

Synthetic studies for the preparation of phosphorus carbonyl rhenacycles with the selenoimidodiphosphinate ligand $[N(\text{SePPh}_2)_2]$

Lucila Márquez-Pallares^a, Jorge Pluma-Pluma^a, Marisol Reyes-Lezama^a,
Marisol Güizado-Rodríguez^a, Herbert Höpfl^b, Noé Zúñiga-Villarreal^{a,*}

^a Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior, 04510 México, D.F., Mexico

^b Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, C.P. 62210 Cuernavaca Morelos, Mexico

Received 13 December 2006; received in revised form 23 December 2006; accepted 23 December 2006

Available online 9 January 2007

Abstract

The synthesis of the rhenacycles $[\text{Re}(\text{CO})_3(\text{PR}_3)\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$, $\text{PR}_3 = \text{PPh}_3$ (**1**), PMePh_2 (**2**), and PMe_2Ph (**3**) by a straightforward high yield procedure is described. Attempts at the preparation of the spiro $[\text{Re}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2-\kappa^2\text{P})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$ resulted in the formation of complexes $[\text{Re}_2(\text{CO})_6\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}_2(\mu-\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ (**4**) and $[\text{Re}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2-\kappa^2\text{P})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa\text{Se}\}]$ (**5**). All new inorganic rhenacycles **1–5** were characterized in solution and in solid state. The X-ray diffraction analysis of $[\text{Re}(\text{CO})_3\text{PPh}_3\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$ showed that its MnSePNPSe ring conformation is sensitive to temperature.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Rhenium(I) complexes; ⁷⁷Se NMR; Carbonyl substitution reactions; Tetraphenyldiselenoimidodiphosphinato complexes; Tertiary phosphines; Bis(diphenylphosphino)ethane

1. Introduction

The coordination of the $[N(\text{EPPH}_2)_2]^-$ (E = O, S, Se) anions has been widely studied over the last years. Their potential applications in a number of fields (e.g. catalysis, metal extraction studies, optoelectronics, NMR shift reagents, to mention but a few) and their capability of joining the metal center in different fashions and, at the same time, adopting several ring conformations in inorganic metallacycles have been two major reasons for their extensive exploration [1]. As far as the coordination chemistry of the $[N(\text{SePPh}_2)_2]$ fragment is concerned it has been found that it binds a wide range of atoms: from main group elements (K [2], group 12 [3]; Al and Ga [4], In [5a,5b], Sn [3,6], Pb [3], Sb [5b,7], Bi [5b,7], Se [8] and Te [9]), transition metals (V and Cr [10], Mn [11a,11b,11c] and Re [11d,11e], Ru [12a,12b,12c], Os

[13a,13b], Co [14], Rh [2,12b,12c], Ir [12b,15], group 10: Ni [16], Pd [2,12c,16,17], Pt [2,12c,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]. Our interest in the structure and reaction chemistry of the $[N(\text{EPPH}_2)_2]^-$ (E = O, S, Se) anions with carbonyl complexes of Mn and Re led us to undertake a systematic study thereof [22,11a,11c]. Recently, we reported the synthesis of the $[\text{Mn}(\text{CO})_{4-x}(\text{L})_x\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$ complexes, where $X = 1$ for L = PPh_3 , and PMePh_2 ; and $X = 2$, for L = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ by two methods [11a]. In the present paper, we describe the synthesis of the rhenacycles $[\text{Re}(\text{CO})_3(\text{PR}_3)\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$, $\text{PR}_3 = \text{PPh}_3$ (**1**), PMePh_2 (**2**), and PMe_2Ph (**3**), using a different method from those employed for the manganese analogs. When the new method was tested to prepare the spiro compound $[\text{Re}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2-\kappa^2\text{P})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$ (whose Mn analog is known [11a]) complexes **4**, $[\text{Re}_2(\text{CO})_6\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}_2(\mu-\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$, and **5**, $[\text{Re}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{CH}_2-$

* Corresponding author. Fax: +52 56 16 22 03.

E-mail address: zuniga@servidor.unam.mx (N. Zúñiga-Villarreal).

$\text{PPh}_2\text{-}\kappa^2\text{P}\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-}\kappa^2\text{Se}\}$ were obtained. All new inorganic rhenacycles **1–5** were characterized in solution and in solid state.

2. Experimental

All preparative work was effected 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. $[\text{ReBr}(\text{CO})_5]$, 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). Methylphenylphosphine, triphenylphosphine, dimethylphenylphosphine, and 1,2-bis(diphenylphosphine)ethane were from Aldrich, Co. Gray selenium was from Fisher Reagents Scientific Company. $\text{HN}(\text{PPh}_2)_2$ [23], $\text{HN}(\text{SePPh}_2)_2$ [17], $[\text{K}\{\text{SePPh}_2\}_2\text{N}\}$ [2], and $[\text{Re}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-}\kappa^2\text{Se}\}]$ [11c] were prepared according to the literature procedures. IR spectra were obtained in solution (4000–580 cm^{-1}) and in KBr disk (4000–200 cm^{-1}) using a Bruker Tensor 27 FT-IR 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 $\text{Ph}_2\text{Se}_2/\text{CDCl}_3$ (set to 463.5 ppm for ^{77}Se), respectively. FAB(+) mass spectra were recorded using a JEOL SX-102A instrument with *m*-nitrobenzyl alcohol as matrix in all cases. The melting points were determined on a Fisher–Johns apparatus and are uncorrected.

2.1. General procedures

2.1.1. Method A

Synthesis of $[\text{Re}(\text{CO})_3(\text{PR}_3)\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-}\kappa^2\text{Se}\}]$ complexes for $\text{PR}_3 = \text{PPh}_3$ (**1**); PMePh_2 (**2**); and PMe_2Ph (**3**).

$\text{K}[\text{N}(\text{SePPh}_2)_2]$, $[\text{ReBr}(\text{CO})_5]$, and PR_3 (for quantities see below) were added to a 100 mL round bottom flask containing 70 mL of dry toluene. After some time under reflux (30 min for **1**, 1 h for **2**, and 1 h 15 min for **3**) the solvent was eliminated under reduced pressure leaving an off-white material. The product was washed with dry hexane (2 × 15 mL) and dissolved in dichloromethane to filter off KBr. Crystallization was effected in a mixture of hexane/dichloromethane at 4 °C for several days yielding crystalline powders in the three cases.

2.1.1.1. $[\text{Re}(\text{CO})_3(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-}\kappa^2\text{Se}\}]$ (1**).** 0.58 g (0.8 mmol) of $\text{K}[\text{N}(\text{SePPh}_2)_2]$, 0.4 g (0.99 mmol) of $[\text{ReBr}(\text{CO})_5]$, and 0.26 g (1.00 mmol) of PPh_3 .

1.04 g, 0.96 mmol 98% yield; M.p. 213–215 °C. IR (KBr): $\nu(\text{CO})$ 2017s, 1928s, 1891s cm^{-1} ; $\nu(\text{P}_2\text{N})$ 1179w,

