Synthesis, Characterization and Coordination Chemistry of Some Selenium-Containing Macrocyclic Schiff Bases

Arunashree Panda,[a] Saija C. Menon,[a] Harkesh B. Singh,*[a] Christopher P. Morley,[b] Robert Bachman,[c] T. Matthew Cocker,[c] and Ray J. Butcher[d]

Keywords: Macrocycles / Selena-aza macrocycles / Palladium / Nickel / Cobalt

The condensation of bis(*o*-formylphenyl) selenide with 1,2-diaminoethane or 1,3-diaminopropane yielded the new macrocyclic ligands **1** and **2** in very good yields. Crystals of **1** are monoclinic, space group $P2_1/c$ with $a = 10.0648(10)$ Å, $b = 37.390(4)$ Å, $c = 8.0073(11)$ Å, Z = 4 and those of **2** are triclinic, space group $P\bar{1}$ with $a = 7.200(3)$, $b = 9.137(3)$, $c = 12.780(6)$ Å, Z = 1. The coordination chemistry of **1** and **2** has been studied with the "soft" metal ion Pd^{II} and "hard" metal ions Ni^{II} and Co^{II}. Reaction of $[PdCl_2(COD)]$ with 1 mol-equiv. of **1** or **2** in refluxing methanol and addition of NH_4PF_6 afforded the Pd^{II} complexes **5** and **6**, respectively. Compound **5** is an unexpected partially hydrolyzed complex. It crystallizes in the tetragonal space group $P4_12_12$ with $a = 10.7737(10)$ Å, $b = 10.7737(10)$ Å, $c = 28.190(5)$ Å, Z = 4. The structure shows the Pd^{II} ion coordinated to a square-planar arrangement of two selenium and two nitrogen atoms. Reaction of $NiCl_2{\cdot}6H_2O$ with **1** or **2** and NH_4PF_6 yielded complexes **7** and **8**, respectively. The assignment of octahedral geometries to $[Ni(L)](PF_6)_2]$ (**7**: L = **1**; **8**: L = **2**) follows from their paramagnetism [$\mu_{\mathrm{eff}} = 3.23$ (**7**), 1.81 (**8**) B.M.] and their UV/Vis spectra. This was also confirmed by single-crystal X-ray studies. The crystal structures of **7** and **8** showed a distorted octahedral nickel center coordinated by two selenium and four nitrogen atoms. **7**: Monoclinic, space group $P2_1/c$; $a = 9.979(2)$ Å, $b = 18.901(4)$ Å, $c = 19.333(4)$ Å; Z = 4. **8**:Orthorhombic, space group $Pna2_1$; $a = 20.277(5)$, $b = 20.865(5)$, $c = 9.416(2)$ Å; Z = 4. The cyclic voltammograms of **7** and **8** in MeCN solution show well-behaved quasi-reversible Ni^{III}/Ni^{II} couples. The analogous Co^{II} complex, $[Co(\mathbf{1})](PF_6)_2]$ (**9**) also shows a quasi-reversible Co^{III}/Co^{II} couple.

Introduction

Currently, a great deal of attention is being focused on macrocyclic ligands because they play an important role in many aspects of chemistry, medicine and the chemical industry.[1] The contrast-enhancing properties of their lanthanide complexes in NMR imaging,[2] their suitability as antibiotics in radioimmunotherapy,[2] their high selectivity in the binding of metal ions,[1,2] and nucleotide bases,[3] and their unique structural features as spacers for crystal engineering[4] are some of the notable applications. In seeking optimum efficiency in their existing and potential applications, numerous macrocyclic ligands with a wide spectrum of electronic and structural features have been designed and synthesized. To date, the majority of these synthetic cyclic ligands contain oxygen,[5] nitrogen,[6] phosphorus[7] and sulfur[8] donor atoms.

The chemical and structural features of macrocyclic metal complexes can be tuned by incorporating different "soft" and "hard" donor atoms in the chelating ring, thereby promoting the stabilization of both low and high oxidation states of the metal center, as well as forcing metal ions to adopt an atypical coordination geometry. In this context, thia[8] and mixed aza-thia[9] crown ethers have been the subject of intense interest in the last few years, particularly as their complexes are useful model compounds for biological systems.[10]

Pinto and co-workers pioneered work on the synthesis of the cyclic selenium ligands. They have reported a series of selena crowns, including $[14]aneSe_4$, $[16]aneSe_4$, and $[24]aneSe_4$.[11] The Pd^{II} complex $[Pd([16]aneSe_4)]^{2+}$ has been shown to possess the *c*,*c*,*c* configuration by Pinto et al.[12] They have also reported the complexes of Cu^I and Cu^{II} with $[16]aneSe_4$ and some new selenium-containing coronands.[13] Reid et al. have reported complexes with a variety of platinum metal centers, viz. $[M([16]aneSe_4)]^{2+}$ (M = Pd or Pt),[14] $[PtX_2([16]aneSe_4)]^+$ (X = Cl, Br),[15] $[MX_2([16]aneSe_4)]^+$ (M = Rh or Ir),[16,17] $[RuX_2([16]aneSe_4)]^{n+}$ ($n = 0$ or 1), and $[MX(PPh_3)([16]aneSe_4)]^+$ (M = Ru or Os).[18] There are limited examples on Ni^{II}[19] and Co^{II}[17] complexes of these selenoethers. Reid et al. have also reported a range of complexes of Cr,[20] Mo, W, Mn, Re Cu, Ag and

---

[a] Department of Chemistry, Indian Institute of Technology,
Powai, Bombay 400076, India
Fax: +91-22-2572-3480
E-mail: chhbsia@chem.iitb.ac.in
[b] Department of Chemistry, University of Wales Swansea,
Singleton Park, Swansea, SA2 8PP, UK
[c] Department of Chemistry, Georgetown University,
Washington DC 20057, USA
[d] Department of Chemistry, Howard University,
Washington DC 20059 USA

DOI: 10.1002/ejic.200400757

Au involving [8]aneSe_2(1,5-diselenacyclooctane), 1,6-diselena-3,4-benzocyclononane, and [16]aneSe_4,[21,22] The main group metal complexation of these selenoethers are only reported for As^{III}, Sb^{III} and Bi^{III}.[23] Recently, Levason et al. have developed some mixed donor selenoether and telluroether macrocyclic ligands and studied their complexation property towards various metal ions.[24]

Cyclic polyselenoethers have also been prepared and their extraction abilities towards transition metal and heavy metal cations determined.[25] The first host molecule containing an Se–Se bond has been synthesized by Tomoda et al.[26] Muralidharan et al. have described a selenium-containing cyclophane and also studied its complexation.[27] Another novel tetraselenide macrocycle has been synthesized by Furukawa and co-workers.[28] Polyselenoether macrocycles have also been synthesized from 3,3-dimethylselenatane which is cyclooligomerized catalytically at 115 °C in the presence of $[Re_2(CO)_9(SeCH_2CMe_2CH_2)]$.[29] Jackson and co-workers have designed and synthesized a novel macrobicyclic cage incorporating N/Se (N_3Se_3) atoms and its Co^{III} complex.[30] Meunier et al. have reported the synthesis of a diselena crown ether[31] and tetraselena crown ethers of three different sizes incorporating several oxygen atoms in the bridge.[32] The complexation of these selenoethers has been achieved by their reaction with mercury(II) iodide. Very recently, they have reported the preparation of new cationic palladium complexes binding to two selena macrocyclic ligands.[33] Zeng et al. has synthesized a calix[4]diselena crown ether which has been tested as sensor for ion selective electrodes.[34] Meng et al. have synthesized a phospha-selena macrocycle and studied their complexation with $Pd^{II}Cl_2$.[35]

In continuation of our work on tellurium-[36] and selenium-containing aza macrocycles[37] we report here the facile synthesis, structure and reactivity of the new 22- and 24-membered Schiff-base macrocycles **1** and **2** along with their coordination chemistry. We also compare their structural behavior and relative donor abilities with their tellurium analogs.

Results and Discussion

Macrocyclic Schiff-Base Ligands

The 22- and 24-membered macrocyclic Schiff bases **1** and **2** with N and Se donor sets were isolated in 91 and 89% yield as colorless solids by use of the [2+2] condensation reaction of bis(*o*-formylphenyl) selenide[37] with 1,2-diaminoethane or 1,3-diaminopropane, respectively, in CH_3CN at room temperature without recourse to a metal ion template (Scheme 1). Secondary intramolecular Se···N interaction (vide infra) plays an important role in the formation of the macrocycles by reducing the unfavorable lone pair−lone pair repulsion between nitrogen atoms. These compounds are soluble in $CHCl_3$ and CH_2Cl_2 but show poor solubility in other common organic solvents and in polar solvents like CH_3OH and DMSO. They could be recrystallized from a $CHCl_3/CH_3CN$ (1:1) mixture.

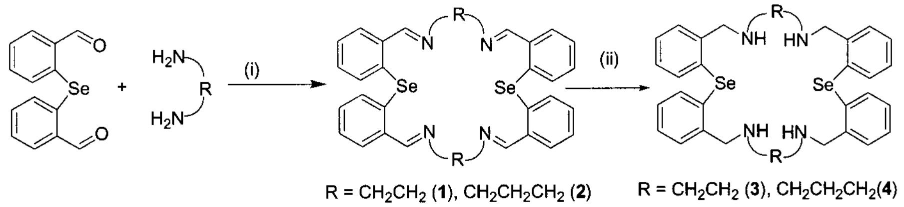
The IR spectra of the crystals of **1** and **2** showed that cyclization had occurred; an imine C=N stretch was present at 1636 and 1632 cm^{-1}, respectively, and no absorptions corresponding to unreacted carbonyl or primary amine were observed. Both the ^1H and ^{13}C NMR spectra of compounds **1** and **2** show resonances corresponding to one quarter of the molecule, suggesting very symmetric structures for the macrocyles. The CH=N proton signals were observed at δ = 8.52 and 8.46 ppm, respectively, being shifted ca.1.8 ppm upfield of the signal of the formyl proton in the starting bis(*o*-formylphenyl) selenide[37] (δ = 10.28 ppm).

