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Synthesis and structure of heavier group 2 metal complexes with diselenoimidodiphosphinato ligand containing Sr–Se and Ba–Se direct bonds

Ravi K. Kottalanka, Srinivas Anga, Salil K. Jana, Tarun K. Panda*

Department of Chemistry, Indian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram, 502205 Andhra Pradesh, India

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We report the mononuclear diselenoimidodiphosphinato strontium and barium complexes of the molecular formula $[\{\eta^2\text{-N}(PPh_2Se)_2\}_2Sr(THF)_2]$ (**2**) and $[\{\eta^2\text{-N}(PPh_2Se)_2\}_2Ba(THF)_3]$ (**3**) which can be obtained by two routes, either by the treatment of metal bis(trimethylsilyl)amide and diselenoimidodiphosphine (**1**) via the elimination of silylamine or salt metathesis reaction involving metal diiodide and potassium salt of diselenoimidodiphosphine. In the solid state structures of **2** and **3**, each of the metal atom is ligated by four selenium atoms from two diselenoimidodiphosphinato ligand moieties and two (for **2**) and three (for **3**) THF molecules to adopt a distorted octahedral geometry around the strontium atom and distorted pentagonal bipyramidal geometry for barium ion. In the complexes **2** and **3**, a direct metal selenium contact is observed. Additionally we also report the synthesis and structure of lithium complex $[\eta^2\text{-N}(PPh_2Se)_2Li(THF)_2]$ (**4**) which was synthesized by using **1** and $LiCH_2SiMe_3$ in THF solution.

1. Introduction

Due to the oxophilic and electropositive nature compared to those of early *d*-transition metals, homoleptic and heteroleptic alkaline earth metal complexes are attractive to the organometallic chemists [1,2]. The alkaline earth metal compounds have recently employed in various catalytic applications to ring-opening polymerization of various cyclic esters [3,4], polymerization of styrene and dienes [5–7], and hydroamination and hydrophosphination reactions of alkenes and alkynes [8]. Exploration of the structure and reactivity of alkaline earth metal species is one of the most important steps to the design and development of efficient homogeneous catalysts; however, full realization of the catalytic potential of these elements still requires substantial advances in understanding their basic coordination and organometallic chemistry. To stabilize these extremely oxophilic and electropositive metals, a wide variety of nitrogen-based ancillary ligands, such as tris(pyrazolyl)borates [1], aminotroponiminates [9], β-diketiminates [10–12], and iminopyrroles [13–15], 1,4-diaza-1,3-butadiene [16,17] have been introduced to prepare well-defined alkaline earth metal complexes revealing that the catalytic activity and selectivity of the alkaline earth metal complexes can be controlled via the well-defined nitrogen-based ligand architecture.

Another important application of alkaline earth metal chalcogenolates is in high temperature superconductors and ferroelectrics. In particular, alkaline earth metal oxide compounds used as suitable precursors [18]. Much less attention has been paid to the alkaline earth metal thiolates and selenates, although many heavier chalcogenates are known as potential dopants for chalcogen-based semiconductors [19]. The chelating ligands having selenium as the donor atom to stabilize the heavier alkaline earth metal complexes are rare. Over the last few years very few calcium selenides have been reported, such as $[(TMEDA)_2Ca(SeSi(SiMe_3)_3)]$ [20], but to date only the solid state structures of $[(THF)_4Ca(SeMes')_2]$ [21] and $[(THF)_2Ca\{(PyCH)\text{–}(Se)PPh_2\}_2]$ [22] have been reported. Full structural characterization of strontium selenides is even scarce [23,24]. The complex having barium selenium bond is limited as the structurally authenticated examples are mostly restricted for the various sulfur derivatives $[\{(H_2O)_2Ba(tmtH_2)_2\}_n]$ (tmt = 2,4,6-trimarcaptotriazine, $S_3C_3N_3$) [25], [([17] crown-6)Ba(hmpa)SMes*][SMes*](Mes* = 2,4,6-$t\text{Bu}_3C_6H_2$) [26], $[Ba(hmpa)_3\{NaPhNNNNC(S)\}_2]$ [27], $[Ba(hmpa)_3(C(S)NOPh_2]$ [28], and few more examples including $[Ba(SCMe_3)_2$ [29], $[Ba(tmeda)_2(SeSi(SiMe_3)_3)_2]$ [20] are reported. Ruhlandt-Senge et al. reported barium selenoates like $[Ba(THF)_4(SeMes^*)_2]$, [([26] crown-6)Ba(hmpa)$_2$(SMes*)$_2$], $[Ba(Py)_3(THF)(SeTrip)_2\}_2]$ (Trip = 2,4,6 $i\text{Pr}_3C_6H_2$), and [Ba([17]crown-6)(SeTrip)$_2$]

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* Corresponding author. Tel.: +91 4023016036; fax: +91 4023016032.
E-mail address: tpanda@iith.ac.in (T.K. Panda).

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[30], however vast potential of this field of chemistry is still to be developed. Recently we also have reported the heavier alkaline earth metal selenium containing complexes $[M(THF)_2\{Ph_2P(Se)N(CHPh_2)\}_2]$ (M = Ca, Sr, Ba) to enrich the field of heavier group 2 metal seleno complexes [31]. In that work we showed that phosphinoselenoic amide ligand are capable to stabilize heavier alkaline earth metals via the formation of a selenium metal bond. In continuation of our study regarding heavier group 2 metal selenoates complexes, we observed that diselenoimidodiphosphinato ligand is introduced to a wide range of metal coordination sphere including alkali metals [32,33], group 12 [34]; group 13 [35,36], group 14 [34,37,38], group 15 [39], group 16 [40,41], transition metals (V and Cr [42]; Mn [43,44] and Re [45]; Ru, Rh, Ir [33,46,47]; Os [48], Co [49]; group 10: Ni [50], Pd [50–53], Pt [32,46,50] and group 11 [53]: and to rare earth metals [54,55]: and this can be due to the flexible nature of the ligand moieties to adopt several metallacyclic ring depending upon coordination to the metal center. To our surprise, the reports for heavier alkaline earth metal diselenoimidodiphosphinato are missing in this series which could give more information about the alkaline earth metal selenoates and therefore there is a scope to develop the heavier alkaline earth metal complexes with diselenoimidodiphosphinato ligand.