745 w cm^{-1} ; $\nu(\text{PSe})$ 538m cm^{-1} . IR (CH_2Cl_2): $\nu(\text{CO})$ 2020s, 1932 m, 1895m cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ/ppm : 8.05 [ddd, $\text{H}_o(\text{PNP})$, $^3J_{\text{H}_o\text{-P}} = 6$ Hz, $^3J_{\text{H}_o\text{-H}_m} = 4$ Hz, $^3J_{\text{H}_o\text{-H}_p} = 2$ Hz]; 7.22 [dt, $\text{H}_p(\text{PNP})$, $^3J_{\text{H}_p\text{-H}_m} = 7$ Hz, $^4J_{\text{H}_p\text{-H}_o} = 2$ Hz]; 7.09 [dt, $\text{H}_m(\text{PNP})$, $^3J_{\text{H}_m\text{-H}_p} = 7$ Hz, $^3J_{\text{H}_m\text{-H}_o} = 4$ Hz, $^4J_{\text{H}_m\text{-P}} = 4$ Hz]; 7.48–7.34 [m, aromatic protons PPh_3]. ^{13}C NMR(^1H) (CDCl_3 , 75.6 MHz): δ/ppm : 137.10 [dd, C_{ipso} (PNP), $J_{\text{C}_{\text{ipso}}\text{-P}} = 107$ Hz, $^3J_{\text{C}_{\text{ipso}}\text{-P}} = 10$ Hz]; 127.65 [d, C_o (PNP), $^3J_{\text{C}_o\text{-P}} = 13$ Hz]; 131.40 [d, C_m (PNP), $^4J_{\text{C}_m\text{-P}} = 13$ Hz]; 130.5 [s, C_p (PNP)]; 137.70 [d, C_{ipso} (PPh_3), $J_{\text{C}_{\text{ipso}}\text{-P}} = 92$ Hz]; 128.30 [d, C_o (PPh_3), $^3J_{\text{C}_o\text{-P}} = 10$ Hz]; 134.30 [d, C_m (PPh_3), $^4J_{\text{C}_m\text{-P}} = 10$ Hz]; 130.20 [s, C_p (PPh_3)]; 190.50 [s, broad, C 2(CO) *trans* to SePNPSe]; 189.75 [s, broad, C (CO) *trans* to PPh_3]. ^{31}P NMR(^1H) (CDCl_3 , 121.7 MHz): δ/ppm : 28.62 [d, (PNP), $^3J_{\text{PNP-PPh}_3} = 18$ Hz, $J_{\text{P-Se}} = 559$ Hz (satellites)]; 9.50 [t, (PPh_3), $^3J_{\text{PNP-PPh}_3} = 18$ Hz]. ^{77}Se NMR(^1H) (CDCl_3 , 57.3 MHz): δ/ppm : -276.45 [dd, $^1J_{\text{PNP-Se}} = 559$ Hz, $^2J_{\text{PPh}_3\text{-Se}} = 30$ Hz]. MS (*m/e*): 1074 [M^+]; 1018 [$\text{M}-2(\text{CO})^+$]; 913 [$\text{M}-3(\text{CO})-(\text{Ph})^+$].

2.1.1.2. $[\text{Re}(\text{CO})_3(\text{PMePh}_2)\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-}\kappa^2\text{Se}\}]$ (2**).** 0.32 g (0.56 mmol) of $\text{K}[\text{N}(\text{SePPh}_2)_2]$, 0.23 g (0.55 mmol) of $[\text{ReBr}(\text{CO})_5]$, and 0.11 g (0.56 mmol) of PMePh_2 .

0.54 g, 0.54 mmol 97% yield; M.p. 205–209 °C. IR (KBr): $\nu(\text{CO})$ 2015s, 1924s, 1896s cm^{-1} ; $\nu(\text{P}_2\text{N})$ 1178w, 744 w cm^{-1} ; $\nu(\text{PSe})$ 538m cm^{-1} . IR (CH_2Cl_2): $\nu(\text{CO})$ 2022s, 1933m, 1898m cm^{-1} . ^1H NMR (CDCl_3 , 300.5 MHz): δ/ppm : 8.07 [ddd, $\text{H}_o(\text{PNP})$, $^3J_{\text{H}_o\text{-P}} = 7$ Hz, $^3J_{\text{H}_o\text{-H}_m} = 4$ Hz, $^3J_{\text{H}_o\text{-H}_p} = 2$ Hz]; 7.26 [dt, $\text{H}_p(\text{PNP})$, $^3J_{\text{H}_p\text{-H}_m} = 8$ Hz, $^4J_{\text{H}_p\text{-H}_o} = 2$ Hz]; 7.14 [dt, $\text{H}_m(\text{PNP})$, $^3J_{\text{H}_m\text{-H}_p} = 8$ Hz, $^3J_{\text{H}_m\text{-H}_o} = 4$ Hz, $^4J_{\text{H}_m\text{-P}} = 4$ Hz]; 7.41–7.65 [m, aromatic protons PMePh_2]; 2.33 [d, $\text{Me}(\text{PMePh}_2)$, $^2J_{\text{H-P}} = 8$ Hz]. ^{13}C NMR(^1H) (CDCl_3 , 75.6 MHz): δ/ppm : 136.90 [dd, C_{ipso} (PNP), $J_{\text{C}_{\text{ipso}}\text{-P}} = 107$ Hz, $^3J_{\text{C}_{\text{ipso}}\text{-P}} = 9$ Hz]; 127.80 [d, C_o (PNP), $^3J_{\text{C}_o\text{-P}} = 14$ Hz]; 131.40 [d, C_m (PNP), $^4J_{\text{C}_m\text{-P}} = 12$ Hz]; 130.00 [s, C_p (PNP)]; 138.00 [d, C_{ipso} (PMePh_2), $J_{\text{C}_{\text{ipso}}\text{-P}} = 94$ Hz]; 128.43 [d, C_o (PMePh_2), $^3J_{\text{C}_o\text{-P}} = 10$ Hz]; 132.43 [d, C_m (PMePh_2), $^4J_{\text{C}_m\text{-P}} = 10$ Hz]; 130.60 [s, C_p (PMePh_2)]; 134.90 [d, C_{ipso} (PMePh_2), $J_{\text{C}_{\text{ipso}}\text{-P}} = 44$ Hz]; 128.30 [d, C_o (PMePh_2), $^3J_{\text{C}_o\text{-P}} = 16$ Hz]; 130.80 [d, C_m (PMePh_2), $^4J_{\text{C}_m\text{-P}} = 11$ Hz], 131.20 [s, C_p (PMePh_2)]; 15.5 [d, $J_{\text{C}_{\text{Me}}\text{-P}} = 31$ Hz]; 190.23 [d, C 2(CO), $^2J_{\text{cis}(\text{C-P})} = 8$ Hz]; 189.75 [d, C (CO), $^2J_{\text{trans}(\text{C-P})} = 8$ Hz]. ^{31}P NMR(^1H) (CDCl_3 , 121.7 MHz): δ/ppm : 27.94 [d, (PNP), $^3J_{\text{PNP-PPh}_3} = 18$ Hz, $J_{\text{P-Se}} = 560$ Hz (satellites)]; -12.10 [t, (PMePh_2), $^3J_{\text{PNP-PPh}_3} = 20$ Hz]. ^{77}Se NMR(^1H) (CDCl_3 , 57.3 MHz): δ/ppm : -289.35 [dd, $^1J_{\text{PNP-Se}} = 560$ Hz, $^2J_{\text{PMePh}_2\text{-Se}} = 34$ Hz]. MS (*m/e*): 1013 [M^+], 985 [$\text{M}-\text{CO}^+$]; 957 [$\text{M}-2(\text{CO})^+$]; 929 [$\text{M}-3(\text{CO})^+$]; 852 [$\text{M}-3(\text{CO})-(\text{Ph})^+$]; 729 [$\text{M}-3(\text{CO})-(\text{PMePh}_2)^+$].

2.1.1.3. $[\text{Re}(\text{CO})_3(\text{PMe}_2\text{Ph})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-}\kappa^2\text{Se}\}]$ (3**).** 0.58 g (0.8 mmol) of $\text{K}[\text{N}(\text{SePPh}_2)_2]$, 0.35 g

(0.86 mmol) of $[\text{ReBr}(\text{CO})_5]$, and 0.12 g (0.86 mmol) of PMe_2Ph .