The observation of a single signal in the ^{77}Se NMR spectra of the macrocycles confirms the equivalence of the two selenium atoms in **1** and **2**. On comparing the values for **1** and **2** (δ = 407, 413 ppm) with those for the corresponding saturated compounds **3** and **4** (δ = 329, 326 ppm), prepared as shown in Scheme 1, a considerable decrease in ^{77}Se chemical shift is noticed. This indicates poorer shielding of the selenium nucleus in the former cases, due to the delocalization of the selenium lone pairs in the five-membered ring formed by the strong Se···N interactions. In **3** and **4**, the Se···N interactions are not significant and hence delocalization of the electron pair is not possible.

The fast electron bombardment (FAB) mass spectra of **1** and **2** were recorded in order to confirm the formation of the [2+2] cyclocondensation products. The selenium-containing fragments could easily be recognized because of their characteristic isotope distribution pattern. In addition to the molecular ion peaks at *m*/*z* = 627 and 657 as the base peaks, the FAB mass spectra clearly show peaks due to the successive loss of groups from the macrocyclic framework.

Crystal Structures of 1 and 2

The crystal structure of **1** consists of discrete molecules and the unit cell contains four of them. The bond lengths and bond angles for a representative molecule are given in



Scheme 1. (i) $NH_2CH_2CH_2NH_2$ or $NH_2CH_2CH_2CH_2NH_2$; (ii) $NaBH_4$, EtOH, reflux.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

Se(1)–C(1A)	1.929(6)	Se(1)–C(1B)	1.941(6)
Se(2)–C(1D)	1.923(7)	Se(2)–C(1C)	1.933(7)
N(1A)–C(7A)	1.261(9)	N(1A)–C(8A)	1.455(9)
N(1B)–C(7B)	1.251(9)	N(1B)–C(8B)	1.472(10)
N(1C)–C(7C)	1.271(9)	N(1C)–C(8C)	1.440(10)
N(1D)–C(7D)	1.233(9)	N(1D)–C(8D)	1.458(9)
C(1A)–Se(1)–C(1B)	100.2(3)	C(1D)–Se(2)–C(1C)	100.9(3)
C(7A)–N(1A)–C(8A)	121.0(6)	C(7B)–N(1B)–C(8B)	117.5(6)
C(7C)–N(1C)–C(8C)	118.8(7)	C(7D)–N(1D)–C(8D)	119.6(6)
C(2A)–C(1A)–Se(1)	121.3(5)	C(6A)–C(1A)–Se(1)	119.3(5)
N(1A)–C(7A)–C(6A)	123.3(6)	N(1A)–C(8A)–C(8C)	111.4(6)
C(2B)–C(1B)–Se(1)	116.2(5)	C(6B)–C(1B)–Se(1)	123.9(5)
N(1B)–C(7B)–C(6B)	122.3(6)	N(1B)–C(8B)–C(8D)	108.7(6)
C(6C)–C(1C)–Se(2)	123.9(5)	C(2C)–C(1C)–Se(2)	116.5(6)
N(1C)–C(7C)–C(6C)	122.0(7)	N(1C)–C(8C)–C(8A)	110.8(6)
C(2D)–C(1D)–Se(2)	123.1(5)	C(6D)–C(1D)–Se(2)	117.9(5)
N(1D)–C(7D)–C(6D)	122.5(7)	N(1D)–C(8D)–C(8B)	111.5(6)

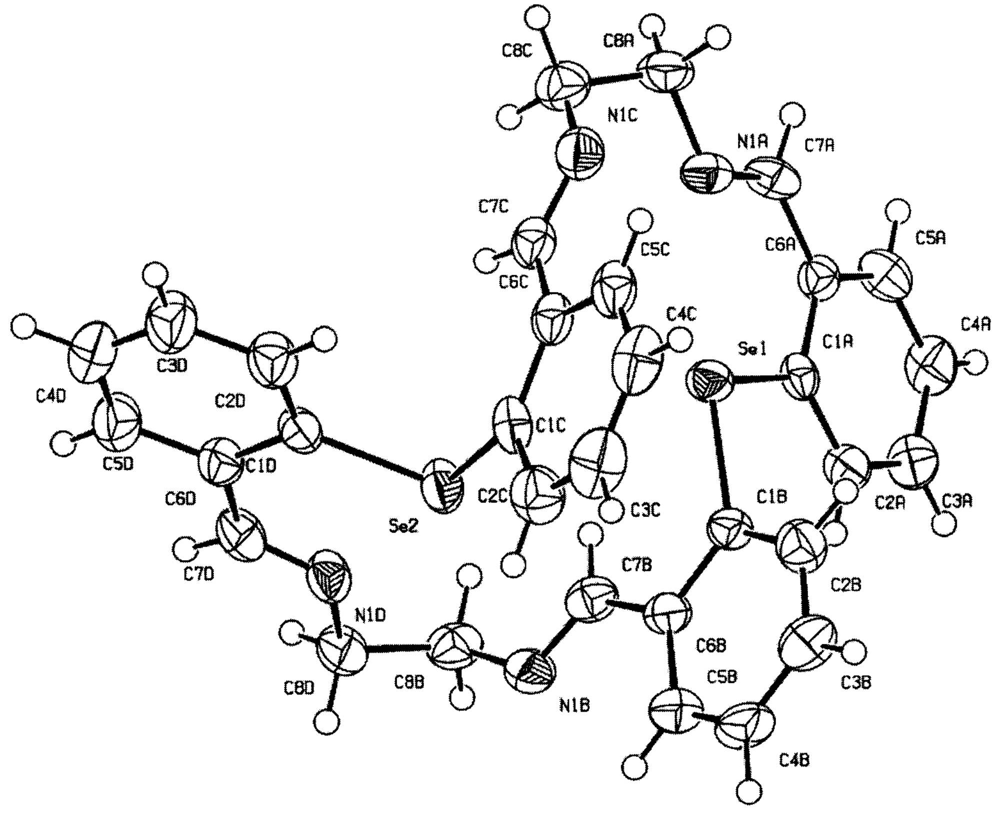


Figure 1. ORTEP diagram for **1**.

Table 1, and the ORTEP diagram is shown in Figure 1. The Se(1)···N(1A) and Se(2)···N(1C) intramolecular distances of 2.723 Å and 2.729 Å are shorter than the sum of the van der Waals radii of Se (2 Å) and sp^2-hybridized N (1.5 Å).[38] Although there are equal chances of coordination of N(1A), N(1B) to the Se(1) atom and N(1C), N(1D) to the Se(2) atom, the N(1B) and N(1D) atoms are not coordinated to Se(1) and Se(2), respectively. Thus, the solid-state geometry of the molecule indicates the presence of only one attractive interaction per selenium atom, i.e. it corresponds to the structure of 10-Se-3 selenurane. The bond configuration at the selenium atom is T-shaped. The C(1B)–Se–C(1A) angle is 100.2(3)°.

The transannular Se···Se distance (3.808 Å) is shorter than the sum of the van der Waals radii (4 Å). Interestingly, the transannular Te···Te bond length (4.979 Å)[36] in the case of the tellurium analog is greater than the sum of the van der Waals radii (4.4 Å). However, the transannular Se···Se distance in **1** is comparable to the Se1···Se2 distance of 3.9315(8) Å in 22-diselenasapphyrin.[39]

Compound **2** crystallized in the triclinic space group $P\bar{1}$. The unit cell contains one molecule. Selected bond lengths

Table 2. Selected bond lengths [Å] and angles [°] for **2**.

Se–C(1B)	1.924(8)	Se–C(1A)	1.930(9)
N(1A)–C(7A)	1.271(11)	N(1A)–C(8A)	1.477(11)
N(1B)–C(7B)	1.242(11)	N(1B)–C(8B)	1.470(10)
C(1B)–Se–C(1A)	97.7(4)	C(7A)–N(1A)–C(8A)	118.0(7)
C(7B)–N(1B)–C(8B)	119.3(8)	C(6A)–C(1A)–Se	122.8(6)
C(2A)–C(1A)–Se	118.3(7)	N(1A)–C(7A)–C(6A)	120.1(8)
N(1A)–C(8A)–C(9)	107.9(7)	C(2B)–C(1B)–Se	122.5(7)
C(6B)–C(1B)–Se	119.6(6)	N(1B)–C(7B)–C(6B)	123.7(8)
N(1B)–C(8B)–C(9)#1	110.0(7)		