In this context, the heavier alkaline earth metal selenium containing complexes $[\{\eta^2\text{-}N(PPh_2Se)_2\}_2Sr(THF)_2]$ (**2**) and $[\{\eta^2\text{-}N(PPh_2Se)_2\}_2Ba(THF)_3]$ (**3**) are presented, which can be prepared in good yield and high purity by two synthetic routes. Thus heavier alkaline earth metal complexes reported herein, **2**–**3**, can be the examples of fewer class of complexes, with a direct selenium-alkaline earth metal contact. Additionally we also present the synthesis and structure of lithium complex $[\eta^2\text{-}N(PPh_2Se)_2Li(THF)_2]$ (**4**) which were obtained by using **1** and $LiCH_2SiMe_3$ in THF solution.

2. Experimental

2.1. General information

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line, or in an argon-filled M. Braun glove box. THF was pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$ and stored in the glove box. ^1H NMR (400 MHz), $^{13}C\{^1H\}$ (100 MHz) and $^{31}P\{^1H\}$ NMR (161.9 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Diselenoimidodiphosphine [56], $[K\{N(Ph_2PSe)_2\}]$ [33], $[M\{N(SiMe_3)_2\}_2(THF)_2]$ [57,58] (M = Sr, Ba), and $LiCH_2SiMe_3$ [59] were prepared according to the literature procedures. SrI_2 and BaI_2 were purchased from Sigma Aldrich and used without further purification.

2.2. Synthesis of $[\{\eta^2\text{-}N(PPh_2Se)_2\}_2Sr(THF)_2]$ (2)

Route 1: in a 10 mL sample vial 2 equivalents (200 mg, 0.368 mmol) of ligand **1** and 1 equivalent of $[Sr\{N(SiMe_3)_2\}_2(THF)_2]$ (101.6 mg, 0.184 mmol) are mixed together with 2 mL of THF. After 6 h of stirring, 2 mL of *n*-pentane was added to the top of it and the reaction mixture was placed in −40 °C freezer. After 12 h, pale green colored crystals of **2** were obtained. Yield 218.3 mg (90%).

Route 2: in a 50 mL pre-dried Schlenk flask potassium salt of ligand **1** $[K\{N(Ph_2PSe)_2\}]$ (200 mg, 0.344 mmol) was mixed with SrI_2 (74.0 mg, 0.172 mmol) in 10 mL of THF solvent at ambient temperature and stirred for 12 h. The white precipitate of KI was filtered off and filtrate was dried under *vacuo*. The resulting white compound was further purified by washing with pentane and crystals of **2** suitable for X-ray analysis can be grown from THF/pentane (1:2 ratios) mixture at −40 °C. Yield 196.3 mg (86%).

^1H NMR (400 MHz, C_6D_6): δ 8.07 (bs, 8H, ArH), 6.90 (bs, 12H, ArH), 3.58 (m, 8H, CH_2 of THF), 1.39 (m, 8H, CH_2 of THF) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 128.2 (ArC), 127.9 (ArC), 127.7(ArC), 67.8 (THF), 25.6 (THF) ppm. $^{31}P\text{–}\{^1H\}$NMR (161.9 MHz, C_6D_6): 43.3 ppm. FT-IR (selected frequencies): 1433 (P–C), 899 (P–N), 539 (P=Se) cm^{-1}.

Elemental analysis: $C_{56}H_{56}N_2O_2P_4Se_4Sr$ (1316.37) calcd. C 51.09 H 4.29 N 2.13; found C 50.88 H 4.06 N 2.01.

2.3. Synthesis of $[\{\eta^2\text{-}N(PPh_2Se)_2\}_2Ba(THF)_3]$ (3)

Route 1: in a 10 mL sample vial two equivalents (200 mg, 0.368 mmol) of ligand **1** and 1 equivalent of $[Ba\{N(SiMe_3)_2\}_2(THF)_2]$ (110.8 mg, 0.184 mmol) were mixed together with 2 mL of THF. After 3 h of stirring at ambient temperature, 2 mL of *n*-pentane was added to it and the reaction mixture was kept in −40 °C freezer. After 12 h pale green colored crystals of **3** were obtained. Yield 225.0 mg (85%).

Route 2: in a 50 mL pre-dried Schlenk flask potassium salt of ligand **1** $[K\{N(Ph_2PSe)_2\}]$ (200 mg, 0.344 mmol) was mixed with BaI_2 (67.3 mg, 0.172 mmol) in 10 mL THF solvent at ambient temperature and stirred for 12 h. The white precipitate of KI was filtered off and filtrate was dried under *vacuo*. The resulting white compound was further purified by washing with pentane and crystals suitable for X-ray analysis are grown from THF/pentane (1:2 ratios) mixture solvent at −40 °C. Yield 202.0 mg (82%).

^1H NMR (400 MHz, C_6D_6): δ 8.16 (bs, 8H, ArH), 6.93–6.98 (m, 12H, ArH), 3.57(m, 12H, CH_2 of THF), 1.38 (m, 12H, CH_2 of THF) ppm. $^{13}C\text{–}\{^1H\}$NMR (100 MHz, C_6D_6): 131.7 (P attached *o*-ArC), 129.9(P attached ArC), 128.1 (P attached *p*-ArC), 127.9 (P attached *m*-ArC), 67.8 (THF), 25.6 (THF) ppm. $^{31}P\text{–}\{^1H\}$NMR (161.9 MHz, C_6D_6): 43.7 ppm. FT-IR (selected frequencies): 1434 (P–C), 934 (P–N), 538 (P=Se) cm^{-1}.