0.57 g, 0.6 mmol 70% yield; M.p. 165–170 °C. IR (KBr): $\nu(\text{CO})$ 2013s, 1918s, 1887s cm^{-1} ; $\nu(\text{P}_2\text{N})$ 1176w, 743w cm^{-1} ; $\nu(\text{PSe})$ 539m cm^{-1} . IR (CH_2Cl_2): $\nu(\text{CO})$ 2019s, 1929m, 1895m cm^{-1} . ^1H NMR (CDCl_3 , 300.5 MHz): δ/ppm : 8.06 [ddd, $\text{H}_o(\text{PNP})$, $^3J_{\text{H}_o-\text{P}} = 8$ Hz, $^3J_{\text{H}_o-\text{H}_m} = 7$ Hz, $^3J_{\text{H}_o-\text{H}_p} = 2$ Hz]; 7.30 [dt, $\text{H}_p(\text{PNP})$, $^3J_{\text{H}_p-\text{H}_m} = 8$ Hz, $^4J_{\text{H}_p-\text{H}_o} = 2$ Hz]; 7.20 [dt, $\text{H}_m(\text{PNP})$, $^3J_{\text{H}_m-\text{H}_p} = 8$ Hz, $^3J_{\text{H}_m-\text{H}_o} = 7$ Hz, $^4J_{\text{H}_m-\text{P}} = 2$ Hz]; 7.38–7.60 [m, aromatic protons PMe_2Ph]; 2.33 [d, $\text{Me}(\text{PMe}_2\text{Ph})$, $^2J_{\text{H}-\text{P}} = 8$ Hz]; 1.76 [dd, $\text{Me}(\text{PMe}_2\text{Ph})$, $^2J_{\text{H}-\text{P}} = 8$ Hz, $^2J_{\text{H}-\text{H}} = 25$ Hz]. ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 75.6 MHz): δ/ppm : 136.90 [dd, C_{ipso} (PNP), $J_{C_{\text{ipso}}-\text{P}} = 105$ Hz, $^3J_{C_{\text{ipso}}-\text{P}} = 8$ Hz]; 127.90 [d, C_o (PNP), $^3J_{C_o-\text{P}} = 14$ Hz]; 131.40 [d, C_m (PNP), $^4J_{C_m-\text{P}} = 13$ Hz]; 129.66 [s, C_p (PNP)]; 138.2 [d, C_{ipso} (PMe_2Ph), $J_{C_{\text{ipso}}-\text{P}} = 97$ Hz]; 128.24 [d, C_o (PMe_2Ph), $^3J_{C_o-\text{P}} = 14$ Hz]; 130.74 [d, C_m (PMe_2Ph), $^4J_{C_m-\text{P}} = 12$ Hz]; 131.20 [s, C_p (PMe_2Ph)]; 15.20 [d, $\text{Me}(\text{PMe}_2\text{Ph})$, $J_{C_{\text{Me}}-\text{P}} = 31$ Hz]; 189.93 [d, C 2(CO), $^2J_{\text{cis}(\text{C}-\text{P})} = 8$ Hz]; 190.17 [d, C (CO), $^2J_{\text{trans}(\text{C}-\text{P})} = 8$ Hz]. ^{31}P NMR $\{^1\text{H}\}$ (CDCl_3 , 121.7 MHz): δ/ppm : 27.56 [d, (PNP), $^3J_{\text{PNP}-\text{PPh}_3} = 21$ Hz, $J_{\text{P}-\text{Se}} = 562$ Hz (satellites)]; -30.22 [t, (PMePh_2), $^3J_{\text{PNP}-\text{PPh}_3} = 21$ Hz]. ^{77}Se NMR $\{^1\text{H}\}$ (CDCl_3 , 57.3 MHz): δ/ppm : -298.25 [dd, $^1J_{\text{PNP}-\text{Se}} = 562$ Hz, $^2J_{\text{PMePh}_2-\text{Se}} = 36$ Hz]. MS (m/e): 951 [M^+]; 895 [$\text{M}-2(\text{CO})^+$]; 867 [$\text{M}-3(\text{CO})^+$]; 790 [$\text{M}-3(\text{CO})-(\text{Ph})^+$]; 729 [$\text{M}-3(\text{CO})-(\text{PMePh}_2)^+$].

2.1.1.4. Reaction of $\text{K}[\text{N}(\text{SePPh}_2)_2]$, $[\text{ReBr}(\text{CO})_5]$, and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. $\text{K}[\text{N}(\text{SePPh}_2)_2]$ (0.2 g, 0.34 mmol), $[\text{ReBr}(\text{CO})_5]$ (0.14 g, 0.34 mmol) and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (0.14 g, 0.34 mmol) were added to a 100 mL round bottom flask containing 70 mL of dry toluene. After 5 h under reflux the solvent was removed under reduced pressure leaving an off-white material. The product was washed with dry hexane (2×15 mL) and dissolved in dichloromethane to filter off KBr. Complexes **4** and **5** were obtained as a mixture being the latter the major product. Both **4** and **5** could be obtained, independently, as main products by Method **B** (see below).

2.1.2. Method B

In a 100 mL round bottom flask with 70 mL of dry toluene $\text{K}[\text{N}(\text{SePPh}_2)_2]$ was added (0.58 g, 0.8 mmol) with 0.41 g (1.0 mmol) of $[\text{ReBr}(\text{CO})_5]$; the reaction mixture was stirred and set to reflux temperature. The reaction was carefully monitored by IR spectroscopy. Once the complex was detected as the only product (20 min) the reaction was allowed to stand at room temperature (25 °C) for around 10 min. PPh_3 (0.18 g, 0.7 mmol) was added to the reaction mixture and set to toluene reflux temperature for 1.5 h. The solvent was evaporated to dryness under reduced pressure leaving a whitish powder. Addition of 25 mL of dichloromethane allowed separation of KBr by filtration. The solvent was reduced under vacuum and crystallization from a mixture of hexane/dichloromethane afforded complex **1** in 90% yield (0.67 g, 0.62 mmol).

Synthesis of $[\text{Re}_2(\text{CO})_6\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}_2-(\mu-\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ (**4**)

In a 100 mL round bottom flask with 70 mL of dry toluene $\text{K}[\text{N}(\text{SePPh}_2)_2]$ was added (0.2 g, 0.34 mmol) with 0.14 g (0.33 mmol) of $[\text{ReBr}(\text{CO})_5]$; the reaction mixture was stirred and set at 82–85 °C. The reaction was carefully monitored by IR spectroscopy. Once the complex $[\text{Re}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$ was detected as the only product (20 min) the reaction was allowed to stand at room temperature (25 °C) for around 10 min. An equimolar amount of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ was added to the reaction mixture and set to toluene reflux temperature for 5 h. An off-white powder was obtained after the solvent was taken away under reduced pressure. Addition of 25 mL of dichloromethane allowed removal of KBr by filtration. The solvent was reduced under vacuum and crystallization from a mixture of hexane/dichloromethane afforded complex **4** in 70% yield and m.p. 200–205 °C. IR (KBr): $\nu(\text{CO})$ 2017s, 1929s, 1895s cm^{-1} ; $\nu(\text{P}_2\text{N})$ 1181w, 744w cm^{-1} ; $\nu(\text{PSe})$ 539m cm^{-1} . IR (CHCl_3): $\nu(\text{CO})$ 2020s, 1936 m, 1904m cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ/ppm : 7.90 [ddd, $\text{H}_o(\text{PNP})$, $^3J_{\text{H}_o-\text{P}} = 7$ Hz, $^3J_{\text{H}_o-\text{H}_m} = 3$ Hz, $^3J_{\text{H}_o-\text{H}_p} = 2$ Hz]; 7.10 [dt, $\text{H}_m(\text{PNP})$, $^3J_{\text{H}_p-\text{H}_m} = 7$ Hz, $^4J_{\text{H}_p-\text{H}_o} = 3$ Hz]; 7.43–7.32 [m, aromatic protons $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ and H_p of PNP]; 2.70 [dd, $\text{H}_{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2}$, $^3J_{\text{H}-\text{H}_{\text{cis}}} = 8$ Hz, $^3J_{\text{H}-\text{H}_{\text{trans}}} = 12$ Hz]. ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 75.6 MHz): δ/ppm : 133.50 [d, C_{ipso} (PNP), $J_{C_{\text{ipso}}-\text{P}} = 90$ Hz]; 128.10 [d, C_o (PNP), $^3J_{C_o-\text{P}} = 15$ Hz]; 133.30 [d, C_m (PNP), $^4J_{C_m-\text{P}} = 11$ Hz]; 131.10 [s, C_p (PNP)]; 133.40 [d, C_{ipso} ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), $J_{C_{\text{ipso}}-\text{P}} = 45$ Hz]; 127.60 [d, C_o ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), $^3J_{C_o-\text{P}} = 14$ Hz]; 131.40 [d, C_m ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), $^4J_{C_m-\text{P}} = 11$ Hz]; 130.90 [s, C_p ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$)]. ^{31}P NMR $\{^1\text{H}\}$ (CDCl_3 , 121.7 MHz): δ/ppm : 28.30 [d, (PNP), $^3J_{\text{PNP}-\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2} = 21$ Hz]; 3.10 [broad s (linewidth = 48 Hz), ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$)].

