(Cl)[$Ph_2PNP(Se)Ph_2$-*P*,*Se*$]_2$}, indicates that the low oxidation state of the rhenium in complex **2** contributes to its stabilization [14a]. This Se atom elimination in the disubstituted {ReO(Cl)[N($SePPh_2)_2]_2$} complex to give {ReO(Cl)[$Ph_2PNP(Se)Ph_2$-*P*,*Se*$]_2$} was attributed to the "hard" character of the $[R\equiv O]^{3+}$ core, which disfavors coordination of the rhenium(V) atom to four 'soft' selenium donors [14b]; thus, the complexes {Re(NMe)Cl_2[N($SePPh_2)_2$-*Se*,*Se′*](PPh_3)},{Re(NMe)Cl-[N($SePPh_2)_2$-*Se*,*Se′*$]_2$}, and {ReN[N($SePPh_2)_2$-*Se*,*Se′*$]_2$}, characterized in solution [14b], proved to be more stable than the oxo-complex and no selenium elimination was observed; therefore, in the present case the carbonyl fragment $M(CO)_4$, M = Mn, Re in complexes **1** and **2**, seems to adequately match the 'softness' of the N($SePPh_2)_2$ fragment to render stable complexes. The failure to obtain the monosubstituted complex [ReO$(Cl)_2${N($SePPh_2)_2$-*Se*,*Se′*}PPh_3] [14b] further points up the stabilization derived from the interaction of the N($SePPh_2)_2$ and $M(CO)_4$ fragments, M = Mn and Re.

3.2. Infrared spectroscopy

The IR spectra of **1** and **2** are very similar, both show four bands in the carbonyl stretching region. The disposition of the carbonyl groups in both **1** and **2** gives rise to a C_{2v} local symmetry corresponding to the $2A_1 + B_1 + B_2$ vibration modes [25]; this carbonyl infrared pattern corresponds to mononuclear complexes where the N($SePPh_2)_2$ ligand is bound through both Se atoms, being the difference in the wave numbers at which the bands appear in these two tetracarbonyl complexes due to the electron density at each metal core. The ν(PSe) band absorptions in **1** (540 cm^{-1}) and **2** (535 cm^{-1}) are close to the corresponding band of the K[N($SePPh_2)_2$] salt (545 cm^{-1}) [4b].

3.3. NMR spectroscopy

The symmetry in both **1** and **2** is evidenced by the NMR spectra in solution; thus, the ^{31}P spectra show one single (each flanked by satellites due to coupling with ^{77}Se and ^{13}C nuclei), 27.0 and 24.3 ppm for **1** and **2**, respectively; the shift for **2** and its $^1J_{P–Se}$ (546 Hz) are intermediate in the range of the ^{31}P NMR shifts and $^{31}P–^{77}Se$ coupling constants reported for the complexes {ReO(Cl)[N($SePPh_2)_2]_2$}, 34.4 ppm, ($^1J_{P–Se} = 525$ Hz) [14a]; {Re(NMe)Cl_2[N($SePPh_2)_2$-*Se*,*Se′*](PPh_3)}, 31.4 ppm, ($^1J_{P–Se} = 532$ Hz); {Re(NMe)-Cl[N($SePPh_2)_2$-*Se*,*Se′*$]_2$}, 27.3 ppm, ($^1J_{P–Se} = 558$ Hz); and {ReN[N($SePPh_2)_2$-*Se*,*Se′*$]_2$}, 21.6 ppm, ($^1J_{P–Se} = 547$ Hz) [14b]. It is interesting to note that the high oxidation state (V) of the oxo, imido or nitrido complexes compared with **2** (formal oxidation state I) does not affect singularly neither the ^{31}P shifts nor the $^{31}P–^{77}Se$ coupling constants. A comparative study of the ^{77}Se NMR shifts of the ligand N($SePPh_2)_2$ with rhenium or manganese complexes cannot be effected due to the lack of data; however, it is noteworthy the quite low frequencies at which the ^{77}Se NMR chemical shifts appear (**1**, −353.2 ppm; **2**, −340.1 ppm) compared with the acid HN($SePPh_2)_2$ (−163 ppm).

The stark differences in ^{77}Se NMR shifts of some reported complexes with similar $^1J_{P–Se}$ within the N($SePPh_2)_2$ ligand (see for example, {Sn[N($SePPh_2)_2$-*Se*,*Se′*$]_2$}, ^{77}Se NMR, $\delta = 9.8$ ppm; $^1J_{P–Se} = 562$ Hz [9b]) suggest that these chemical shifts are not straightforwardly related to the P–Se coupling constants; a thorough understanding of the effects whereby the ^{77}Se NMR shifts are governed in these systems is yet to be found.

3.4. Structural studies

Suitable crystals of **1** for the single-crystal X-ray diffraction investigation were obtained from a 4:1 mixture of CH_2Cl_2/hexane at 4 °C for several days. Complex **2** could be crystallized from a saturated hexane solution at room temperature left overnight, the crystals so obtained were appropriate for the X-ray analysis. The crystals of complexes {$M(CO)_4[Ph_2P(Se)NP(Se)Ph_2$-*Se*,*Se′*]}, M = Mn, **1** and M = Re, **2** are monoclinic, of space group *C*2/c with *Z* = 4 molecules related by a center of inversion in the unit cell. The molecular structure **2** including its atom numbering scheme is shown on Fig. 2. The X-ray solid state structures of these complexes are quite similar; therefore, the following discussion applies to both Mn and Re molecules **1** and **2**.