Elemental analysis: $C_{60}H_{64}BaN_2O_3P_4Se_4$ (1438.22) calcd. C 50.11 H 4.49 N 1.95; found C 50.02 H 3.93 N 1.73.

2.4. Synthesis of $[\eta^2\text{-}N(PPh_2Se)Li(THF)_2]$ (4)

In a 10 mL sample vial one equivalent (100 mg, 0.184 mmol) of ligand **1** and one equivalent of $LiCH_2SiMe_3$ (17.4 mg, 0.184 mmol) were mixed together along with 2 mL of THF. After 6 h of stirring at ambient temperature, 2 mL of *n*-pentane was added onto it and kept in −40 °C. After 3 h cube shaped colourless crystals of **4** were obtained. Yield 114.8 mg (90%). ^1H NMR (400 MHz, C_6D_6): δ 8.38–8.44 (m, 8H, ArH), 7.04–7.08 (m, 8H, ArH), 6.95–6.99 (m, 4H, ArH), 3.49 (m, 8H, CH_2 of THF), 1.26 (m, 8H, CH_2 of THF) ppm. $^{13}C\text{–}\{^1H\}$ NMR (100 MHz, C_6D_6): δ 142.6 (P-ArC),141.7 (P-ArC), 131.6 (P attached *o*-ArC), 131.5 (P attached *o*-ArC), 129.6 (P attached *p*-ArC), 128.1 (P attached *m*-ArC), 127.6 (P attached *m*-ArC), 68.3 (THF), 25.3 (THF) ppm. $^{31}P\text{–}\{^1H\}$NMR (161.9 MHz, C_6D_6): δ 42.9 ppm. FT-IR (selected frequencies): ν = 1432 (P–C), 931 (P–N), 540 (P=Se) cm^{-1}.

Elemental analysis: $C_{32}H_{36}LiNO_2P_2Se_2$ (693.42) calcd. C 55.43 H 5.23 N 2.02; found C 54.99 H 5.01 N 1.87.

2.5. Single crystal X-ray structure determinations

Single crystals of compounds **2**–**4** were grown from a solution of THF/pentane mixture (1:2) under inert atmosphere at a temperature of −40°C. In each case a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made on an Oxford Supernova X-calibur Eos CCD detector with graphite-monochromatic CuKα (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarized below. The structures were solved by direct methods (SIR92) [60] and refined on F^2 by full-matrix least-squares methods; using SHELXL-97 [61]. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The function R_1 and wR_2 were $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 926079 (**2**), 926077 (**3**), 926078 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223 336 033; email: deposit@ccdc.cam.ac.uk).

2: $C_{56}H_{56}N_2O_2P_4Se_4Sr$; $FW = 1316.37$; (CCDC 926079), Orthorhombic, $P\,b\,c\,a$; lattice constants $a = 10.9194(6)$ Å, $b = 17.2140(6)$ Å, $c = 29.4632(9)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 5538.1(4)$ Å^3; $T = 150(2)$ K, $\lambda = 1.54184$ Å; $Z = 4$; $D_{calc} = 1.579$ g cm^{-3}; $\mu(\text{Cu-}K_\alpha) = 5.781$ mm^{-1}; $\theta_{max.} = 70.77$; 14,408 [$R_{int} = 0.0423$] independent reflections measured, of which 5242 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.547 and −0.601 e/A^{-3}; 313 parameters, $R1$ ($I > 2\sigma(I)$) = 0.0370; w$R2$ (all data) = 0.1045.

3: $C_{60}H_{64}BaN_2O_3P_4Se_4$; $FW = 1438.18$; (CCDC 926077), monoclinic, $C\,2/c$; lattice constants $a = 33.7336(18)$ Å, $b = 11.8971(10)$ Å, $c = 18.1604(10)$ Å; $\alpha = \gamma = 90°$, $\beta = 104.155$; $V = 7067.1(8)$ Å^3; $T = 150(2)$ K, $\lambda = 1.54184$ Å; $Z = 4$; $D_{calc} = 1.352$ g cm^{-3}; $\mu(\text{Cu-}K_\alpha) = 7.88$ mm^{-1}; $\theta_{max.} = 70.96$; 14,980 [$R_{int} = 0.0392$] independent reflections measured, of which 6696 were considered observed with $I > 2\sigma(I)$; max. Residual electron density 2.720 and −0.819 e/A^{-3}; 335 parameters, $R1$ ($I > 2\sigma(I)$) = 0.0688; w$R2$ (all data) = 0.2321.

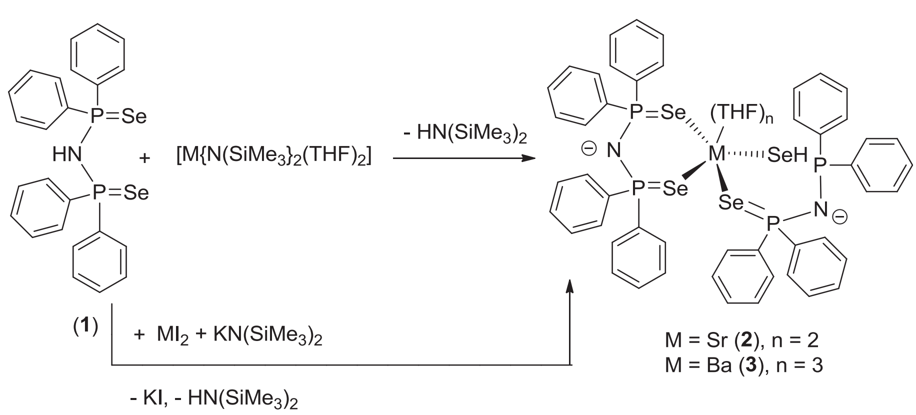
4: $C_{32}H_{36}LiNO_2P_2Se_2$; $FW = 693.42$; (CCDC 926078), monoclinic, $C\ c$; lattice constants $a = 22.0095(5)$ Å, $b = 9.1496(2)$ Å, $c = 17.3861(5)$ Å; $\alpha = \gamma = 90°$, $\beta = 113.821(3)$; $V = 3202.92(14)$ Å^3; $T = 150(2)$ K, $\lambda = 1.54184$ Å; $Z = 4$; $D_{calc} = 1.438$ g cm^{-3}; $\mu(\text{Cu-}K_\alpha) = 4.052$ mm^{-1}; $\theta_{max.} = 70.69$; 6127 [$R_{int} = 0.0200$] independent reflections measured, of which 3804 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.538 and −0.642 e/A^{-3}; 335 parameters, $R1$ ($I > 2\sigma(I)$) = 0.0292; w$R2$ (all data) = 0.0770.