Complex $[\text{Re}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2-\kappa^2\text{P})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa\text{Se}\}]$ (**5**), was obtained in the same manner as **4** with half equimolar amount of added phosphine (0.07 g, 0.17 mmol) and a shorter reflux time (30 min). **5** was isolated in 50% yield; M.p. 207–210 °C. IR (KBr): $\nu(\text{CO})$ 2024s, 1949s, 1912s cm^{-1} ; $\nu(\text{P}_2\text{N})$ 1181w, 739 w cm^{-1} ; $\nu(\text{PSe})$ 536m cm^{-1} . IR (CHCl_3): $\nu(\text{CO})$ 2035s, 1964 m, 1918 m cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ/ppm : 7.80 [ddd, $\text{H}_o(\text{PNP}_{\text{coord.}})$, $^3J_{\text{H}_o-\text{H}_m} = 7$ Hz, $^3J_{\text{H}_o-\text{P}} = 3$ Hz, $^3J_{\text{H}_o-\text{H}_p} = 2$ Hz]; 7.60 [ddd, $\text{H}_o(\text{PNP}_{\text{decoord.}})$, $^3J_{\text{H}_o-\text{H}_m} = 13$ Hz, $^3J_{\text{H}_o-\text{P}} = 4$ Hz, $^3J_{\text{H}_o-\text{H}_p} = 2$ Hz]; 7.1 [dt, $\text{H}_m(\text{PNP})$, $^3J_{\text{H}_m-\text{H}_p} = 7$ Hz, $^3J_{\text{H}_m-\text{H}_o} = 7$ Hz, $^4J_{\text{H}_m-\text{P}} = 3$ Hz]; 7.55–7.15 [m, aromatic protons $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$]. ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 75.6 MHz): δ/ppm : 136.00 [d, C_{ipso} ($\text{PNP}_{\text{coord.}}$), $J_{C_{\text{ipso}}-\text{P}} = 90$ Hz]; 127.30 [d, C_o ($\text{PNP}_{\text{coord.}}$), $^3J_{C_o-\text{P}} = 10$ Hz]; 132.40 [d, C_m ($\text{PNP}_{\text{coord.}}$), $^4J_{C_m-\text{P}} = 12$ Hz]; 130.40 [s, C_p ($\text{PNP}_{\text{coord.}}$)]; 141.20 [d, C_{ipso} ($\text{PNP}_{\text{decoord.}}$), $J_{C_{\text{ipso}}-\text{P}} = 96$ Hz]; 128.70 [d, C_o ($\text{PNP}_{\text{decoord.}}$), $^3J_{C_o-\text{P}} = 10$ Hz]; 132.80 [d, C_m ($\text{PNP}_{\text{decoord.}}$), $^4J_{C_m-\text{P}} = 12$ Hz]; 130.80 [s, C_p ($\text{PNP}_{\text{decoord.}}$)]; 133.60 [d, C_{ipso} ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), $J_{C_{\text{ipso}}-\text{P}} = 46$ Hz]; 127.20 [d, C_o ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$)],

$^3J_{C_{\alpha}-P} = 4$ Hz]; 131.90 [d, C_m ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), $^4J_{C_m-P} = 11$ Hz], 129.10 [s, C_p ($\text{Ph}_2\text{-PCH}_2\text{CH}_2\text{PPh}_2$); 191.23 [d, C (CO), $^2J_{\text{trans}(C-P)} = 9$ Hz]; 190.46 [d, C (CO), $^2J_{\text{trans}(C-P)} = 9$ Hz]; 188.45 [d, C (CO), $^2J_{\text{cis}(C-P)} = 7$ Hz]. ^{31}P NMR{ ^1H } (CDCl_3 , 121.7 MHz): δ/ppm : 32.80 [d, ($\text{PNP}_{\text{decoord.}}$), $^3J_{\text{PNP-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2} = 17$ Hz]; 26.10 [d, ($\text{PNP}_{\text{coord.}}$), $^3J_{\text{PNP-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2} = 17$ Hz]; 26.90 [d, ($\text{Ph}_2\text{-PCH}_2\text{CH}_2\text{PPh}_2$), $^3J_{\text{PNP-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2} = 17$ Hz]. MS (m/e): 1211 [M^+]; 1155 [$\text{M}-(\text{CO})^+$]; 1127 [$\text{M}-2(\text{CO})^+$]; 669 [$\text{M}-\text{PNP}^+$]; 641 [$\text{M}-\text{PNP}-(\text{CO})^+$]; 585 [$\text{M}-\text{PNP}-3(\text{CO})^+$].

2.1.3. Method C

A 100 mL round bottom flask was charged with 70 mL of dry toluene, $[\text{ReBr}(\text{CO})_5]$ (0.5 g, 1.23 mmol), and PPh_3 (0.32 g, 1.23 mmol). After 30 min at reflux temperature the phosphine substitution complex $[\text{ReBr}(\text{CO})_4\{\text{PPh}_3\}]$ was the major product detected by IR $\nu(\text{CO})$. The reaction was allowed to stand at room temperature (25 °C) for around 10 min. $\text{K}[\text{N}(\text{SePPh}_2)_2]$ (0.72 g, 1.23 mmol) was added and the reaction mixture set to reflux temperature for 30 min. Toluene was removed under reduced pressure leaving a whitish powder. KBr was filtered off from a solution of 25 mL of dichloromethane. Elimination of dichloromethane under reduced pressure and crystallization from a mixture of hexane/dichloromethane afforded complex **1** in 84% yield (1.11 g, 1.03 mmol).

2.2. Crystal data

See Tables 1–3.

2.3. Crystal structure determinations

Data for complexes **1–5** were collected at 100(2) K on a Bruker Smart Apex CCD diffractometer 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 1.994, -1.233 for **1**; 1.935, -0.923 for **1a**; 2.345, -1.658 for **2**; 1.935, -0.923 for **3**; 1.207, -1.453 for **4**; and 2.708, $-2.577 \text{ e}\text{\AA}^{-3}$ for **5**. In the case of **1** one of the CHCl_3 molecules is disordered. The C–H hydrogen atoms for this solvent have not been included. Suitable crystals of **1a** were obtained from CDCl_3 at 25 °C for several days; while crystals for **1**, **3**, and **5** were obtained from a 1:1 mixture of $\text{CHCl}_3/\text{hexane}$ at -10 °C. Adequate crystals of **2** were grown from a $\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:1 solution at 4 °C. There are two independent molecules in the asymmetric unit of complex **2**. Adequate crystals of **4** were grown from a THF solution at 4 °C. There are three THF molecules in the asymmetric unit of **4**, one of them is disordered. The molecule is located at a crystallographic special position.

3. Results and discussion

3.1. Syntheses

Complex **1**, $[\text{Re}(\text{CO})_3(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$, was prepared by three methods: in Method A $[\text{ReBr}(\text{CO})_5]$, PPh_3 , and $\text{K}[\text{N}(\text{SePPh}_2)_2]$ were reacted under toluene reflux for 30 min (see Scheme 1 for the three methods). Method B consisted in the formation of $[\text{Re}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$ [**11c**] followed by addition of PPh_3 to give **1**; the reaction time amounted to 1 h and 50 min. Preparation of $[\text{ReBr}(\text{CO})_4\{\text{PPh}_3\}]$ and subsequent reaction in situ with $\text{K}[\text{N}(\text{SePPh}_2)_2]$ constituted Method C with a total reaction time of 1 h. Reaction times were determined by IR spectroscopy monitoring in the $\nu(\text{CO})$ region.

From Scheme 1, it can be seen that the best route for the preparation of complex **1** is Method A (greatest yield and

Table 1
Crystal data for **1** and **1a**

	1	1a
Empirical formula	$\text{C}_{47.5}\text{H}_{37.5}\text{Cl}_{7.5}\text{NO}_3\text{P}_3\text{ReSe}_2$	$\text{C}_{45}\text{H}_{35}\text{NO}_3\text{P}_3\text{ReSe}_2$
M	1373.2	074.77
Temperature (K)	100(2)	100(2)
Crystal size (mm)	$0.42 \times 0.25 \times 0.21$	$0.42 \times 0.39 \times 0.06$
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	22.924(3)	9.6096(7)
b (Å)	10.354(1)	9.7098(8)
c (Å)	24.049(3)	21.298(2)
α (°)	90	92.120(1)
β (°)	116.42(1)	94.819(1)
γ (°)	90	93.196(1)
V (Å ³)	5112.4(10)	1975.5(3)
Z	4	2
θ Range for data collection (°)	1.70–25.00	1.92–25.00
Reflections collected	25 784	19 060
Independent reflections (R_{int})	8794 (0.0419)	6945 (0.0535)
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0407$, $wR_2 = 0.0984$	$R_1 = 0.0366$, $wR_2 = 0.0850$
R indices (all data)	$R_1 = 0.0463$, $wR_2 = 0.1012$	$R_1 = 0.0401$, $wR_2 = 0.0872$