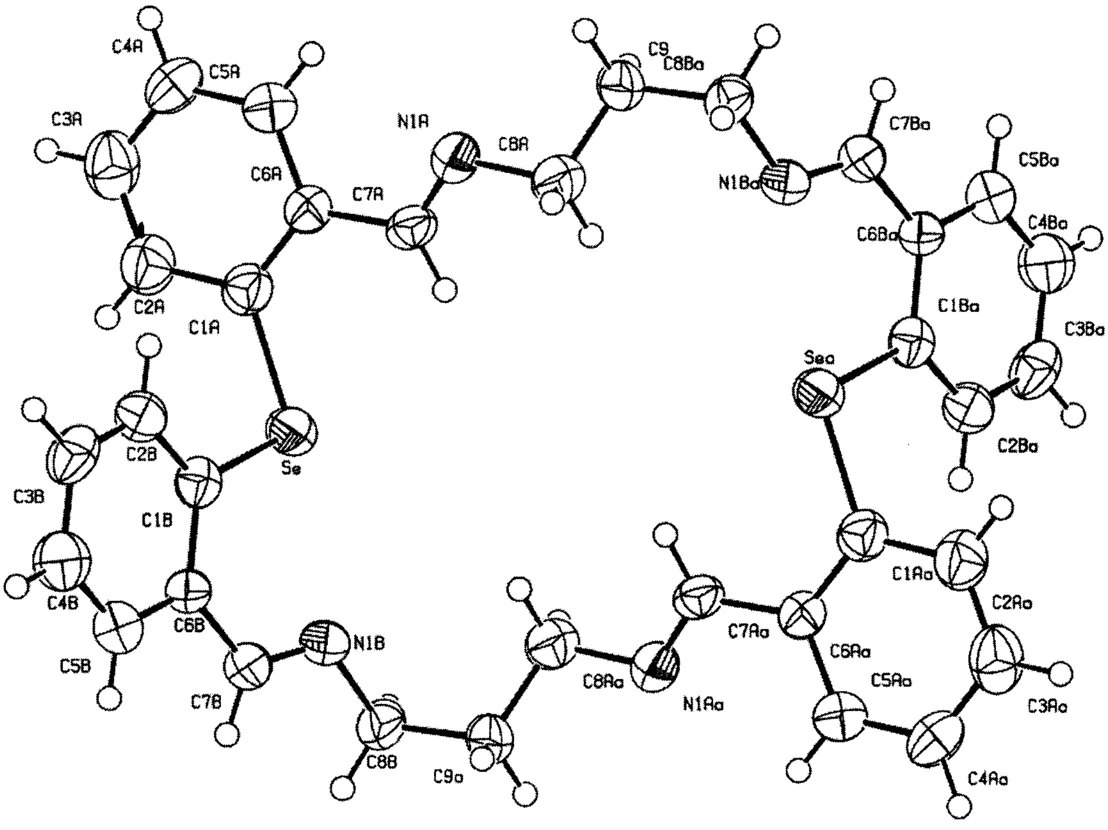


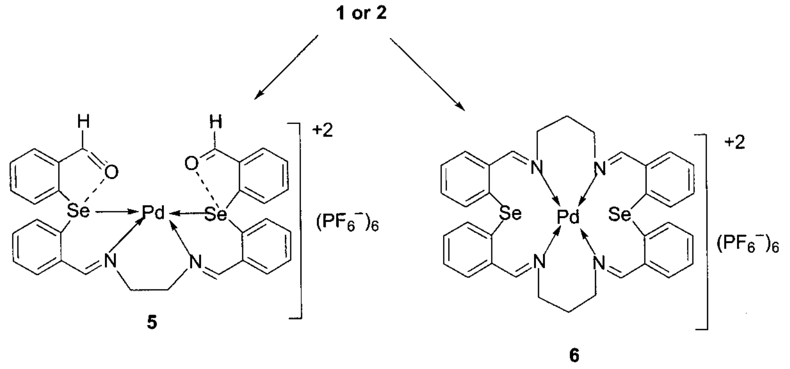
Figure 2. ORTEP diagram for **2**.

and angles are provided in Table 2. The ORTEP view is given in Figure 2. The solid-state geometry of the molecule indicates the presence of only one attractive Se···N interaction per selenium atom, i.e. it corresponds to the structure of 10-Se-3 selenurane. The intramolecular Se···N(1B) distance is 2.773 Å slightly longer than the equivalent distances in **1**. The geometry around the selenium atom is T-shaped, with the C(1B)–Se(1)–C(1A) angle being 97.7(4)°. The transannular Se···Se distance (7.229 Å) is much longer than the sum of van der Waals radii (4 Å) and also greater than the corresponding Se···Se distance (3.808 Å) observed in the 22-membered macrocycle **1**.

Reactions of 1 and 2 with Pd^{II}

The reaction of **1** or **2** with 1 equiv. of [PdCl$_2$(COD)] (COD = 1,5-cyclooctadiene) in refluxing methanol afforded a yellow solution, which gave a yellow precipitate of complex **5** or **6**, respectively, in quantitative yield upon addition of PF$_6^-$ counterions (Scheme 2). Slow concentration of an MeCN solution of **5** yielded yellow crystals of the complex. These complexes are air-stable in the solid state. They are insoluble in chlorinated solvents and hydrocarbons but soluble in MeCN, MeNO$_2$, acetone, DMF and DMSO.

The IR spectra of the complexes confirm the presence of PF$_6^-$ anion {836 [ν(P–F)], 556 [δ(F–P–F)] cm^{-1}} and display the characteristic ν(C=N) stretching frequency around 1640 and 1637 cm^{-1}, respectively, shifted slightly compared with the ν(C=N) stretching frequencies of 1650 (**1**) and 1653 cm^{-1} (**2**) for the free ligands. The ^{1}H NMR spectrum of **5** shows a peak at δ = 10.1 ppm corresponding to two aldehydic protons and at δ = 8.89 ppm corresponding to two azomethine protons. The IR spectrum also shows a peak corresponding to ν(C=O) stretching at 1667 cm^{-1}, which implies that of the four CH=N bonds, two are hydrolyzed to −CHO groups. This hydrolysis may be due to excessive strain in the ring due to the planar geometry en-



Scheme 2. Reagents: (i) $Pd(COD)Cl_2$, MeOH, reflux; (ii) NH_4PF_6.

forced by the metal ion. However, a similar reaction of the Pd^{II} precursor with the 22-membered tellurium analog gives the cationic complex $[Pd(L)](PF_6)_2$ [L = macrocycle derived from bis(*o*-formylphenyl) telluride and 1,2-diaminoethane] without any hydrolysis.[36] This may be due to the larger hole size of the tellurium analog. The ^{77}Se NMR spectrum of **5** exhibits a single signal at δ = 411 ppm showing that the selenium atoms are equivalent. The FAB mass spectrum of the complex shows peaks with the correct isotope distribution pattern at *m*/*z* = 855, 709, 605 corresponding to [**5** $-$ PF_6], [**5** $-$ $2PF_6$] and [**5** $-$ Pd $-$ 2 PF_6]. The formulation of the product **5** as $[Pd\{(C_6H_4(CHO)SeC_6H_4CHNCH_2)_2\}](PF_6)_2$ was confirmed by a crystal structure determination (vide infra).

The elemental analysis data for **6** were in accordance with the formation of a 1:1 product. The ^1H NMR spectrum of **6** shows a single peak at δ = 8.66 ppm for the azomethine protons and the ^{13}C NMR spectrum shows a peak at δ = 170 ppm for the azomethine carbon atoms, confirming the equivalence of the four azomethine groups. The quintuplet and the triplet for the CH_2–CH_2–CH_2 and the NH–CH_2–CH_2 protons are found in the deshielded region at δ = 3.64 and 4.83 ppm compared with δ = 2.00 and 3.61 ppm for the free ligand **2**, thus confirming the coordination of all the nitrogen atoms to the Pd^{II} ion. The large ring size of **2** (24-membered and Se···Se distance 7.229 Å) probably mitigates against coordination of the selenium atoms to Pd^{II}. A single signal was observed in the ^{77}Se NMR spectrum at δ = 441 ppm, which confirmed the identical environment around each selenium atom. The molecular ion peak was not observed in the FAB mass spectrum of **6**. However, the highest recorded peak was found at *m*/*z* = 905, corresponding to [6^+ $-$ PF_6]. Similar observations have been reported by Reid et al.,[14,17] The peak at *m*/*z* = 761 was assignable to [**6** – 2 PF_6]. The base peak at *m*/*z* = 434 corresponded to $[(CH_2)_2N{=}CH(C_6H_4)Se(C_6H_4)CH{=}NCH_2Pd]$. In addition, the spectrum clearly shows peaks due to the fragmentation of the macrocyclic framework. The crystal structure of **6**, which was isolated as yellow needles, could not be solved due to a crystallographic problem. The formulation of **6** as $[Pd(\mathbf{2})](PF_6)_2$ is, however, assured on the basis of the analytical data, IR, ^1H, ^{13}C, ^{77}Se NMR spectroscopy and mass spectrometry.

Crystal Structure of 5

Complex **5** crystallizes in a tetragonal crystal system with four molecules in the unit cell. Figure 3 shows the structure of a representative molecule and confirms the hydrolysis of two of the azomethine bonds in the starting material **1**. Selected bond lengths and angles are given in Table 3. The structure of **5** shows that the palladium ion is bound to two selenium and two nitrogen atoms. The average Pd–N distance, 2.019(6) Å, is in excellent agreement with the sum of the Pauling single bond covalent radii for palladium (1.31 Å) and nitrogen (0.7 Å).[38] The average Pd–Se bond length 2.3973(11) Å is close to that reported in a range of other palladium complexes of selenium-containing ligands.[40–42] It is also comparable to the Pd–Se distances [2.4191(5), 2.4183(5) Å] in $[PdL](PF_6)_2$ (L = diselena macrocycle),[33] although shorter than the Pd–Se bond lengths of 2.428(1) Å and 2.435(2) Å in $[Pd([16]ane\text{-}Se_4)](PF_6)_2{\cdot}2\,MeCN$.[14] The Se–Pd–N and N–Pd–Se angles are 93.3(2)° and 169.7(2)°, respectively, which implies that the complex has a distorted square-planar geometry. The Se···O distance 2.855 Å shows that selenium atom is weakly coordinated to the oxygen atom. This bond length can be compared to the selenium···oxygen contacts 2.888(3) Å in α-selenazofurin.[44] The geometry around the Se atom is V-shaped. The C(1A)–Se–C(1B) angle of 96.7(4)° is 3.5° smaller than the C(1A)–Se–C(1B) angle (100.2(3)°] in **1**.

Reactions of 1 and 2 with Ni^{II}

The reaction of $NiCl_2{\cdot}6H_2O$ with 1 equiv. of **1** or **2** in refluxing methanol followed by the addition of an excess of PF_6^- afforded air-stable, brown and greenish yellow paramagnetic complexes **7** or **8**, respectively (Scheme 3). Complex **7** could be recrystallized by the slow diffusion of diethyl ether into an MeCN solution. Complex **8** was isolated as green needles from methanol. The compounds are soluble in MeCN, $MeNO_2$, acetone, DMSO and DMF. The elemental analysis data of the complexes **7** and **8** suggested the formation of a 1:1 product in each case. The infrared spectroscopic measurements showed the presence of the PF_6^- anion. The $\nu_{C=N}$ absorption for **7** and **8** was found at 1650 and 1628 cm^{-1}, respectively. The electronic spectra of