3. Results and discussion

The heavier alkaline earth metal complexes **2** and **3** were prepared in good yield by two synthetic routes. In the first route the diselenoimidodiphosphine (**1**) is treated with alkaline earth metal bis(trimethylsilyl)amide in THF at ambient temperature to afford the respective strontium and barium complexes of molecular formula $[\{\eta^2\text{-N(PPh}_2\text{Se)}_2\}_2\text{Sr(THF)}_2]$ (**2**) and $[\{\eta^2\text{-N(PPh}_2\text{Se)}_2\}_2\text{Ba(THF)}_3]$ (**3**) via the elimination of volatile bis(trimethylsilyl) amine. In second method, the compounds **2** and **3** can also be obtained by the reaction of respective alkaline earth metal diiodides with potassium salt of diselenoimidodiphosphine $[\text{K}\{\text{N(Ph}_2\text{PSe)}_2\}]$ which was prepared according to the literature procedure involving **1** and potassium bis-trimethylsilylamide [33]. The novel alkaline earth metal complexes **2**–**3** were characterized by analytical/spectroscopic techniques and the molecular structures of both strontium and barium diselenoimidodiphosphinato complexes were determined by single crystal X-ray diffraction analyses (Scheme 1).

A strong absorption at 539 cm^{-1} (for **2**), and 538 cm^{-1} (for **3**) in FT IR spectra indicates the evidence of P=Se bond into the each complex. However, the P=Se bond stretching frequencies for compound **2** and **3** is shifted to lower value compared to the neutral ligand **1** (595 cm^{-1}) due slight elongation of P–Se bond [56]. In ^{1}H NMR spectra, the amino proton of the ligand **1** which was present at 4.42 ppm is absent. The multiplet signals at 3.49 and 1.26 ppm (for **2**) 3.58 and 1.39 ppm (for **3**) can be assigned for solvated THF molecules coordinated to the metal centre. One set of signals for the phenyl protons are also observed which is in the same range to that of ligand **1** indicating no significant effect of metal atoms onto the phenyl groups due to complex formation. In ^{31}P{^{1}H} NMR spectra, in complexes **2**–**3**, all the phosphorus atoms present in the two diselenoimidodiphosphinato moieties are chemically equivalent and show only one signal at 43.3 ppm and 43.7 ppm respectively and these values are significantly high field shifted to that of compound **1** (52.6 ppm) upon coordination of strontium or barium atom onto the selenium atom of the diselenoimidodiphosphinato ligand. This observation is opposite to our previous studies where we noticed a down field shift for the resonance of phosphorus atoms (71.9 ppm for Ca, 71.8 ppm for Sr and 71.9 for Ba) bound to heavier alkaline earth metals compared to free phosphinoselenoic amido ligand (58.0 ppm) [31].

Although there has been ongoing interest in alkaline earth organometallics [62] and particularly in the cyclopentadienyl chemistry of these elements [63], **2**–**3** represents – to the best of our knowledge – the first diselenoimidodiphosphinato alkaline earth



Scheme 1. Synthesis of diselenoimidodiphosphinato strontium (**2**) and barium (**3**) complexes by two synthetic routes.