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

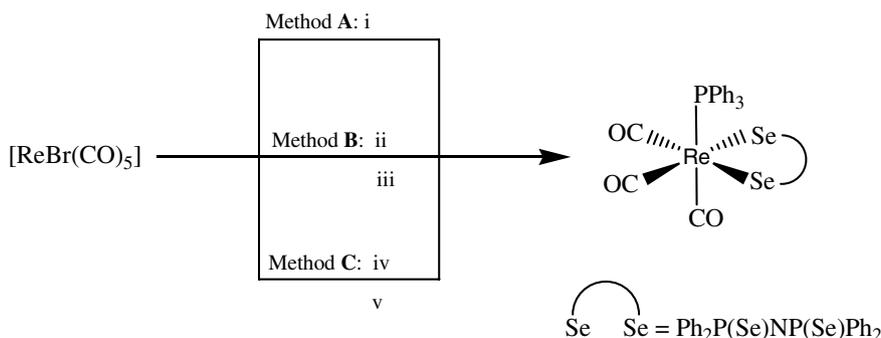
	2	3
Empirical formula	C ₄₀ H ₃₃ NO ₃ P ₃ ReSe ₂	C ₃₅ H ₃₁ NO ₃ P ₃ ReSe ₂ · CHCl ₃
<i>M</i>	1012.7	1070.1
Temperature (K)	100(2)	100(2)
Crystal size (mm)	0.37 × 0.31 × 0.26	0.42 × 0.36 × 0.24
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	22.815(2)	10.500(1)
<i>b</i> (Å)	17.082(1)	17.058(2)
<i>c</i> (Å)	24.623(2)	22.056(3)
β (°)	110.763(1)	102.676(2)
<i>V</i> (Å ³)	7515.3(11)	3854.1(8)
<i>Z</i>	8	4
θ Range for data collection (°)	1.53–26.00	1.52–25.00
Reflections collected	77 313	36 043
Independent reflections (<i>R</i> _{int})	14 748 (0.0823)	6798 (0.0548)
Final <i>R</i> indices [<i>F</i> ² > 2σ(<i>F</i> ²)]	<i>R</i> ₁ = 0.0524, <i>wR</i> ₂ = 0.1030	<i>R</i> ₁ = 0.0315, <i>wR</i> ₂ = 0.0767
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0676, <i>wR</i> ₂ = 0.1094	<i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0780

Table 3
Crystal data for **4** and **5**

	4	5
Empirical formula	C ₈₀ H ₆₄ N ₂ O ₆ P ₆ Re ₂ Se ₄ · 6THF	C ₅₃ H ₄₄ NO ₃ P ₄ ReSe ₂ · CHCl ₃
<i>M</i>	2456.02	1330.26
Temperature (K)	100(2)	100(2)
Crystal size (mm)	0.24 × 0.22 × 0.18	0.36 × 0.42 × 0.48
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.0339(7)	11.1159(7)
<i>b</i> (Å)	26.733(2)	13.1897(8)
<i>c</i> (Å)	17.183(1)	18.363(1)
α (°)		87.265(1)
β (°)	94.045(1)	87.644(1)
γ (°)		86.650(1)
<i>V</i> (Å ³)	5055.7(5)	3854.1(8)
<i>Z</i>	2	2
θ Range for data collection (°)	1.41–25.00	1.55–25.00
Reflections collected	24 359	25 692
Independent reflections (<i>R</i> _{int})	8842 (0.0541)	9404 (0.0392)
Final <i>R</i> indices [<i>F</i> ² > 2σ(<i>F</i> ²)]	<i>R</i> ₁ = 0.0506, <i>wR</i> ₂ = 0.0957	<i>R</i> ₁ = 0.0477, <i>wR</i> ₂ = 0.1322
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0654, <i>wR</i> ₂ = 0.1011	<i>R</i> ₁ = 0.0505, <i>wR</i> ₂ = 0.1343

shortest reaction time). Similar results were obtained with PMePh₂ and PMe₂Ph. The complexes here reported are stable in the solid state and no decomposition was observed after several days in solution.

In an attempt to prepare the *spiro* complex [Re(CO)₂(Ph₂PCH₂CH₂PPh₂-κ²P){Ph₂P(Se)NP(Se)Ph₂-κ²Se}] we carried out the reaction shown in Eq. (1) in equimolar amounts



Scheme 1. All reactions' steps were conducted under toluene reflux. (i) K[N(SePPh₂)₂], PPh₃, 30 min, 98% yield. (ii) K[N(SePPh₂)₂], 20 min. (iii) PPh₃, 1 h, 90% yield. (iv) PPh₃, 30 min. (v) K[N(SePPh₂)₂], 30 min, 84% yield.



After 5 h of reaction a mixture of complexes **4** and **5** was detected being **5** the major product. Complex **4** could be prepared with 70% yield starting from $[\text{Re}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}]$ and an equimolar amount of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ under toluene reflux for 5 h (Method B). Complex $[\text{Re}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\kappa^2\text{P})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa\text{Se}\}]$, **5**, was obtained in 50% yield when half the equimolar amount of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ was added to a toluene solution of $[\text{Re}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}]$ and set to reflux for 30 min. These results contrast with the reactivity of $[\text{Mn}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}]$ with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, where the complex *spiro*- $[\text{Mn}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\kappa^2\text{P})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}]$ was isolated with 74% using equimolar amounts of the starting materials [11a]. The impossibility of elimination of one CO group by the Se atom in **5** precludes the formation of *spiro*- $[\text{Re}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\kappa^2\text{P})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}]$. So far no manganese analogs of **4** or **5** are known; although the manganese analog of **4** has been proposed as an intermediate to *spiro*- $[\text{Mn}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\kappa^2\text{P})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}]$ [11a].

3.2. Infrared spectroscopy

Complexes **1–3** and **5** present three bands (in solution) in the $\nu(\text{CO})$ carbonyl region corresponding to the $2A' + A''$ vibration modes [24] 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. In the case of **1–3** both selenium atoms of the PNP ligand bind to the metal center; while in **5** the PNP ligand is attached to the rhenium by only one selenium atom. The IR spectrum of **4** shows three carbonyl bands (2020s, 1936s, and 1904m cm^{-1} in CHCl_3) arising from a *fac* arrangement at each metal center of the dinuclear complex. A comparison of the IR carbonyl band frequencies between **4** and **5** (2035s, 1964s, and 1918m cm^{-1} in CHCl_3) shows a greater electron density at the metal center of **4**. This can be accounted for by a stronger π acidity of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ with respect to the PNP ligand and/or a stronger σ donor capacity of the latter.

The $\nu(\text{PSe})$ vibration in $(\text{H}[\text{N}(\text{SePPh}_2)_2])$ appears at 595 and 546 cm^{-1} in KBr [2]; in complexes **1–5** the corresponding band appears between 536 and 539 cm^{-1} . Complex **5** shows at 553 cm^{-1} a band arising from the non coordinated $\text{P}=\text{Se}$ moiety.

3.3. NMR spectroscopy

Complexes **1–3** show symmetrical coordination of the $\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2$ ligand in solution as evidenced by the appearance of one signal in ^{31}P and ^{77}Se NMR spectra. The ^{77}Se NMR chemical shifts do not show any trend; it is expected that accumulation of more ^{77}Se NMR data will unfold the governing effects on the chemical shifts in these systems. Notwithstanding, we note that ^{77}Se NMR not only reflects the symmetry in complexes **1–3**, but also gave insight into the interaction of the P–Se atoms through the $^1J_{\text{P-Se}}$ coupling constants (Table 4).

The P–Se coupling constant values vary in the order $[\text{Re}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}] < \mathbf{1} \sim \mathbf{2} \sim \mathbf{3} < \text{HN}(\text{SePPh}_2)_2$. The higher electron density at the metal center in complexes **1**, **2**, and **3** compared with $[\text{Re}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}]$ leads to a stronger interaction of the P–Se atoms in the $\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2$ ligand as evidenced by the $^1J_{\text{P-Se}}$ coupling constants. The strongest P–Se interaction is observed in the acid $\text{HN}(\text{SePPh}_2)_2$, where the selenium and phosphorus atoms are bound displaying a $^1J_{\text{P-Se}}$ of 788 Hz. Interestingly, the $^1J_{\text{P-Se}}$ coupling constants do not seem to be sensitive to the oxidation state of the metal to which the $\text{N}(\text{SePPh}_2)_2$ ligand is attached as shown in Table 4; where a set of $\text{Re}(\text{V})$ complexes exhibit similar $^1J_{\text{P-Se}}$ coupling constants to those reported in this work.