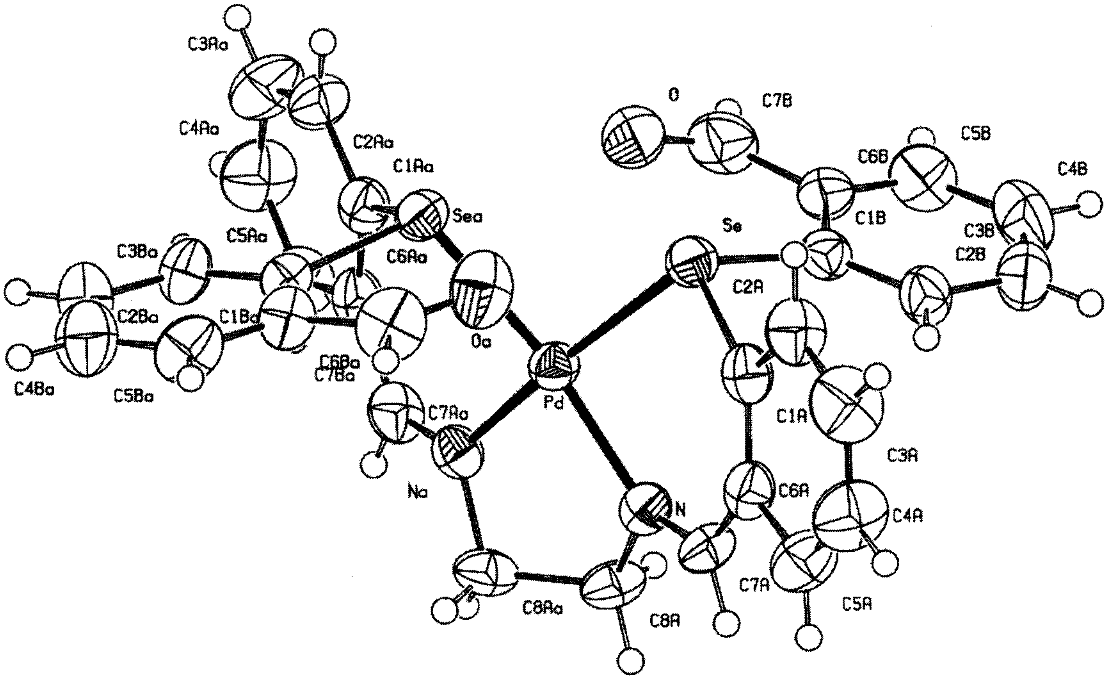
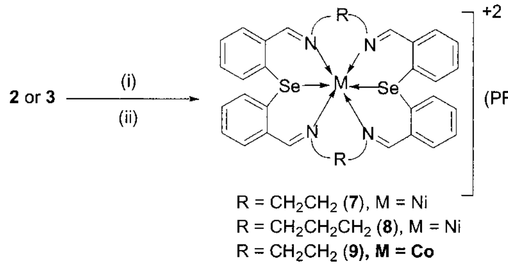


Figure 3. ORTEP diagram for **5**.

Table 3. Selected bond lengths [Å] and angles [°] for **5**.

Pd–N	2.019(6)	Pd–Se	2.3973(11)
Se–C(1A)	1.924(8)	Se–C(1B)	1.954(9)
N–C(7A)	1.297(9)	N–C(8A)	1.470(10)
O–C(7B)	1.197(13)	C(1B)–Se–Pd	106.7(2)
N–Pd–N#1	83.7(4)	N–Pd–Se	93.3(2)
N#1–Pd–Se	169.7(2)	N–Pd–Se#1	169.7(2)
N#1–Pd–#Se1	93.3(2)	Se–Pd–Se#1	91.24(5)
C(1A)–Se–C(1B)	96.7(4)	C(1A)–Se–Pd	101.7(3)
C(7A)–*N*–C(8A)	118.7(7)	C(7A)–*N*–Pd	128.3(6)
C(8A)–*N*–Pd	111.2(5)	C(2A)–C(1A)–Se	115.1(7)
C(6A)–C(1A)–Se	124.0(6)	N–C(7A)–C(6A)	128.7(8)
N–C(8A)–C(8A) #1	108.5(6)	C(2B)–C(1B)–Se	119.7(6)
C(6B)–C(1B)–Se	121.1(6)	O–C(7B)–C(6B)	126.4(10)

the complexes **7** and **8** were recorded at room temperature in CH_3CN in the range of 190–900 nm. The solution-phase electronic spectra (> 200 nm) of the ligands **1** and **2** consist of two intense bands centered at 290 and 335 nm which can be assigned to π–π* transitions. The intense peak found at 295 nm in each case may be attributed to a charge-transfer transition. Three spin-allowed transitions are expected for d^8 Ni^{II} complexes in an octahedral field. For the complex **7** there are three intense bands at 310, 452, and 804, which may be assigned to the interligand π–π* and d–d transitions. The solid-state UV/Vis spectrum also shows similar peaks at 800, 458, and 312 nm confirming the stability of the complex in the solution state. Complex **8** shows peaks at 872 (7.3), 560 (8.2) and 446 (24.3) nm in acetonitrile solution. These may be assigned to a combination of intraligand π–π* and d–d transitions. The solid-state UV/Vis spectra shows peaks at 866, 552 and 452 nm confirming the stability of complex in solution.



Scheme 3. Reagents: (i) $NiCl_2·6H_2O$ or $CoCl_2·6H_2O$; (ii) MeOH, reflux, NH_4PF_6.

In the FAB mass spectrum the highest recorded peak for complex **7** was found at *m*/*z* = 997. This was assigned to [**7** + H_2O]. The peak at *m*/*z* = 831 corresponds to [**7** − PF_6]. The base peak was found at *m*/*z* = 686 and can be assigned to [**7** – 2 PF_6]. For complex **8** a peak at *m*/*z* = 733 was found as the base peak, which can be assigned to [**8** − 2

PF_6 + H_2O]. A peak at m/z = 712 corresponds to [**8** – 2 PF_6]. The cyclic voltammograms of **7** and **8** revealed well-behaved quasi-reversible (ΔE = 100 mV at scan rate = 100 $mV{\cdot}s^{-1}$) Ni^{III}/Ni^{II} couples, with $E_{1/2}$ = 1.42 V and 1.55 V, respectively.

The assignment of octahedral geometries to [Ni(**1**)]$(PF_6)_2$ (**7**) and [Ni(**2**)]$(PF_6)_2$ (**8**) follows from their paramagnetism, μ_{eff} = 3.06 and 3.25 B.M., respectively, which indicates S = 1. This was confirmed by single-crystal X-ray studies (vide infra).

Crystal Structures of 7 and 8

Complex **7** crystallizes as a monohydrate in the monoclinic system (space group $P2_1/c$) with four molecules in the

Table 4. Selected bond lengths [Å] and angles [°] for **7**.

Ni–N(2B)	2.048(5)	Ni–N(2A)	2.053(5)
Ni–N(1B)	2.055(5)	Ni–N(1A)	2.073(5)
Ni–Se(1)	2.4890(10)	Ni–Se(2)	2.5517(10)
Se(1)–C(11B)	1.920(6)	Se(1)–C(11A)	1.937(6)
Se(2)–C(21A)	1.933(6)	Se(2)–C(21B)	1.942(6)
N(1A)–C(17A)	1.269(7)	N(1A)–C(18A)	1.471(7)
N(2A)–C(27A)	1.275(7)	N(2A)–C(28A)	1.481(7)
N(1B)–C(17B)	1.274(7)	N(1B)–C(18B)	1.489(8)
N(2B)–C(27B)	1.271(7)	N(2B)–C(28B)	1.478(8)
N(2B)–Ni–N(2A)	98.8(2)	N(2B)–Ni–N(1B)	79.0(2)
N(2A)–Ni–N(1B)	177.7(2)	N(2B)–Ni–N(1A)	95.3(2)
N(2A)–Ni–N(1A)	77.9(2)	N(1B)–Ni–N(1A)	101.3(2)
N(2B)–Ni–Se(1)	167.6(2)	N(2A)–Ni–Se(1)	93.37(13)
N(1B)–Ni–Se(1)	88.72(13)	N(1A)–Ni–Se(1)	85.26(13)
N(2B)–Ni–Se(2)	84.57(14)	N(2A)–Ni–Se(2)	86.62(14)
N(1B)–Ni–Se(2)	94.11(13)	N(1A)–Ni–Se(2)	164.32(14)
Se(1)–Ni–Se(2)	98.24(3)	C(11B)–Se(1)–C(11A)	97.7(2)
C(11B)–Se(1)–Ni	98.3(2)	C(11A)–Se(1)–Ni	99.1(2)
C(21A)–Se(2)–C(21B)	97.7(3)	C(21A)–Se(2)–Ni	95.1(2)
C(21B)–Se(2)–Ni	95.8(2)	C(17A)–N(1A)–C(18A)	119.2(5)
C(17A)–N(1A)–Ni	133.6(4)	C(18A)–N(1A)–Ni	106.8(4)
C(27A)–N(2A)–C(28A)	115.9(5)	C(27A)–N(2A)–Ni	129.6(4)
C(28A)–N(2A)–Ni	112.6(4)	C(17B)–N(1B)–C(18B)	116.3(5)
C(17B)–N(1B)–Ni	128.5(4)	C(18B)–N(1B)–Ni	112.5(4)
C(27B)–N(2B)–C(28B)	119.9(5)	C(27B)–N(2B)–Ni	132.2(4)
C(28B)–N(2B)–Ni	107.8(4)	C(12A)–C(11A)–Se(1)	118.2(5)
C(16A)–C(11A)–Se(1)	121.4(4)	N(1A)–C(17A)–C(16A)	125.8(6)
N(1A)–C(18A)–C(28A)	108.9(5)	C(22A)–C(21A)–Se(2)	115.6(5)
C(26A)–C(21A)–Se(2)	123.2(5)	N(2A)–C(27A)–C(26A)	125.5(6)
N(2A)–C(28A)–C(18A)	110.9(5)	N(1B)–C(17B)–C(16B)	127.8(5)
C(22B)–C(21B)–Se(2)	117.6(5)	C(26B)–C(21B)–Se(2)	122.2(5)
N(2B)–C(27B)–C(26B)	124.4(6)	N(2B)–C(28B)–C(18B)	109.5(6)

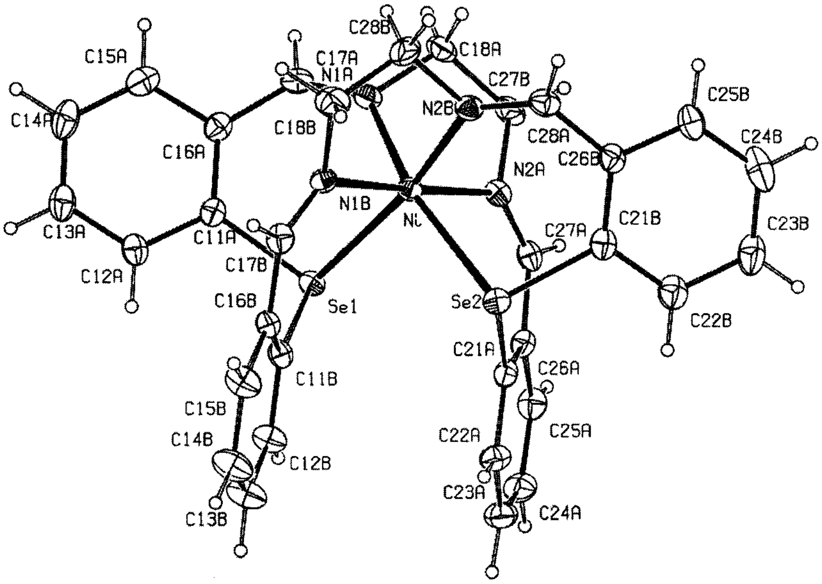


Figure 4. ORTEP diagram for **7**.