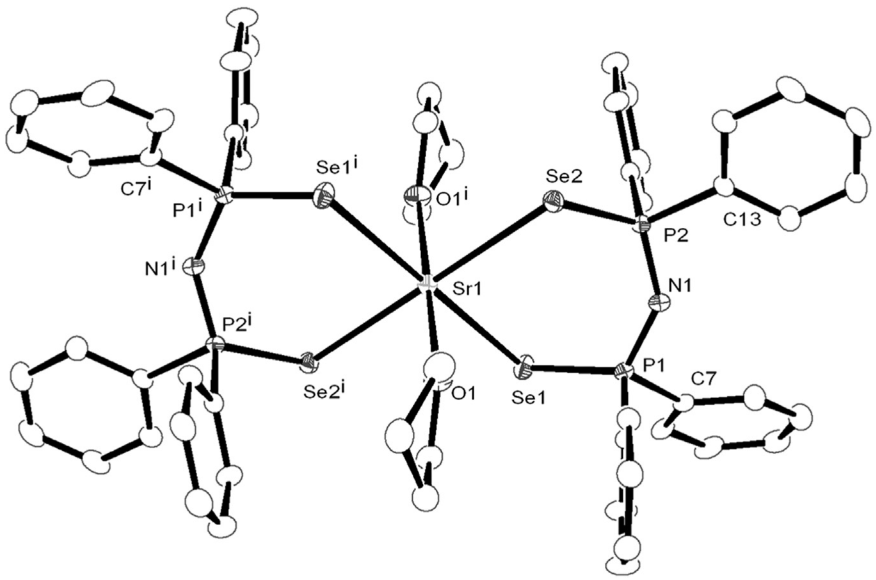


Fig. 1. ORTEP diagram of **2** with thermal displacement parameters drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]. P(1)–N(1) 1.588(3), P(2)–N(1) 1.581(3), P(1)–Se(1) 2.1515(8), P(2)–Se(2) 2.1583(8), P(1)–C(1) 1.822(3), P(1)–C(7) 1.819(3), P(2)–C(13) 1.821(3), P(2)–C(19) 1.823(3), Sr(1)–Se(1) 3.1013(4), Sr(1)–Se(1)^{i} 3.1013(3), Sr(1)–Se(2) 3.1262(3), Sr(1)–Se(2)^{i} 3.1262(3), Sr(1)–O(1) 2.523(2) Sr(1)–O(1)^{i} 2.523(2) N(1)–P(1)–Se(1) 120.79(10), N(1)–P(2)–Se(2) 120.01(10), P(1)–N(1)–P(2) 141.44(18), Se(1)–Sr(1)–Se(2) 94.512(9), P(1)–Se(1)–Sr(1) 104.96(2), P(2)–Se(2)–Sr(1) 103.23(2), N(1)–P(1)–C(1) 106.95(14), N(1)–P(1)–C(7) 105.39(14), N(1)–P(2)–C(13) 105.45(14), N(1)–P(2)–C(19) 110.25(14), O(1)–Sr(1)–Se(1) 91.43(6), O(1)^{i}–Sr(1)–Se(1) 88.57(6), O(1)^{i}–Sr(1)–O(1) 180.0, O(1)–Sr(1)–Se(2) 86.89(6), O(1)–Sr(1)–Se(2)^{i} 93.11(6).

metal complexes. Therefore, their molecular structures in the solid state were determined by X-ray diffraction analysis. The strontium complex **2** crystallizes in orthorhombic space group *P bca* having four molecules in the unit cell. Structural parameters for compound **2** are given in experimental section. The molecular structure of compound **2** is shown in Fig. 1. In the centrosymmetric molecule **2**, the coordination polyhedron is formed by two monoanionic $\{N(Ph_2P(Se))\}^-$ ligands, and two THF molecules which are *trans* to each other. Each $\{N(Ph_2P(Se)\}^-$ ligand coordinates to the strontium atom via chelation of two selenium atoms having a distance of 3.1013(4) Å. The amido nitrogen is not coordinating to the strontium atom as Sr1–N1 distance of 4.422 Å is very high. The Sr1–Se distance (3.1013(4) and 3.1262(3) Å) are within the range of Sr–Se distance 3.1356(9) Å for $[Sr(THF)_2\{Ph_2P(Se)N(CHPh_2)\}_2]$ reported by us [31], (3.138(7)–3.196(9) Å) for $[(THF)_3Sr(Se_2PPh_2)_2]$ published very recently by Westerhausen et al., and (3.066(1) Å) for the complex $[Sr\{Se(2,4,6\text{-}t\text{Bu}_3C_6H_2)\}_2(THF)_4]$ [24]. The center metal is additionally ligated by two THF molecules having Sr–O distance of 2.523(2) Å to adopt the strontium atom distorted octahedron geometry. The P1–N1–P2 angle of 141.44(18)° is slightly more than that (130.3(3)° and 133.1(3))° of diselenoimidodiphosphinato cobalt complex $[Co\{N(Ph_2PSe)_2\}_2]$ reported by Novosad et al. [49] Thus two six-membered metallacycles Sr1–Se1–P1–N1–P2–Se2 and Sr1–Se1^{i}–P1^{i}–N1^{i}–P2^{i}–Se2^{i} are formed due to ligation of two ligand moieties via selenium atoms. The plane containing P1, Se1, Sr1 makes a dihedral angle of 28.39° with the plane having P2, Se2, Sr1 atoms. The six-membered $SrSe_2P_2N$ metallacycle is nonplanar and adopt a twisted boat conformation. For the metallacycle Sr1–Se1–P1–N1–P2–Se2, the atoms P2 and Se1 reside 0.668 Å and 0.521 Å above the mean plane having Sr1, Se1, P1, N1, P2, Se2 atoms respectively whereas Sr1 (0.076 Å), Se2 (0.092 Å), N1(0.046 Å) and P1(0.312 Å) are located below the mean plane.

The P–Se bond distances (2.1515(8) and 2.1583(8) Å) and P–N bond distances (1.588(3) and 1.581(3) Å) are within the range to that of (2.0992(14) and 2.1913(13) Å) and (1.577(7) and 1.609(4) Å) respectively for $[Co\{N(Ph_2PSe)_2\}_2]$ [49].

In contrast to the strontium complex **2**, barium diselenoimidodiphosphinato complex **3** crystallizes in the monoclinic space group *C*2/c having four molecules of **3** in the unit cell. The details of the structural parameters are given in the experimental section. The solid state structure of the complex **3** is given in Fig. 2. Similar with strontium complex, in the barium complex **3,** the coordination polyhedron is formed by two $\{\{N(Ph_2PSe)_2\}^-$ ligands, and three THF molecules. As expected from the larger atomic radius of Ba^{2+} [64], Ba1–O (2.707(5), 2.796(8) Å), and Ba1–Se (3.3842(8), 3.3524(8) Å) distances are elongated in comparison with the corresponding values determined for the Sr^{2+} complexes **2** (Sr–O 2.523(2) Å and Sr–Se 3.1013(4) and 3.1262(3) Å). However the Ba–O and Ba–Se distances are within the range to that (Ba–O 2.716(6) and Ba–Se 3.3553(10) Å) our previously observed barium compound $[Ba(THF)_2\{Ph_2P(Se)N(CHPh_2)\}_2]$ [31] and also within the range of reported value 3.2787(11) Å for the complex $[Ba(THF)_4(SeMes^*)_2]$ (Mes* = $2,4,6\text{-}t\text{Bu}_3C_6H_2$) and 3.2973(3) Å for $[Ba(Py)_3(THF)\text{-}(SeTrip)_2\}_2]$ (Trip = 2,4,6 $i\text{Pr}_3C_6H_2$) reported by Ruhlandt-Senge et al. [23]. Thus the central atom barium adopts a distorted pentagonal bipyramidal geometry due to coordination from two **1** moieties and three THF molecules. Two six-membered metallacycles Ba1–Se1–P1–N1–P2–Se2 and Ba1–Se1^{i}–P1^{i}–N1^{i}–P2^{i}–Se2^{i} are formed due to ligation of two ligand moieties via selenium atoms. In complex **3**, the six-membered $BaSe_2P_2N$ metallacycle is nonplanar and adopts a twisted boat conformation similar to that of strontium complex **2**. For the metallacycle Ba1–Se1–P1–N1–P2–Se2, the atoms P2 and Se1 reside 0.437 Å and 0.527 Å above the mean plane having Ba1, Se1, P1, N1, P2, Se2 atoms respectively whereas Ba1 (0.140 Å), Se2 (0.129 Å), N1(0.083 Å) and P1(0.613 Å) are located below the mean plane. Similar to strontium complex, no interaction between the amido nitrogen and barium atom was observed. Nevertheless complex **3** is another example of barium seleno complex having barium selenium direct contact.