3.4. Structural studies

The geometry around the rhenium center in the complexes herein reported is slightly distorted octahedral with the carbonyl groups in *fac* disposition. The molecular structure of **1** including its atom numbering scheme is shown in Fig. 1 together with some selected bond distances and angles.

Table 4
 ^{77}Se NMR shifts and coupling constants in CDCl_3

Compound	δ (ppm)	$^1J_{\text{P-Se}}$ /Hz	Reference
$[\text{Re}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}]$	–340.1	546	[11c]
1	–276.5	559	This work
2	–289.4	560	This work
3	–298.3	561	This work
$[\text{ReO}(\text{Cl})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}_2]^{\text{a}}$	–	525	[11e]
<i>cis</i> - $\text{Re}(\text{NMe})\text{Cl}_2\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}-(\text{PPh}_3)$	–	532, 540	[11d]
$[\text{Re}(\text{NMe})\text{Cl}\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}_2]$	–	558	[11d]
$[\text{ReN}\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\kappa^2\text{Se}\}_2]$	–	547	[11d]
$\text{HN}(\text{SePPh}_2)_2$	–156.6	788	

^a In CD_2Cl_2 .

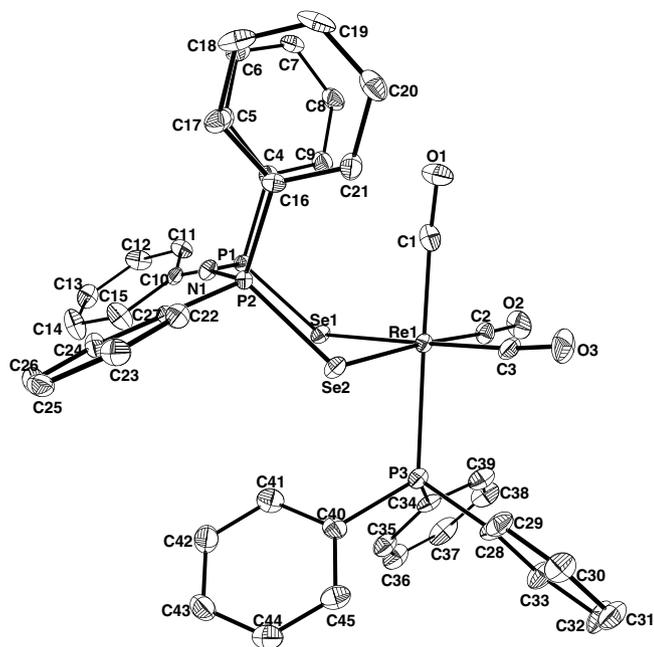


Fig. 1. Molecular structure of **1** including atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Re(1)–Se(1) 2.6382(6), Re(1)–Se(2) 2.6277(6), Se(1)–P(1) 2.193(2), P(1)–N(1) 1.594(5); P(1)–N(1)–P(2) 128.7(3), Se(1)–Re(1)–Se(2) 91.18(2), N(1)–P(1)–Se(1) 117.8(2), P(1)–Se(1)–Re(1) 105.82(4).

When complex **1** was left in CDCl_3 at 25 °C for several days, in an nmr tube, suitable crystals for the X-ray structural analysis of **1a** were obtained. The molecular structure of **1a** including its atom numbering scheme is shown in Fig. 2 together with some selected bond distances and angles.

The six-membered metallacycle SePNPSeRe in complexes **1** and **1a** differ in conformation: in **1** the ring presents a chair conformation, while in **1a** the boat conformation is observed. The nitrogen and the rhenium atoms are positioned at the apices in both rings. The change in conformation can be ascribed to the higher temperature at which crystals were grown.

The molecular structures of **2** and **3** including their atom numbering scheme are shown in Figs. 3 and 4, respectively, together with some selected bond distances and angles.

In the asymmetric unit of **2** there are two independent molecules whose structures are similar. The SePNPSeRe ring conformation in **2** can be best described as a half chair and in **3** the conformation is that of a chair. The chair conformation is shared by the dinuclear complex **4** (the molecular structure of **4** including its atom numbering scheme is shown in Fig. 5 together with some selected bond distances and angles).

The diselenoimidodiphosphinato ligand is symmetrically coordinated to Re through both selenium atoms in complexes **1**, **1a–4**; the Re–Se bond lengths are equivalent within experimental error (av. 2.6396(6) Å for complexes **1**, **1a–4**) indicating a covalent interaction ($\Sigma_{\text{cov}}(\text{Re}, \text{Se}) = 2.76 \text{ Å}$) [25]. The P–Se and P–N bond distances in the SePNPSe backbone are also equivalent (av. P–Se and P–N:

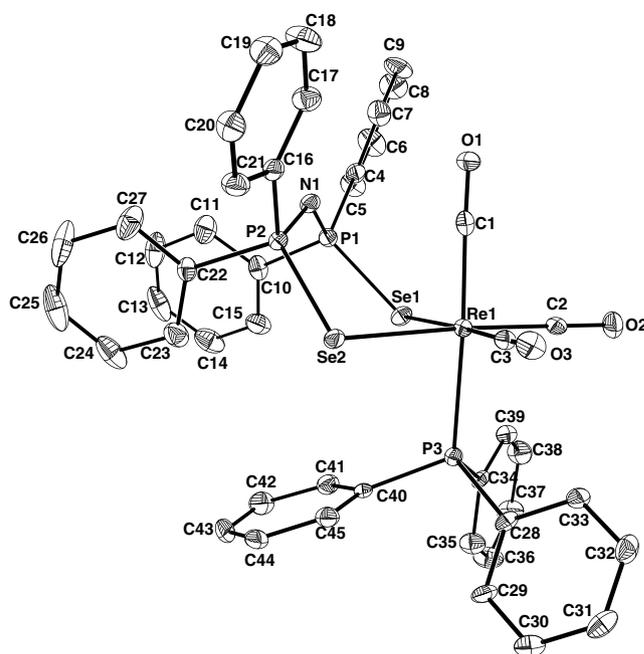


Fig. 2. Molecular structure of **1a** including atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Re(1)–Se(1) 2.6403(5), Re(1)–Se(2) 2.6318(5), Se(1)–P(1) 2.174(1), P(1)–N(1) 1.590(4); P(1)–N(1)–P(2) 133.6(3), Se(1)–Re(1)–Se(2) 95.15(2), N(1)–P(1)–Se(1) 119.8(2), P(1)–Se(1)–Re(1) 106.06(4).

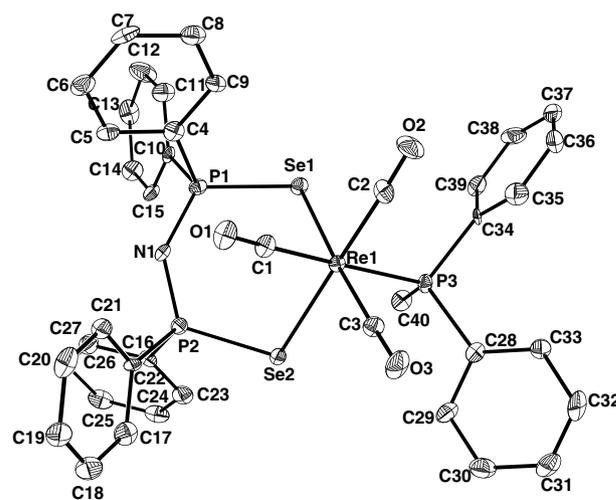


Fig. 3. Molecular structure of **2** including atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Re(1)–Se(1) 2.6386(7), Re(1)–Se(2) 2.6451(7), Se(1)–P(1) 2.171(2), P(1)–N(1) 1.594(6); P(1)–N(1)–P(2) 138.4(4), Se(1)–Re(1)–Se(2) 88.43(2), N(1)–P(1)–Se(1) 119.1(2), P(1)–Se(1)–Re(1) 99.98(5).