unit cell. Selected bond lengths and bond angles for a representative molecule are listed in Table 4. The ORTEP diagram is shown in Figure 4. The structure shows the nickel(II) ion occupying the macrocyclic cavity, bound through the four nitrogen and two selenium donor atoms. The angles around the nickel ion lie in the range 84.57(14)–98.24(3)° and 164.32(14)–177.7(2)° deviating only slightly from those expected for regular octahedral geometry. The two selenium atoms are mutually *cis* to each other. The Ni–Se distances [2.489(10) and 2.552(10) Å] are significantly

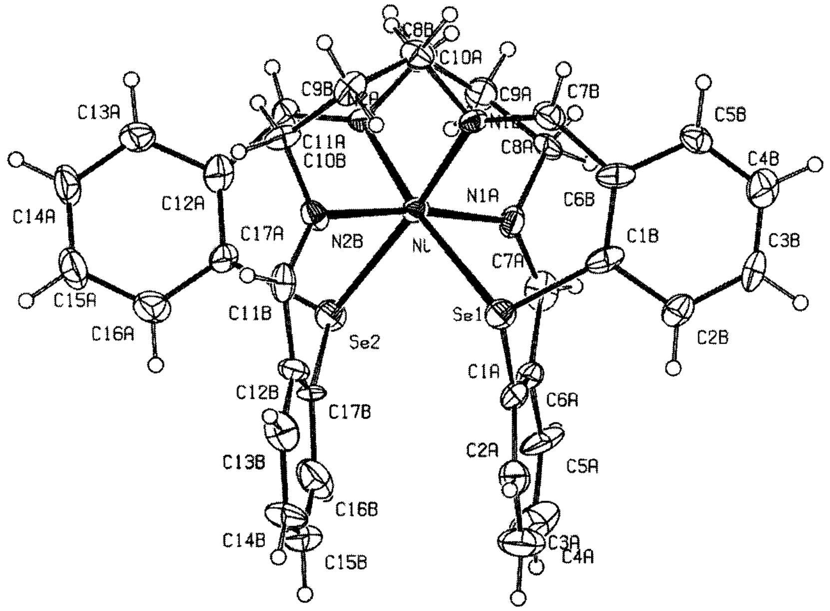


Figure 5. ORTEP diagram for **8**.

Table 5. Selected bond lengths [Å] and angles [°] for **8**.

Ni–N(2A)	2.072(12)	Ni–N(1A)	2.079(13)
Ni–N(2B)	2.086(13)	Ni–N(1B)	2.104(12)
Ni–Se(1)	2.558(2)	Ni–Se(2)	2.578(3)
Se(1)–C(1A)	1.874(19)	Se(1)–C(1B)	1.907(18)
Se(2)–C(17B)	1.927(16)	Se(2)–C(17A)	1.939(17)
N(1A)–C(7A)	1.29(2)	N(1A)–C(8A)	1.471(18)
N(2A)–C(11A)	1.283(19)	N(2A)–C(10A)	1.466(19)
N(1B)–C(7B)	1.281(19)	N(1B)–C(8B)	1.495(18)
N(2B)–C(11B)	1.281(19)	N(2B)–C(10B)	1.486(18)
N(2A)–Ni–N(2B)	94.6(5)	N(1A)–Ni–N(2B)	172.1(5)
N(2A)–Ni–N(1B)	93.4(4)	N(1A)–Ni–N(2A)	88.8(5)
N(1A)–Ni–N(1B)	97.2(5)	N(2B)–Ni–N(1B)	89.7(5)
N(2A)–Ni–Se(1)	172.2(4)	N(1A)–Ni–Se(1)	84.4(4)
N(2B)–Ni–Se(1)	92.6(4)	N(1B)–Ni–Se(1)	83.7(3)
N(2A)–Ni–Se(2)	85.4(3)	N(1A)–Ni–Se(2)	88.8(4)
N(2B)–Ni–Se(2)	84.4(3)	N(1B)–Ni–Se(2)	173.9(4)
Se(1)–Ni–Se(2)	98.29(9)	C(1A)–Se(1)–C(1B)	97.1(7)
C(1A)–Se(1)–Ni	97.9(5)	C(1B)–Se(1)–Ni	95.7(4)
C(17B)–Se(2)–C(17A)	96.7(7)	C(17B)–Se(2)–Ni	95.8(5)
C(17A)–Se(2)–Ni	96.8(5)	C(7A)–N(1A)–C(8A)	114.3(14)
C(7A)–N(1A)–Ni	125.7(12)	C(8A)–N(1A)–Ni	119.9(10)
C(11A)–N(2A)–C(10A)	117.5(13)	C(11A)–N(2A)–Ni	128.0(11)
C(10A)–N(2A)–Ni	114.4(10)	C(7B)–N(1B)–C(8B)	115.1(13)
C(7B)–N(1B)–Ni	129.6(11)	C(8B)–N(1B)–Ni	115.3(9)
C(11B)–N(2B)–C(10B)	114.9(13)	C(11B)–N(2B)–Ni	124.7(11)
C(10B)–N(2B)–Ni	119.8(9)	C(2A)–C(1A)–Se(1)	116.5(14)
C(6A)–C(1A)–Se(1)	122.9(12)	N(1A)–C(7A)–C(6A)	129.4(18)
N(1A)–C(8A)–C(9A)	111.5(14)	N(2A)–C(10A)–C(9A)	111.6(13)
N(2A)–C(11A)–C(12A)	128.0(15)	C(12A)–C(17A)–Se(2)	121.2(13)
C(16A)–C(17A)–Se(2)	117.6(13)	C(6B)–C(1B)–Se(1)	123.0(13)
C(2B)–C(1B)–Se(1)	118.4(12)	N(1B)–C(7B)–C(6B)	126.2(16)
C(9B)–C(8B)–N(1B)	112.5(13)	N(2B)–C(10B)–C(9B)	112.5(13)
N(2B)–C(11B)–C(12B)	130.7(15)	C(12B)–C(17B)–Se(2)	124.7(12)
C(16B)–C(17B)–Se(2)	116.0(14)		

different, but comparable to those in [NiPyPySe$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ [2.479(2), 2.477(2) [Å][27] and *trans*-[NiCl$_2$(MeSeCH$_2$CH$_2$SeMe)$_2$] [2.5581(9), 2.5536(9) Å],[19] respectively.

The single-crystal X-ray structure determination of **8** alsoshowed a distorted octahedral arrangement of the four nitrogen atoms and two selenium atoms around the central metal ion. Figure 5 shows the coordination sphere around the Ni^{II} ion and Table 5 summarizes selected bond lengths and bond angles. The complex crystallizes in a chiral space group *Pna*2$_1$ with four molecules in the unit cell. The Ni–Se distances [2.558(2), 2.578(3) Å] are slightly longer than those in **7**, and resemble those [2.568(2), 2.567(2) Å] in [(CO)$_3$Mn(μ-2-SC$_4$H$_3$S)$_3$Ni(μ-SePh)$_3$Fe(CO)$_3$]$^-$.[45] The C(1A)–Se(1)–C(1B) angle of 97.1(7)° deviates slightly (0.6°) from that in the ligand **2**.

Reaction of 1 with Co^{II}

The reaction of CoCl$_2$·6H$_2$O with 1 equiv. of **1** in refluxing methanol afforded a black solution. Addition of excess NH$_4$PF$_6$ yielded a black crystalline precipitate of complex **9** (Scheme 3). The air-stable complex **9** is insoluble in chlorocarbons and hydrocarbons. However, it dissolves in coordinating solvents such as MeCN, DMF, or DMSO. Rapid decomposition by displacement of the aza-selena macrocycle **1** occurs in the solvent DMSO. This was confirmed by ^{1}H NMR spectroscopic studies on the compound in [D$_6$]DMSO. A similar type of observation has been made by Reid et al. for the seven-coordinate Mo^{II} and W^{II} species derived from the selenoether ligands 1,5,9,13-tetraselenacyclohexadecane ([16]aneSe$_4$) and 1,6-diselena-3,4-benzocyclononane.[21] The elemental analysis data confirmed a 1:1 stoichiometry for the complex. The peaks at 838 and 554 cm^{-1} in the infrared spectrum were assigned to ν(P–F), δ(F–P–F). The peak at 1644 cm^{-1} was due to ν(C=N) stretching. In the UV/Vis spectrum of **9** an intense band was found centered at 290 nm, which may be due to a charge-transfer transition. Two further bands at 340 and 515 nm may be attributed to a combination of π–π* and d–d transitions. The FAB mass spectrum shows a low-intensity peak at m/z = 975 corresponding to the molecular ion [M]. The peak at m/z = 832 is for [**9** − PF$_6$]. The base peak at m/z = 687 corresponds to [**9** − 2 PF$_6$].

A powder sample of the paramagnetic black Co^{II} complex had μ_{eff} = 1.81 B.M., which indicates that it has a low-spin configuration (S = 1/2). Elemental analysis data, IR, UV/Vis, ^{77}Se NMR and FAB mass spectra, and magnetic susceptibility data are consistent with the formula of the complex **9** being [Co(**1**)](PF$_6$)$_2$. Cyclic voltammetry in acetonitrile solution reveals a well-behaved quasi-reversible (ΔE = 72 mV) Co^{III}/Co^{II} couple having $E_{1/2}$ = 0.17 V.

Conclusions

The Schiff-base condensation reaction of 1,2-diaminoethane or 1,3-diaminopropane with bis(*o*-formylphenyl) selenide yields the 22- and 24-membered [2+2] ligands **1** and **2**, respectively. Here the Se···N intramolecular interaction acts as a template in the formation of the ring. Macrocycles **1** and **2** have contrasting conformations. Whereas the transannular Se···Se distance in **1** is 3.808 Å, in **2** the distance is 7.229 Å. The Pd^{II} complex of **1** is isolated as a partially hydrolyzed complex. This is in contrast to the tellurium analog where the macrocycle is intact. The hydrolysis probably occurs due to the ring strain imposed by the square-planar geometry. The Ni^{II} complexes of **1** and **2** also show contrasting behavior. The former crystallises in an achiral space group ($P2_1/c$) whereas the latter crystallises in a chiral space group ($Pna2_1$).