Lithium complex: alkali metal salts are important precursors for salt metathesis reaction. Various alkali metal salts of $\{N(PR_2Se)_2\}$ ligand are known, however the $[Li\{N(P(^{i}pr)_2Se)_2\}]$ was prepared by

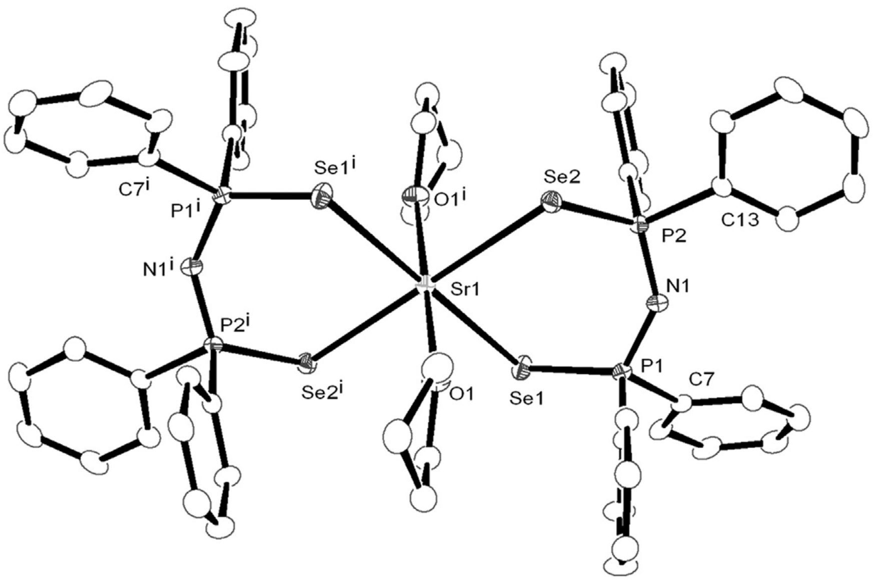
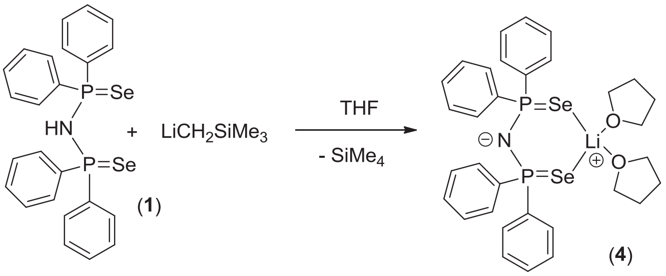


Fig. 2. ORTEP diagram of **3** with thermal displacement parameters drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]. P(1)–N(1) 1.588(5), P(2)–N(1) 1.585(5), P(1)–Se(1) 2.1393(14), P(2)–Se(2) 2.1440(17), P(1)–C(1) 1.818(6), P(1)–C(7) 1.819(6), P(2)–C(13) 1.821(7), P(2)–C(19) 1.811(6), Ba(1)–Se(1) 3.3842(8), Ba(1)–Se(1)^{i} 3.3842(8), Ba(1)–Se(2) 3.3524(8), Ba(1)–Se(2)^{i} 3.3524(8), Ba(1)–O(1) 2.796(8), Ba(1)–O(2) 2.707(5), Ba(1)–O(2)^{i} 2.707(5), N(1)–P(1)–Se(1) 119.5(2), N(1)–P(2)–Se(2) 121.0(2), P(1)–N(1)–P(2) 135.3(3), Se(1)–Ba(1)–Se(2) 82.371(19), P(1)–Se(1)–Ba(1) 101.68(4), P(2)–Se(2)–Ba(1) 114.06(5), N(1)–P(1)–C(1) 103.8(3), N(1)–P(1)–C(7) 110.1(3), N(1)–P(2)–C(13) 107.9(3), N(1)–P(2)–C(19) 105.0(3), O(2)–Ba(1)–O(1) 76.69(14), O(2)–Ba(1)–O(2)^{i} 153.4(3), O(1)–Ba(1)–Se(2) 67.253(17), O(2)–Ba(1)–Se(2) 78.68(11).

Chivers et al. involving the reaction of *n*-BuLi and [HN(P(^{i}Pr)$_2$Se)$_2$] in the presence of TMEDA at −78° [32]. Here we report an alternative method to synthesize the lithium salt of diselenoimidodiphosphinato ligand without using TMEDA. The treatment of **1** with LiCH$_2$SiMe$_3$ in 1:1 M ratio in THF at ambient temperature afforded the lithium salt of molecular formula [η^2-N(PPh$_2$Se)Li(THF)$_2$] (**4**) through the elimination of volatile tetramethylsilane in good yield (Scheme 2). The compound **4** was characterized by analytical/spectroscopic technique and the solid state structure of the complex **4** was determined by single crystal X-ray diffraction analysis.