2.175(1) and 1.592(5) Å in complexes **1**, **1a–4**). In $\text{Ph}_2\text{P}(\text{Se})\text{NHP}(\text{Se})\text{Ph}_2$ 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 lengthening of both –P–Se bond distances as well as the shortening of both P–N bond distances in complexes **1**, **1a–4** are indicative of electron delocalization over the $\text{ReSe}_2\text{P}_2\text{N}$ metallacycle. The difference in the PNP angles attests to the flexibility of

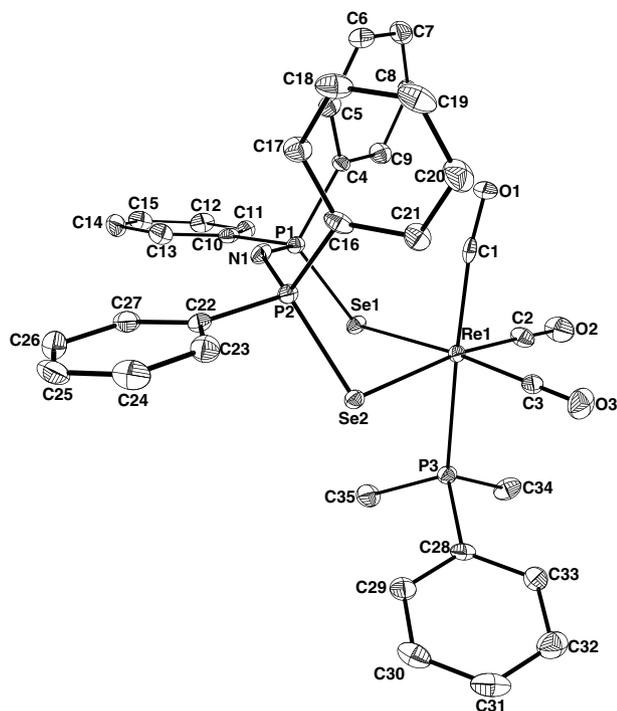


Fig. 4. Molecular structure of **3** including atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths (Å) and ($^{\circ}$): Re(1)–Se(1) 2.6485(5), Re(1)–Se(2) 2.6450(5), Se(1)–P(1) 2.180(1), P(1)–N(1) 1.598(4); P(1)–N(1)–P(2) 134.7(2), Se(1)–Re(1)–Se(2) 88.80(2), N(1)–P(1)–Se(1) 119.7(1), P(1)–Se(1)–Re(1) 102.45(3).

the SePNPSe backbone (PNP angle of **1** = 128.7(3) $^{\circ}$ and PNP angle of **2** = 138.4(4) $^{\circ}$; lowest and greatest PNP angle, respectively): from existing data no trend between PNP angle and ring conformation can be drawn.

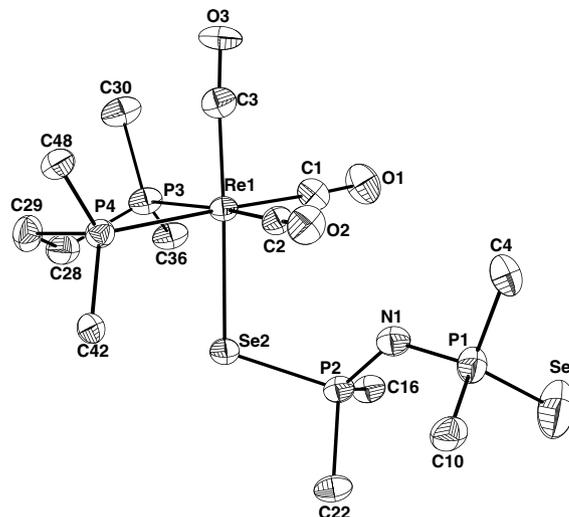


Fig. 6. Molecular structure of **5** with atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths (Å) and angles ($^{\circ}$): Re(1)–Se(2) 2.6227(7), Se(1)–P(1) 2.106(2), Se(2)–P(2) 2.180(2), P(2)–N(1) 1.579(6), N(1)–P(1) 1.601(6); P(1)–N–P(2) 130.2(4). Only *ipso* carbons are shown for clarity.

Fig. 6 shows a three dimensional representation with corresponding atom numbering scheme and some selected bond lengths and angles of complex **5**.

The inorganic selenium ligand in **5** binds in a monodentate fashion. The P–Se bond distance is shorter for the uncoordinated P–Se than for the coordinated P–Se group (2.106(2) vs. 2.180(2) Å, resp.). Bis(diphenylphosphine)ethane coordinates to build a five-membered ring. The PNP angle in complex **5** measures 130.2(4) $^{\circ}$; and is greater than the corresponding PNP angle in **1**; although in the latter

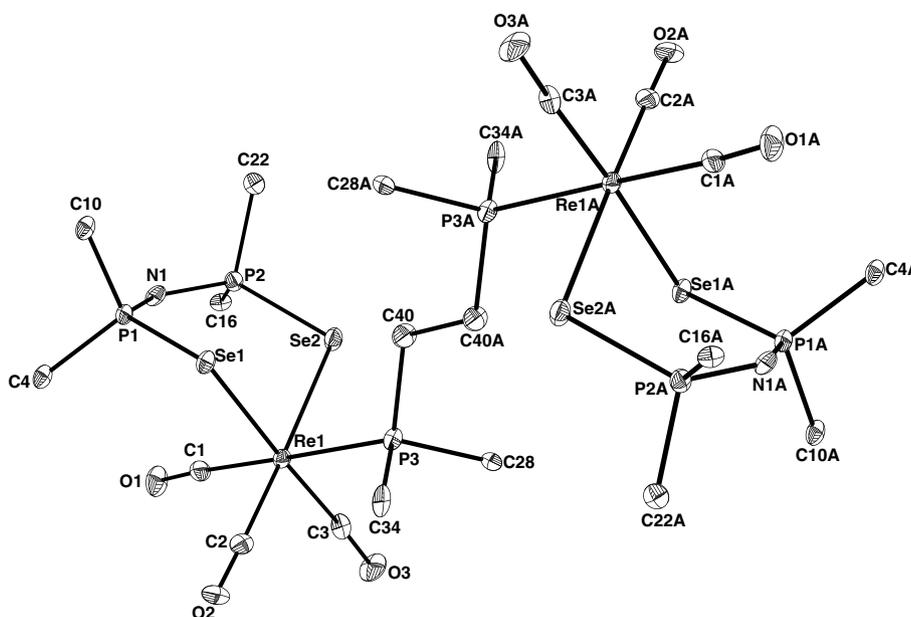


Fig. 5. Molecular structure of **4** including atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths (Å) and angles ($^{\circ}$): Re(1)–Se(1) 2.6450(7), Re(1)–Se(2) 2.6356(7), Se(1)–P(1) 2.160(2), P(1)–N(1) 1.594(5); P(1)–N(1)–P(2) 135.7(4), Se(1)–Re(1)–Se(2) 88.09(2), N(1)–P(1)–Se(1) 118.0(2), P(1)–Se(1)–Re(1) 101.12(5). Only *ipso* carbons are shown for clarity.

the inorganic ligand $N(\text{SePPh}_2)_2$ chelates to form a metallocycle.

4. Conclusions

A simple, straightforward method for the preparation of complexes of the type $[\text{Re}(\text{CO})_3(\text{PR}_3)\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2-\kappa^2\text{Se}\}]$ was found. Although an understanding of the effects governing the ^{77}Se NMR shifts in the imidodiselenodiphosphinato systems, upon coordination, is yet to be found; we could establish that the oxidation state of the rhenium atom does not influence on the magnitude of the ^{77}Se coupling constants, $^1J_{\text{P-Se}}$, in the complexes with imidodiselenodiphosphinato ligands. It was found a new ligating mode for the $\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2$ ligand (monocoordinate monometallic fashion) within the realm of imidodiselenodiphosphinato-rhenium complexes.

Supplementary material

CCDC 629243, 629244, 629245, 629246, 629247 and 629248 contain the supplementary crystallographic data for **1**, **1a**, **2**, **3**, **4** and **5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

The authors thank Messrs E. García-Ríos, L. Velasco-Ibarra, and M.N. Zavala-Segovia for technical assistance (Instituto de Química, UNAM) and Dr. Vojtech Jancik for invaluable help with some X-ray crystal structure determinations. N.Z.-V. gratefully acknowledges funding from PAPIIT (DGAPA-UNAM) through grant IN217706-2 and the CONACyT through Grant P47263-Q. M.G.-R. thanks UNAM for a postdoctoral stipend. M.R.-L. deeply acknowledges a Ph.D. stipend from CONACyT through Grant P47263-Q. L.M.-P. thanks PAPIIT (DGAPA-UNAM) for an undergraduate stipend through Grant IN217706-2.