Experimental Section

General: Bis(*o*-formylphenyl) selenide[37] and [PdCl$_2$(COD)][46] were prepared according to reported procedures. Air-sensitive reactions were carried out under inert conditions. Solvents were purified by standard techniques and were freshly distilled prior to use. 1,2-Diaminoethane (en) and 1,3-diaminopropane (pn) were reagent grade and were distilled prior to use. Melting points were recorded in capillary tubes and are uncorrected. IR spectra were recorded as KBr pellets with a Nicolet Impact 400 FT-IR spectrometer (4000–400 cm^{-1}). Electronic absorption spectra were obtained in CHCl$_3$/CH$_3$CN at 25 °C in a 1-cm quartz cuvette with a thermostatted Shimadzu UV-2100 apparatus and reflectance spectra was recorded with a UV-160A spectrophotometer. ^{1}H, ^{13}C and ^{77}Se NMR spectra were recorded with a Varian VXR 300S spectrometer at the indicated frequencies. Chemical shifts cited were referenced to TMS (^{1}H, ^{13}C NMR) as internal, Me$_2$Se (^{77}Se) as external standard. Elemental analyses were performed with a Carlo–Erba model 1106 elemental analyzer. Fast atom bombardment (FAB) mass spectra were recorded at room temperature with a JEOL SX 102 DA-6000 mass spectrometer/data system using xenon (6 kV, 10 mV) as the bombarding gas. The acceleration voltage was 10 kV and *m*-nitrobenzyl alcohol was used as the matrix with positive-ion detection. In the case of clusters due to the presence of more than one isotope, the value given is for the most intense peak. Magnetic susceptibilities of powdered samples were determined at room temperature with a Faraday balance, standardized with mercury tetracyanocobaltate(II) [χ = 16.44 × 10^{-6} cm^3·mol^{-1}]. The molar susceptibilities were corrected for diamagnetism using Pascal's constants. The effective magnetic moments were calculated using the expression $\mu_{\text{eff}} = 2.83(\chi_m \times T)^{1/2}$. Cyclic Voltammetry (CV) experiments were performed with a Scanning Potentiostat EG and G PARC Model 362 instrument which consists of a one-compartment cell with platinum working and counter electrodes and a standard Ag/AgCl reference electrode. Tetrabutylammonium tetrafluoroborate (Aldrich) was used as the supporting electrolyte. All solutions were purged with nitrogen before the CV data were recorded. Measurements were conducted in 0.1 mol·dm^{-3} Bu$_4$NBF$_4$ in acetonitrile with sample concentration 0.05 mM. Ferrocene was taken as standard.

Synthesis of Macrocyclic Schiff Base 1: A solution of bis(*o*-formylphenyl) selenide (0.15g, 0.5 mmol) in acetonitrile (100 mL) was added to a stirred solution of 1,2-diaminoethane (0.030 g, 0.5 mmol) in acetonitrile (100 mL) over a period of 1 h. The mixture was stirred overnight and the precipitated colorless powder was filtered off, washed with acetonitrile and recrystallized from CHCl$_3$/CH$_3$CN (1:1). Yield: 0.14g, 91%. M.p. 218–220 °C. C$_{32}$H$_{28}$N$_4$Se$_2$ (627.31): calcd. C 61.35, H 4.50, N 8.94; found C

61.18, H 4.71, N 8.63. IR (KBr): ṽ = 636 ν(C=N) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.52 (s, 4 H), 7.72 (dd, J = 7.7 H, 4 Hz), 7.28 (t, J = 7.37 Hz, 4 H), 7.16 (t, J = 7.29 Hz, 4 H), 7.09 (dd, J = 7.93 Hz, 4 H), 3.67 (s, 8 H, CH$_2$) ppm. ^{13}C NMR (75.42 MHz, CDCl$_3$, 25 °C): δ = 163.72 (CH=N), 136.25, 134.65, 133.88, 130.74, 130.16, 127.31 (aromatic C), 62.24 (N–CH$_2$) ppm. ^{77}Se NMR (57.22 MHz, CDCl$_3$): δ = 407 ppm. MS (FAB): m/z = 627 [M$^+$], 307, 298, 284, 272, 245, 233, 184, 165, 154, 136, 117, 104, 91, 71.

Synthesis of Macrocyclic Schiff Base 2: This was prepared as described for **1** from bis(o-formylphenyl) selenide (0.15g, 0.5 mmol) and 1,3-diaminopropane (0.037g, 0.5 mmol). The colorless powder was washed with acetonitrile and recrystallized from CHCl$_3$/CH$_3$CN (1:1). Yield: 0.15 g, 89%. M.p. 225–227 °C (dec.). $C_{34}H_{32}N_4Se_2$ (654.57): calcd. C 62.39, H 4.93, N 8.56; found C 62.18, H 5.04, N, 8.69. IR (KBr): ṽ = 1653 ν(C=N), 1632 ν(C=N) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.46 (s, $-CH{=}N-$, 4 H), 7.64–7.16 (m, 16 H, aromatic H), 3.61 (t, 8 H, N–CH_2–CH$_2$), 2.01 (quint, 4 H, –CH$_2$–CH_2–CH$_2$–) ppm. ^{13}C NMR (75.42 MHz, CDCl$_3$): δ = 162.58 (azomethine C), 136.92, 134.34, 133.78, 130.60, 130.18, 127.18 (aromatic C), 56.87 (N–CH$_2$–CH$_2$), 30.07 (N–CH$_2$–CH$_2$–) ppm. ^{77}Se NMR (57.22 MHz, CDCl$_3$): δ = 413 ppm. MS (FAB): m/z = 657 [M$^+$], 327, 307, 284, 245, 204, 165, 154, 136, 117, 107, 91, 77, 65, 41.

Synthesis of Complex 5: The ligand **1** (0.1 g, 0.16 mmol) was taken up in a two-necked round-bottomed flask with 20 mL of methanol. This was brought to reflux and then [PdCl$_2$(COD)] (0.045 g, 0.16 mmol) was added. The suspension immediately changed color to a clear yellow solution. This was allowed to reflux for an additional 15 min. Then it was filtered and an excess of NH$_4$PF$_6$ was added to the filtrate. Immediately a yellow powder precipitated. This could be recrystallized by slow concentration of an MeCN solution of the complex. Yield: 0.12 g, 76%. M.p. 208–210 °C (dec.). $C_{30}H_{24}F_1N_2O_2P_{22}PdSe_2$ (998.78): calcd. C 36.08, H 2.42, N 2.80; found C 35.92, H 2.46, N 2.55. IR (KBr): ṽ = 1667 ν(C=O), 1640 ν(C=N) cm^{-1}. ^{1}H NMR (300 M Hz, [D$_6$]DMSO): δ = 10.05 (s, 2 H, aldehydic H), 8.88 (s, 2 H, azomethine H), 8.34–6.61 (m, 16 H, aromatic H), 3.81–3.52 (m, 4 H, =NCH_2–CH_2N=) ppm. ^{77}Se NMR (57.22 M Hz, [D$_6$]DMSO): δ = 411 ppm. MS (FAB): m/z = 855 [M$^+$− PF$_6$], 709 [M$^+$ – 2 PF$_6$], 525, 495, 467, 439, 420, 391, 329, 307, 289, 245.

Synthesis of Complex 6: This was prepared as described for **5** by the addition of [PdCl$_2$(COD)] (0.043 g, 0.15 mmol) to the ligand **2** (0.1 g, 0.15 mmol) in methanol. Recrystallization by the slow diffusion of diethyl ether into a nitromethane solutionas afforded **6** as yellow needles. Yield: 0.14 g, 87.5%. M.p. 220–222 °C (dec.). $C_{34}H_{32}F_{12}N_4P_2PdSe_2$ (1050.90): calcd. C 38.86, H 3.07, N 5.33; found C 39.11, H 2.93, N 5.39. IR (KBr): ṽ = 1637 ν(C=N), 836 ν(P–F), 556 δ(F–P–F) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.66 (s, 4 H, azomethine H), 7.60–8.06 (m, 24 H, aromatic H), 3.64 (quint, 4 H, NCH$_2$–CH_2–CH$_2$N), 4.82 (t, 8 H, NCH_2–CH$_2$–CH_2N) ppm. ^{13}C NMR (75.42 MHz, [D$_6$]DMSO): δ = 170.18 (azomethine C), 137.60, 135.38, 135.18, 131.84, 130.75, 119.08 (aromatic C), 62.46 (N–CH$_2$–CH$_2$), 32.22 (CH$_2$–CH$_2$–CH$_2$) ppm. ^{77}Se NMR (57.22 MHz, [D$_6$]DMSO): δ = 441 ppm. MS (FAB): m/z = 905 [M$^+$ − PF$_6$], 761 [M$^+$ − 2 PF$_6$], 577, 551, 539, 512, 487, 469, 434 (base peak), 247.

Synthesis of Complex7: The ligand **1** (0.1 g, 0.16 mmol) was added to methanol (20 mL) under nitrogen. This was brought to reflux and then NiCl$_2$·6H$_2$O (0.038 g, 0.16 mmol) was added. The suspension changed to a clear red solution within 5 min. It was allowed to reflux for an additional 15 min. The solution was filtered and to the filtrate an excess of NH$_4$PF$_6$ was added. Immediately a brown precipitate was obtained which was filtered and washed with methanol. Yield: 0.15 g, 96%. M.p. 258–260 °C (dec). $C_{32}H_{28}F_{12}N_4NiP_2Se_2\cdot H_2O$ (993.17): calcd. C 38.70, H 3.04, N 5.64; found C 38.25, H 3.04, N 5.95. IR (KBr): ṽ = 1650 ν(C=N), 830 ν(P–F), 555 δ(F–P–F) cm^{-1}. UV/Vis (MeCN): $\lambda_{\text{max.}}$ (ε) = 295 (14 330), 345 (2950), 435 (579), 805 nm (58 mol^{-1}·dm^3·cm^{-1}); μ_{eff} = 3.23 B.M.. MS (FAB): m/z = 831 [M$^+$ − PF$_6$], 686 [M$^+$ − 2 PF$_6$], 372, 343, 291, 273, 242, 178, 153, 120.