In ^{1}H NMR spectra of **4**, the coordinated THF molecules appear at 3.49 and 1.26 ppm as multiplet along with the phenyl protons in the expected range. The ^{31}P{^{1}H} NMR spectra one singlet is observed at 42.9 ppm indicating both the phosphorus atoms are magnetically equivalent. Compound **4** was recrystallized from THF/pentane (1:2) and crystallizes in monoclinic space group *Cc* having four molecules in the unit cell. The solid state structure of the complex **4** is given in Fig. 3. The details of the structural parameters are given in Section 2. The coordination polyhedron of the complex **4** is formed by the chelation of two selenium atoms of the ligand moiety along with two THF molecules. No interaction between amido nitrogen and lithium atoms was observed. Li–Se distances 2.598(7) and 2.606(7) Å are within the range to that of (2.556(9) and 2.52(8) Å) previously reported [η^2-N(P(^{i}pr)$_2$Se)Li(TMEDA)] complex [32]. The Li–O distances of 1.950(7) and 1.932(7) Å are within the reported values. The lithium atom adopts a distorted tetrahedral geometry due to the ligation of two selenium atoms and two THF molecules.



Scheme 2. Synthesis of diselenoimidodiphosphinato lithium compound **4**.

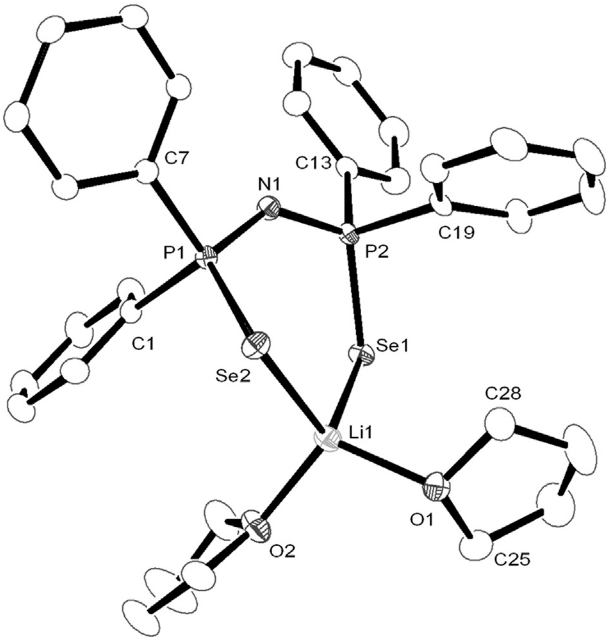


Fig. 3. ORTEP diagram of **4** with thermal displacement parameters drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]. P(1)–N(1) 1.594(3), P(2)–N(1) 1.597(3), P(1)–Se(2) 2.1453(9), P(2)–Se(1) 2.1462(9), P(1)–C(1) 1.827(3), P(1)–C(7) 1.819(4), P(2)–C(13) 1.822(3), P(2)–C(19) 1.825(3), Li(1)–Se(1) 2.598(7), Li(1)–Se(2) 2.606(7) Li(1)–O(1) 1.950(7), Li(1)–O(2) 1.932(7), N(1)–P(1)–Se(2) 120.19(12), N(1)–P(2)–Se(1) 119.79(11), P(1)–N(1)–P(2) 133.7(2), Se(1)–Li(1)–Se(2) 113.2(2), P(1)–Se(2)–Li(1) 93.27(15), P(2)–Se(1)–Li(1) 98.44(15), N(1)–P(1)–C(1) 108.56(16), N(1)–P(1)–C(7) 103.27(16), N(1)–P(2)–C(13) 104.41(16), N(1)–P(2)–C(19) 108.17(17), O(2)–Li(1)–O(1) 109.7(3), O(2)–Li(1)–Se(1) 105.5(3), O(1)–Li(1)–Se(1) 105.5(3), O(2)–Li(1)–Se(2) 111.9(3).

The six-membered ring $LiSe_2P_2N$ formed by Li1, Se1, P1, N1, P2, Se2 atoms are not coplanar and adopt a twisted boat conformation similar to that of strontium complexes **2** and **3.** For the metallacycle Li1–Se1–P2–N1–P1–Se2, the atoms Se2 (0.403 Å), P2 (0.509 Å), N1 (0.013 Å) above the weighted least-squares best plane having Ba1, Se1, P1, N1, P2, Se2 atoms whereas Li1 (0.053 Å), P1 (0.566 Å) and Se1 (0.280 Å) are located below the mean plane.

4. Conclusion

In conclusion, we have reported the missing group 2 metal complexes of diselenoimidodiphosphinato by synthesizing strontium and barium complexes via two synthetic routes using diselenoimidodiphosphinato ligand. In first method silylamide route and in the second method salt metathesis route was used to prepare the target compounds. Strontium complex **2** adopted distorted octahedral geometry whereas geometry of the larger barium atom in complex **3** can be best described as distorted pentagonal bipyramidal and the M–Se bond distances are increasing from Sr–Se to Ba–Se bond. Finally, synthesis of the lithium diselenoimidodiphosphonato complex was achieved by the deprotonation of the ligand with $LiCH_2SiMe_3$, and the molecular structure of the lithium complex obtained was disclosed by the X-ray analysis.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.04.056.