References

- [1] (a) I. Haiduc, in: J.A. McCleverty, T.J. Meyer (Eds.), *Comprehensive Coordination Chemistry II*, Elsevier Ltd., Amsterdam, 2003, pp. 323–347; (b) C. Silvestru, J.E. Drake, *Coord. Chem. Rev.* 223 (2001) 117–216; (c) T.Q. Ly, J.D. Woollins, *Coord. Chem. Rev.* 176 (1998) 451–481; (d) P. Bhattacharyya, J.D. Woollins, *Polyhedron* 14 (1995) 3367–3388.
- [2] P. Bhattacharyya, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, *J. Chem. Soc., Dalton Trans.* (1995) 2489–2495.
- [3] V. García-Montalvo, J. Novosad, P. Kilian, J.D. Woollins, A.M.Z. Slawin, P. García y García, M. López-Cardoso, G. Espinosa-Pérez, R. Cea-Olivares, *J. Chem. Soc., Dalton Trans.* (1997) 1025–1029.
- [4] M.-A. Muñoz-Hernández, A. Singer, D.A. Atwood, R. Cea-Olivares, *J. Organomet. Chem.* 571 (1998) 15–19.
- [5] (a) K. Darwin, L.M. Gilby, P.R. Hodge, B. Piggott, *Polyhedron* 18 (1999) 3729–3733; (b) R. Cea-Olivares, V. García-Montalvo, J. Novosad, J.D. Woollins, R.A. Toscano, G. Espinosa-Pérez, *Chem. Ber.* 129 (1996) 919–923.
- [6] (a) L. Flores-Santos, R. Cea-Olivares, S. Hernández-Ortega, R.A. Toscano, V. García-Montalvo, J. Novosad, J.D. Woollins, *J. Organomet. Chem.* 544 (1997) 37–41; (b) R. Cea-Olivares, J. Novosad, J.D. Woollins, A.M.Z. Slawin, V. García-Montalvo, G. Espinosa-Pérez, P. García y García, *Chem. Commun.* (1996) 519–520.
- [7] D.J. Crouch, M. Helliwell, P. O'Brien, J.-H. Park, J. Waters, D.J. Williams, *J. Chem. Soc., Dalton Trans.* (2003) 1500–1504, In this work the selenium ligand is $[\text{iPr}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{iPr}_2]$ and the coordination mode is κ^2 .
- [8] R. Cea-Olivares, G. Canseco-Melchor, V. García-Montalvo, S. Hernández-Ortega, J. Novosad, *Eur. J. Inorg. Chem.* (1998) 1573–1576.
- [9] J. Novosad, S.V. Lindeman, J. Marek, J.D. Woollins, *St. Husebye, Heteroatom Chem.* 9 (1998) 615–621.
- [10] V. Béreau, P. Sekar, C.C. McLauchlan, J.A. Ibers, *Inorg. Chim. Acta* 308 (2000) 91–96.
- [11] (a) J.M. Germán-Acacio, M. Reyes-Lezama, N. Zúñiga-Villarreal, *J. Organomet. Chem.* 691 (2006) 3223–3231; (b) D. Maganas, S.S. Staniland, A. Grigoropoulos, F. White, S. Parsons, N. Robertson, P. Kyritsis, G. Pneumatikakis, *Dalton Trans.* (2006) 2301–2315; (c) N. Zúñiga-Villarreal, J.M. Germán-Acacio, A.A. Lemus-Santana, M. Reyes-Lezama, R.A. Toscano, *J. Organomet. Chem.* 689 (2004) 2827–2832; (d) R. Rossi, A. Marchi, L. Marvell, L. Magon, M. Peruzzini, U. Casellato, R. Graziani, *J. Chem. Soc., Dalton Trans.* (1993) 723–729; (e) R. Rossi, A. Marchi, L. Marvelli, M. Peruzzini, U. Casellato, R. Graziani, *J. Chem. Soc., Dalton Trans.* (1992) 435–437.
- [12] (a) W.-H. Leung, K.-K. Lau, Q.-F. Zhang, W.-T. Wong, B. Tang, *Organometallics* 19 (2000) 2084–2089; (b) M. Valderrama, R. Contreras, M.P. Lamata, F. Viguri, D. Carmona, F.J. Lahoz, S. Elipe, L.A. Oro, *J. Organomet. Chem.* 607 (2000) 3–11; (c) P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, *J. Chem. Soc., Dalton Trans.* (1998) 2467–2475.
- [13] (a) J. Parr, M.B. Smith, M.R.J. Elsegood, *J. Organomet. Chem.* 664 (2002) 85–93; (b) Q.-F. Zhang, K.-K. Lau, J.L.C. Chim, T.K.T. Wong, W.-T. Wong, I.D. Williams, W.-H. Leung, *J. Chem. Soc., Dalton Trans.* (2000) 3027–3033.
- [14] J. Novosad, M. Necas, J. Marek, P. Veltsistas, Ch. Papadimitriou, I. Haiduc, M. Watanabe, J.D. Woollins, *Inorg. Chim. Acta* 290 (1999) 256–260.
- [15] (a) M.-K. Lau, K.-M. Cheung, Q.-F. Zhang, Y. Song, W.-T. Wong, I.D. Williams, W.-H. Leung, *J. Organomet. Chem.* 689 (2004) 2401–2410; (b) J. Parr, M.B. Smith, A.M.Z. Slawin, *J. Organomet. Chem.* 588 (1999) 99–106.
- [16] C. Papadimitriou, P. Veltsistas, J. Novosad, R. Cea-Olivares, A. Toscano, P. García y García, M. López-Cardoso, A.M.Z. Slawin, J.D. Woollins, *Polyhedron* 16 (1997) 2727–2729.
- [17] P. Bhattacharyya, J. Novosad, J. Phillips, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, *J. Chem. Soc., Dalton Trans.* (1995) 1607–1613.
- [18] (a) H. Liu, N.A.G. Bandeira, M.J. Calhorda, M.G.B. Drew, V. Félix, J. Novosad, F. Fabrizi de Biani, P. Zanello, *J. Organomet. Chem.* 689 (2004) 2808–2819; (b) S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, A. Silvestru, C. Silvestru, *Inorg. Chim. Acta* 347 (2003) 16–22; (c) J.D.E.T. Wilton-Ely, A. Schier, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* (2001) 3647–3651; (d) J.D.E.T. Wilton-Ely, A. Schier, H. Schmidbaur, *Inorg. Chem.* 40 (2001) 4656–4661;

- (e) A.M.Z. Slawin, M.B. Smith, J.D. Woollins, *Polyhedron* 18 (1999) 1135–1140.
- [19] (a) C.G. Pernin, J.A. Ibers, *Inorg. Chem.* 39 (2000) 1222–1226;
(b) C.G. Pernin, J.A. Ibers, *Inorg. Chem.* 38 (1999) 5478–5483.
- [20] C.G. Pernin, J.A. Ibers, *Inorg. Chem.* 39 (2000) 1216–1221.
- [21] M. Geissinger, J. Magull, *Z. Anorg. Allg. Chem.* 623 (1997) 755–761.
- [22] (a) A.A. Lemus-Santana, M. Reyes-Lezama, N. Zúñiga-Villarreal, R.A. Toscano, G. Espinosa-Pérez, *Organometallics* 25 (2006) 1857–1860;
(b) N. Zúñiga-Villarreal, M. Reyes-Lezama, G. Espinosa-Pérez, *J. Organomet. Chem.* 645 (2002) 54–58;
(c) N. Zúñiga-Villarreal, M. Reyes-Lezama, G. Espinosa-Pérez, *Anal. Sci.* 18 (2002) 611–612;
- (d) N. Zúñiga-Villarreal, M. Reyes-Lezama, G. Espinosa, *J. Organomet. Chem.* 626 (2001) 113–117;
- (e) N. Zúñiga-Villarreal, M. Reyes-Lezama, S. Hernández-Ortega, C. Silvestru, *Polyhedron* 17 (1998) 2679–2685;
- (f) N. Zúñiga-Villarreal, C. Silvestru, M. Reyes-Lezama, S. Hernández-Ortega, C. Alvarez Toledano, *J. Organomet. Chem.* 496 (1995) 169–174.
- [23] F.T. Wang, J. Najdzionek, K.L. Leneker, H. Wasserman, D. Braitsch, *Synth. React. Inorg. Met.-Org. Chem.* 8 (1978) 119–125.
- [24] L.E. Orgel, *Inorg. Chem.* 1 (1962) 25–29.
- [25] For the covalent radius of selenium see: J.E. Huheey, E.A. Keiter, R.L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, HarperCollins College, New York, 1993, p. 292, The empirical covalent radius of rhenium is 1.59 Å.