The six-membered ring is in a twist conformation (see Fig. 3. for **2**), being the metal and the nitrogen atoms at the apices. The Mn–Se bond distance in **1**, 2.5417(4) Å, is indicative of its covalent nature ($\sum_{cov}$(Mn, Se) = 2.56 Å) [26]. The covalent nature of the Re–Se in **2** is reflected in its bond distance, 2.6434(4) Å, a shorter Re–Se distance was reported for the complex [ReO(OEt)($Ph_2PNP(Se)Ph_2$-*P*,*Se*$)_2$], 2.562(1) Å, where the Re(V) atom is said to be involved in a covalent interaction with the chalcogen [14b]. The MSePNPSe bond distances within the metalacycles indicate the well known electron delocalization found in most N($SePPh_2)_2$ complexes. The metal centers in **1** and **2**, formally M(I), M = Mn, Re; are coordinated to four carbonyl groups and one bidentate [N($SePPh_2)_2$] ligand in a distorted octahedral environment.

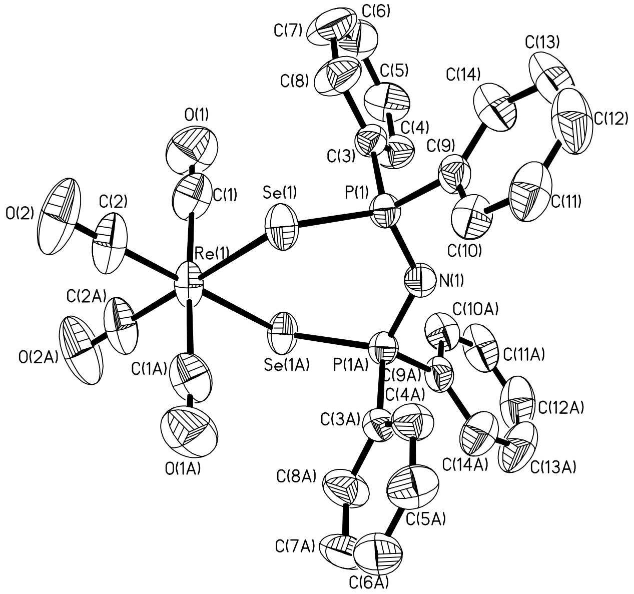

Fig. 2. The molecular structure of **2** including the atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Re(1)–Se(1) 2.6434(4), Se(1)–P(1) 2.1774(8), P(1)–N(1) 1.5897(17); P(1)–N(1)–P(1a) 130.4(2), Se(1)–Re(1)–Se(1a) 99.079(16), N(1)–P(1)–Se(1) 118.01(11), P(1)–Se(1)–Re(1) 106.47(3).

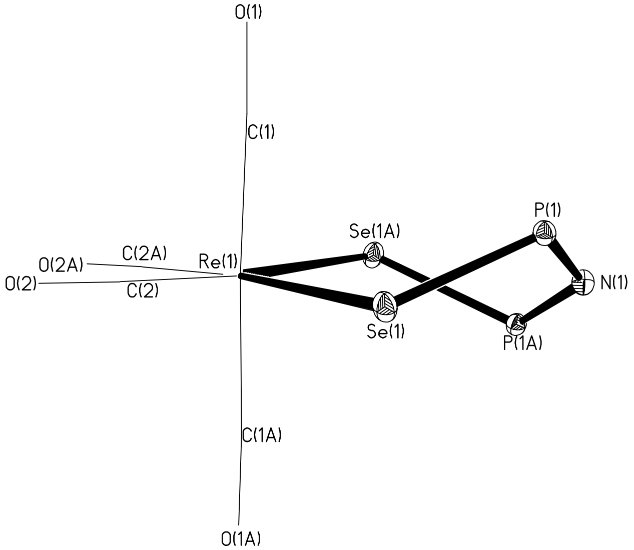

Fig. 3. Side-on view of **2** showing the twist conformation.

4. Conclusions

The existence of **1**, {$Mn(CO)_4[Ph_2P(Se)NP(Se)Ph_2$-*Se*,*Se′*]}, shows that the ligands $N(SePPh_2)_2$ as well as $N(SPPh_2)_2$ [23] can stabilize Mn in a low oxidation state; this greatly contrasts with $N(OPPh_2)_2$, where aerial oxidation of {$Mn(CO)_4[Ph_2P(O)NP(O)Ph_2$-*O*,*O′*]} leads to the stable octahedral, violet Mn(III) complex {$Mn[Ph_2P(O)NP(O)Ph_2$-*O*,*O′*$]_3$} [24]. The formation of **2** evidences that both, low and high, oxidation states Re and Os [16] complexes with $N(SePPh_2)_2$ can be stabilized by this selenium fragment; although the lack of structural characterization in the solid state for the Re(V) complexes with $N(SePPh_2)_2$ [14] suggests their diminished stability compared to **2**.

5. Supplementary material

Supplementary data (atomic coordinates, bond lengths and angles and thermal parameters) have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 229271 for **1** and 229270 for **2**. Copies of the data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. or http://www.ccdc.cam.ac.uk).

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