Table 6. Crystal data and structure refinement for **1**, **2** and **5**.

	1	**2**	**5**
Empirical formula	$C_{32}H_{28}N_4Se_2$	$C_{34}H_{32}N_4Se_2$	$C_{30}H_{24}F_{12}N_2O_2P_2PdSe_2$
Formula mass	626.50	654.56	998.77
Crystal system	monoclinic	triclinic	tetragonal
Space group	$P2_1/c$	$P\bar{1}$	$P4_12_12$
a [Å]	10.0648(10)	7.200(3)	10.7737(10)
b [Å]	37.390(4)	9.137(3)	10.7737(10)
c [Å]	8.0073(11)	12.780(6)	28.190(5)
α [°]	90	72.78(3)	90
β [°]	112.978(8)	76.40(4)	90
γ [°]	90	69.00(3)	90
V [Å^3]	2774.3(6)	741.8(5)	3272.1(7)
Z	4	1	4
d(calcd.) [Mg/m^3]	1.500	1.465	2.027
Temp. [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
Range of θ [°]	2.74–25.00	2.46–27.49	2.67–29.99
Data collected	$\pm h$, $+k$, $+l$		$+h$, $+k$, $-l$
Abs. coeff. [mm^{-1}]	2.694	2.522	2.993
Obsd. reflections [$I > 2\sigma$]	4782	2581	2677
Final $R(F)$ [$I > 2\sigma$][a]	0.0556	0.0717	0.0499
$wR(F^2)$ indices [$I > 2\sigma$]	0.1270	0.1769	0.0837
Data/restraints/parameters	4718/0/371	2581/0/198	2677/64/358
Goodness of fit on F^2	1.045	1.098	1.039

[a] Definitions: $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{1/2}$.

Table 7. Crystal data and structure refinement for **7** and **8**.

	7	**8**
Empirical formula	$C_{32}H_{30}F_{12}N_4NiOP_2Se_2$	$C_{34}H_{32}F_{12}N_4NiP_2Se_2$
Formula mass	993.17	1003.21
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a [Å]	9.979(2)	20.277(5)
b [Å]	18.901(4)	20.865(5)
c [Å]	19.333(4)	9.416(2)
α [°]	90	90
β [°]	100.94(2)	90
γ [°]	90	90
V [Å^3]	3580.4(13)	3983.5(17)
Z	4	4
d(calcd) [Mg/m^3]	1.842	1.673
Temp. [K]	293(2)	293(2)
λ [Å]	0.71073	0.71073
Range of θ [°]	2.69–27.50	2.37–26.24
Data collected	$+h$, $+k$, $\pm l$	$+h$, $+k$, $+l$
Abs. coeff. [mm^{-1}]	2.762	2.482
Obsd. reflections [$I > 2\sigma$]	8074	2792
Final $R(F)$ [$I > 2\sigma$][a]	0.0586	0.0561
$wR(F^2)$ indices [$I > 2\sigma$]	0.1108	0.1225
Data/restraints/parameters	8073/0/516	2792/1/496
Goodness of fit on F^2	1.030	1.025
Absolute structure parameter	–	0.01(3)

[a] Definitions: $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{1/2}$.

Synthesis of Complex 8: This was prepared similarly from ligand **2** (0.1 g, 0.15 mmol) and $NiCl_2 \cdot 6H_2O$ (0.036 g, 0.15 mmol). It was recrystallized by the slow diffusion of diethyl ether into a nitromethane solution. Yield: 0.13 g, 87%. M.p. 258–260 °C (dec.). $C_{34}H_{32}F_{12}N_4NiP_2Se_2 \cdot H_2O$ (1021.23): calcd. C 39.99, H 3.30, N 5.48; found C 39.57, H 3.22; N 5.98. IR (KBr): $\tilde{\nu}$ = 1628 ν(C=N) 834, 753, 557 cm^{-1}. UV/Vis (MeCN): $\lambda_{\text{max.}}$ (ε) = 295 (12 200), 335 (3650), 565 nm (24 mol^{-1}·dm^3·cm^{-1}); μ_{eff} = 3.25 B.M.. MS (FAB): m/z = 733 [$M^+ - PF_6 + H_2O$], 712 [$M^+ - PF_6$], 577, 407, 386, 327, 306, 251, 224.

Synthesis of Complex 9: This was prepared according to the method used for the preparation of the complex **7** by adding $CoCl_2 \cdot 6H_2O$ (0.038 g, 0.16 mmol) to the ligand **1** (0.1 g, 0.16 mmol) in 20 mL methanol. Yield: 0.12 g, 75%. M.p. 226–228 °C (dec.). $C_{32}H_{28}CoF_{12}N_4P_2Se_2$ (975.38): calcd. C 39.41, H 2.89, N 5.74; found C 38.50, H 2.96, N 5.66. IR (KBr): $\tilde{\nu}$ = 1644 ν(C=N), 838 ν(P–F), 554 (δ(F–P–F) cm^{-1}. UV/Vis: (MeCN): $\lambda_{\text{max.}}$ (ε) = 290 (13 240), 340 (6640), 515 nm (1100 mol^{-1}·dm^3·cm^{-1}); μ_{eff} = 1.81 B.M. MS (FAB): m/z = 975 [M^+], 832 [$M^+ - PF_6$], 687 [$M^+ - 2\,PF_6$, base peak], 373, 343, 309, 291, 242, 152, 120.

X-ray Crystallographic Study: The diffraction measurements for compound **1**, **2**, **5**,**7** and **8** were performed at room temperature (293 K) with a Siemens R3m/V diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The unit cell was determined from 25 randomly selected reflections using the automatic search index and least-squares routine. The data were corrected for Lorentz, polarization and absorption effects. A semiempirical absorption correction from ψ-scans was applied to the data of **5** and **7**. The maximum and minimum transmission values of the correction factors for compounds **5** and **7** were 0.2761 and 0.2170 and 0.5048 and 0.4442, respectively. The structures were solved by routine heavy-atom (using SHELXS[47]) and Fourier methods and refined by full-matrix least squares, the non-hydrogen atoms with anisotropic and the hydrogen atoms with fixed isotropic thermal parameters of 0.07 Å^2 using SHELXL93.[48] The hydrogen atoms were partially located from difference electron-density maps and the rest were fixed at calculated positions. Scattering factors were from common sources.[49] Some details of data collection and refinement are given in Tables 6 and 7. CCDC-148626 (**1**), -148627 (**2**), -148630 (**5**), -148631 (**7**) and -148632 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We are grateful to the Department of Science and Technology (DST), New Delhi and Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy, Bombay for funding this work. Additional help from the Regional Sophisticated Instrumentation Center (RSIC), Indian Institute of Technology (IIT), Bombay for 300 MHz NMR spectroscopy, and RSIC, CDRI Lucknow for mass spectrometry, is gratefully acknowledged. R. J. B. wishes to acknowledge the DOD-ONR program for funds to upgrade the diffractometer.

[1] a) L. F. Lindoy, in: *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, **1989**; b) B. Dietrich, P. Viout, J.-M. Lehn, *Macrocyclic Chemistry: Aspects of Organic and Inorganic Supramolecular Chemistry*, Wiley-VCH, Weinheim, **1993**; c) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, Wiley-VCH, Weinheim, **1995**; d) J. W. Steed, J. L. Atwood, in: *Supramolecular Chemistry*, Wiley, Chichester, **2000**; e) H. Dodziuk, *Introduction to Supramolecular Chemistry*, Kluwer Academic Pub., Dordrecht, **2002**.

[2] V. Alexander, *Chem. Rev.* **1995**, *95*, 273.

[3] S. Goswami, A. D. Hamilton, *J. Am. Chem. Soc.* **1989**, *111*, 3425.

[4] A. J. Blake, W. Li, V. Lippolis, M. Schröder, *Chem. Commun.* **1997**, 1943.

[5] a) G. W. Gokel, L. J. Barbour, S. L. De Wall, E. S. Meadows, *Coord. Chem. Rev.* **2001**, *222*, 127; b) K. Gloe, H. Graubaum, M. Wust, T. Rambusch, W. Seichter, *Coord. Chem. Rev.* **2001**, *222*, 103; c) J. W. Steed, *Coord. Chem. Rev.* **2001**, *215*, 171.

[6] a) A. Bianchi, E. Garcia-España, K. Bowman-James (Eds.), *Supramolecular Chemistry of Anions*, Wiley-VCH, New York, **1997**; b) H. Elias, *Coord. Chem. Rev.* **1999**, *187*, 37; c) C. L. Kranemann, B. Costisella, P. Eilbracht, *Tetrahedron Lett.* **1999**, *40*, 7773; d) J. Nelson, V. McKee, G. Morgan, *Prog. Inorg. Chem.* **1998**, *47*, 167; R. Ibrahim, S. Tsuchiya, S. Ogawa, *J. Am. Chem. Soc.* **2000**, *122*, 12174; e) D. Utz, F. W. Heinemann, F. Hampel, D. T. Richens, S. Schindler, *Inorg. Chem.* **2003**, *42*, 1430.

[7] a) K. Brandt, I. Porwolik-Czomperlik, M. Siwy, T. Kupka, R. A. Shaw, D. B. Davies, M. B. Hursthouse, G. D. Sykara, *J. Am. Chem. Soc.* **1997**, *119*, 12432; b) M. Dreiss, M. Faulhaber, H. Pritzkow, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*,1892; c) F. Mercier, F. Laporte, L. Richard, F. Mathey, M. Schröder, M. Regitz, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 947; d) K. Brandt, I. Porwolik-Czomperlik, M. Siwy, T. Kupka, R. A. Shaw, S. Ture, A. Clayton, D. B. Davies, M. B. Hurdthouse, G. D. Sykara, *J. Org. Chem.* **1999**, *64*, 7299; e) L. Escriche, J. A. Munoz, R. Kivekas, R. Sillampaa, J. Casabo, *Eur. J. Inorg. Chem.* **2002**, 3258; f) R. J. Baker, P. G. Edwards, *J. Chem. Soc., Dalton Trans.* **2002**, 2960; g) L. Escriche, J. A. Munoz, R. Kivekas, R. Sillampaa, J. Casabo, *Eur. J. Inorg. Chem.* **2002**, 3258; h) S. Ekici, M. Nieger, R. Glaum, E. Niecke, *Angew. Chem. Int. Ed.* **2003**, *42*, 435.

[8] a) R. Schibli, R. Alberto, U. Abram, S. Abram, A. Egli, P. A. Schubiger, T. A. Kaden, *Inorg. Chem.* **1998**, *37*, 3509; b) A. J. Blake, W. Li, V. Lippolis, M. Schröder, *Chem. Commun.* **1998**, 1943; c) S. Brooker, T. C. Davidson, *Chem. Commun.* **1997**, 2007; d) T. Tsuchiya, T. Shimizu, K. Hirabayashi, N. Kamigata, *J. Org. Chem.* **2003**, *68*, 3480 .and references cited therein; e) M. Vetrichelvan, Yee-Hing Lai, K. F. Mok, *Dalton Trans.* **2003**, 295 .and references cited therein.

[9] a) P. Comba, A. Kühner, *Eur. J. Inorg. Chem.* **1999**, 509; b) P. Comba, A. Kühner, A. Peters, *J. Chem. Soc. Dalton Trans.* **1999**, 509; c) P. Comba, J. Ensling, P. Gütlich, A. Kühner, A. Peters, H. Pritzkow, *Inorg. Chem.* **1999**, *38*, 3316 .and references cited therein; d) P. D. Metelski, Y. Fu, K. Khan, T. W. Swaddle, *Inorg. Chem.* **1999**, *38*, 3103; e) P. Osvath, A. M. Sargeson, A. McAuley, R. E. Mendelez, S. Subramanian, M. J. Zaworotko, L. Broge, *Inorg. Chem.* **1999**, *38*, 3634; f) S. Galijasevic, K. Krylova, M. J. Koenigbauer, G. S. Jaeger, J. D. Bushendorf, M. J. Heeg, L. A Ochrymowycz, M. J. Taschner, D. B. Rorabacher, *Dalton Trans.* 2003, 1577; g) M. Arca, A. J. Blake, V. Lippolis, D. R. Montesu, J. McMaster, L. Tei, M. Schröder, *Euro. J. Inorg. Chem.* **2003**, 1232; h) P. J. Wilson, A. J. Blake, P. Mountford, M. Schröder, *Inorg. Chim. Acta* **2003**, *345*, 44; i) C. Ma, F. Li, D. Wang, H. Yin, *J. Organomet. Chem.* **2003**, *667*, 5.

[10] V. McKee, *Adv.Inorg. Chem.* **1993**, *40*, 323.

[11] R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J-H. Gu, B. D. Johnston, B. M. Pinto, *J. Am. Chem. Soc.* **1989**, *111*, 6582.

[12] R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J. Gu, B. M. Pinto, X. Zhou, *Inorg. Chem.* **1996**, *35*, 3667.

[13] a) R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J. Gu, B. M. Pinto, *J. Organomet. Chem.* **1991**, *411*, 147; b) R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J. Gu, B. M. Pinto, X. Zhou, *J. Am. Chem. Soc.* **1990**, *112*, 3706; c) R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J-H. Gu, S. Mehta, B. M. Pinto, X-M. Zhou, *Inorg. Chem.* **2000**, *39*, 2558.

[14] a) N. R. Champness, P. F. Kelly, W. Levason, G. Reid, A. M. Z. Slawin, D. J. Williams, *Inorg. Chem.* **1995**, *34*, 651; b) N. R. Champness, W. Levason, J. J. Quirk, G. Reid, *Polyhedron* **1995**, *14*, 2753.

[15] W. Levason, J. J. Quirk, G. Reid, C. S. Frampton, *Inorg. Chem.* **1994**, *33*, 6120.

[16] P. F. Kelly, W. Levason, G. Reid, D. J. Williams, *J. Chem. Soc., Chem. Commun.* **1993**, 1716.

[17] W. Levason, J. J.Quirk, G. Reid, *J. Chem. Soc., Dalton Trans.* **1996**, 3713.

[18] W. Levason, J. J. Quirk, G. Reid, S. M. Smith, *J. Chem. Soc., Dalton Trans.* **1997**, 3719.

[19] M. K. Davies, W. Levason, G. Reid, *J. Chem. Soc., Dalton Trans.* **1998**, 2185.

[20] W. Levason, G. Reid, S. M. Smith, *Polyhedron* **1997**, *16*, 4253.

[21] M. K. Davies, M. C. Durrant, W. Levason, G. Reid, R. L. Richards, *J. Chem. Soc., Dalton Trans.* **1999**, 1077.

[22] D. G. Booth, W. Levason, J. J. Quirk, G. Reid, S. M. Smith, *J. Chem. Soc., Dalton Trans.* **1997**, 3493.

[23] a) A. J. Barton, A. R. J. Genge, W. Levason, G. Reid, *J. Chem. Soc., Dalton Trans.* **2000**, 2163; b) A. J. Barton, N. J. Hill, W. Levason, B. Patel, G. Reid, *Chem. Commun.* **2001**, 95; c) A. J. Barton, N. J. Hill, W. Levason, G. Reid, *J. Chem. Soc., Dalton Trans.* **2001**, 1621; d) J. Barton, N. J. Hill, W. Levason, G. Reid, *J. Am. Chem. Soc* **2001**, *123*, 11801; e) N. J. Hill, W. Levason, G. Reid, *Inorg. Chem.* **2002**, *41*, 2070; f) N. J. Hill, W. Levason, R. Patel, G. Reid, M. Webster, *Dalton Trans.* **2004**, 980.

[24] a) W. Levason, S. D. Orchard, G. Reid, *Chem. Commun.* **2001**, 427; b) M. J. Hesford, W. Levason, M. L. Matthews, S. D. Orchard, G. Reid, *Dalton Trans.* **2003**, 2434; c) M. J. Hesford, W. Levason, M. L. Matthews, G. Reid, *Dalton Trans.* **2003**, 2852.

[25] T. Kumagi, S. Akabori, *Chem. Lett.* **1989**, 1667.

[26] S. Tomoda, M. J. Iwaoka, *J. Chem. Soc., Chem. Commun.* **1990**, 231.

[27] S. Muralidharan, M. Hojjatie, M. Firestone, H. Freiser, *J. Org. Chem.* **1989**, *54*, 393.

[28] a) H. Fujihara, M. Yabe, M. Ikemori, N. Furukawa, *J. Chem. Soc. Perkin. Trans. 1* **1993**, 2145; b) H. Fujihara, M. Yabe, N. Furukawa, *J. Chem. Soc., Perkin. Trans. 1* **1996**, 1783.

[29] R. Adams, K. T. McBride, *J. Chem. Soc., Chem. Commun.* **1997**, 525.

[30] R. Bhula, A. P. Arnold, G. J. Gainsford, W. G. Jackson, *J. Chem. Soc., Chem. Commun.* **1996**, 143.

[31] A. Mazouz, J. Bodiguel, P. Meunier, B. Gautheron, *Phosphorus, Sulfur Silicon* **1991**, *61*, 247.

[32] A. Mazouz, P. Meunier, M. M. Kubicki, B. Hanquet, R. Amardeil, C. Bornet, A. Zahidi, *J. Chem. Soc., Dalton Trans.* **1997**, 1043.

[33] C. Bornet, R. Amardeil, P. Meunier, J. C. Daran, *J. Chem. Soc., Dalton Trans.* **1999**, 1039.

[34] X. Zeng, X. Han, L. Chen, Q. Li, F. Xu, X. He, Z. Zhang, *Tetrahedron Lett.* **2002**, *43*, 131.

[35] J. L. Li, J. B. Meng, Y. M. Wang, J. T. Wang, T. Matsuura, *J. Chem. Soc., Perkin Trans. 1* **2001**, 1140.

[36] a) S. C. Menon, H. B. Singh, R. P. Patel, S. K. Kulshereshtha, *J. Chem. Soc., Dalton Trans.* **1996**, 1203; b) S. C. Menon, A. Panda, H. B. Singh, R. J. Butcher, *J. Chem. Soc., Chem. Commun.* **2001**, 143; c) S. C. Menon, A. Panda, H. B. Singh, R. P. Patel, S. K. Kulshereshtha, W. L. Darby, R. J. Butcher, *J. Organomet. Chem.* **2004**, *689*, 1452.

[37] a) A. Panda, S. C. Menon, H. B. Singh, R. J. Butcher, *J. Organomet. Chem.* **2001**, *623*, 87; b) S. Panda, H. B. Singh, R. J. Butcher, *Chem. Commun.* **2004**, 322.

[38] J. E. Huheey, E. A. Keiter, R. L. Keiter, in *Inorganic Chemistry: Principles of structure and reactivity*, HarperCollins College Publishers, New York, **1993**.

[39] S. J. Narayanan, B. Sridevi, T. K. Chandrashekar, A. Vij, R. Roy, *Angew. Chem. Int. Ed.* **1998**, *37*, 3394.

[40] S. Ford, P. K. Khanna, C. P. Morley, M. D. Vaira, *J. Chem. Soc., Dalton Trans.* **1999**, 791.

[41] R. Cao, W. Su, M. Hong, W. Zhang, W. Wong, J. Lu, *J. Chem. Soc., Chem. Commun.* **1998**, 2083.

[42] R. Oilunkaniemi, R. S. Laitinen, M. Ahlgrén, *J. Chem. Soc., Chem. Commun.* **1999**, 585.

[43] a) W. Nakanishi, S. Hayashi, S. Toyota, *J. Chem. Soc., Chem. Commun.* **1996**, 371; b) W. Nakanishi, S. Hayashi, S. Toyota,

J. Org. Chem. **1998**, *63*, 8790; c) P. G. Jones, M. C. Ramirez de Arellano, *J. Chem. Soc., Dalton Trans.* **1996**, 2713.
[44] B. M.Goldstein, F. Takusagawa, H. M. Berman, P. C. Srivastava, R. K. Robins, *J. Am. Chem. Soc.* **1985**, *107*, 1394.
[45] W. Liaw, C. Lee, L. Horng, G. Lee, S. Peng, *Organometallics* **1999**, *18*, 782.
[46] D. Drew, J. R. Doyle, *Inorg. Synth.* **1972**, *13*, 47.
[47] G. M. Sheldrick, *Crystallographic Computing 3*, Oxford University Press, Oxford, **1985**, p. 175.
[48] G. M. Sheldrick, *SHELX93, Program for Crystal Structure Determination*, University of Göttingen, **1993**.
[49] *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, **1974**, vol. 4, p. 99.

Received: September 13, 2004