References

[1] S. Harder, Chem. Rev. 110 (2010) 3852–3876.
[2] S. Kobayashi, Y. Yamashita, Acc. Chem. Res. 44 (2011) 58–71.
[3] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, Chem. Rev. 104 (2004) 6147–6176.
[4] C.M. Thomas, Chem. Soc. Rev. 39 (2010) 165–173.
[5] X. Xu, Y. Chen, G. Zou, Z. Ma, G. Li, J. Organomet. Chem. 695 (2010) 1155–1162.
[6] Y. Sarazin, D. Rosca, V. Poirier, T. Roisnel, A. Silvestru, L. Maron, J.-F. Carpentier, Organometallics 29 (2010) 6569–6577.
[7] Y. Sarazin, B. Liu, T. Roisnel, L. Maron, J.-F. Carpentier, J. Am. Chem. Soc. 133 (2011) 9069–9087.
[8] P. Jochmann, T.S. Dols, T.P. Spaniol, L. Perrin, L. Maron, J. Okuda, Angew. Chem. Int. Ed. 48 (2009) 5715–5719 (and the references therein).
[9] M.H. Chisholm, J.C. Gallucci, K. Phomphrai, Inorg. Chem. 43 (2004) 6717–6725.
[10] C.F. Caro, P.B. Hitchcock, M.F. Lappert, Chem. Commun. (1999) 1433–1434.
[11] S. Harder, Organometallics 21 (2002) 3782–3787.
[12] S. Datta, P.W. Roesky, S. Blechert, Organometallics 26 (2007) 4392–4394.
[13] J. Jenter, R. Koppe, P.W. Roesky, Organometallics 30 (2011) 1404–1413.
[14] H. Hao, S. Bhandari, Y. Ding, H.W. Roesky, J. Magull, H.G. Schmidt, M. Noltemeyer, C. Cui, Eur. J. Inorg. Chem. (2002) 1060–1065.
[15] Y. Matsuo, H. Tsurugi, T. Yamagata, K. Mashima, Bull. Chem. Soc. Jpn. 76 (2003) 1965–1968.
[16] T.K. Panda, K. Yamamoto, K. Yamamoto, H. Kaneko, Y. Yang, H. Tsurugi, K. Mashima, Organometallics 31 (2012) 2268–2274.
[17] T.K. Panda, H. Kaneko, O. Michel, H. Tsurugi, K. Pal, K.W. Toernroos, R. Anwander, K. Mashima, Organometallics 31 (2012) 3178–3184.
[18] K.G. Caulton, L.G. Hubert-Pfalzgraf, Chem. Rev. 90 (1990) 969–995.
[19] T.P. Hanusa, Chem. Rev. 93 (1993) 1023–1036.
[20] D.E. Gindelberger, J. Arnold, Inorg. Chem. 33 (1994) 6293–6299.
[21] U. Englich, K. Ruhland-Senge, Z. Anorg. Allg. Chem. 627 (2001) 851–856.
[22] C. Kling, H. Ott, G. Schwab, D. Stalke, Organometallics 27 (2008) 5038–5042.
[23] K. Ruhlandt-Senge, K. Davis, S. Dalal, U. Englich, M.O. Senge, Inorg. Chem. 34 (1995) 2587–2592.
[24] T.M.A. Al-Shboul, G. Volland, H. Gorls, S. Krieck, M. Westerhausen, Inorg. Chem. 51 (2012) 7903–7912.
[25] K. Henke, D.A. Atwood, Inorg. Chem. 37 (1998) 224–227.
[26] S. Chadwick, U. Englich, K. Ruhlandt-Senge, Chem. Commun. (1998) 2149–2150.
[27] F.A. Banbury, M.G. Davidson, A. Martin, P.R. Raithby, R. Snaith, K.L. Verhorevoort, D.S. Wright, J. Chem. Soc. Chem. Commun. (1992) 1152–1154.
[28] P. Mikulcik, P.R. Raithby, R. Snaith, D.S. Wright, Angew. Chem. Int. Ed. 30 (1991) 428–430.
[29] A.P. Purdy, A.D. Berry, C.F. George, Inorg. Chem. 36 (1997) 3370–3375.
[30] K. Ruhlandt-Senge, U. Englich, Chem. Eur. J. 6 (2000) 4063–4070.
[31] R.K. Kottalanka, K. Naktode, S. Anga, Hari Pada Nayek, T.K. Panda, Dalton Trans. 42 (2013) 4947–4956.
[32] S.D. Robertson, T. Chivers, Dalton Trans. (2008) 1765–1772.
[33] P. Bhattacharyya, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1995) 2489–2495.
[34] V. Garcia-Montalvo, J. Novosad, P. Kilian, J.D. Woollins, A.M.Z. Slawin, P. Garcia y Garcia, M. Loepez-Cardoso, G. Espinosa-Perez, R. Cea-Olivares, J. Chem. Soc. Dalton Trans. (1997) 1025–1029.
[35] M.-A. Munoz-Hernandez, A. Singer, D.A. Atwood, R. Cea-Olivares, J. Organomet. Chem. 571 (1998) 15–19.
[36] K. Darwin, L.M. Gilby, P.R. Hodge, B. Piggott, Polyhedron 18 (1999) 3729–3733.
[37] L. Flores-Santos, R. Cea-Olivares, S. Hernandez-Ortega, R.A. Toscano, V. Garcia-Montalvo, J. Novosad, J.D. Woollins, J. Organomet. Chem. 544 (1997) 37–41.
[38] R. Cea-Olivares, J. Novosad, J.D. Woollins, A.M.Z. Slawin, V. Garcıá-Montalvo, G. Espinosa-Perez, P. Garcia y Garcia, Chem. Commun. (1996) 519–520.
[39] D.J. Crouch, M. Helliwell, P. O'Brien, J.-H. Park, J. Waters, D.J. Williams, J. Chem. Soc. Dalton Trans. (2003) 1500–1504.
[40] R. Cea-Olivares, G. Canseco-Melchor, V. Garcia-Montalvo, S. Hernandez-Ortega, J. Novosad, Eur. J. Inorg. Chem. (1998) 1573–1576.
[41] J. Novosad, S.V. Lindeman, J. Marek, J.D. Woollins, St. Husebye, Heteroatom Chem. 9 (1998) 615–621.
[42] V. Bereau, P. Sekar, C.C. McLauchlan, J.A. Ibers, Inorg. Chim. Acta 308 (2000) 91–96.
[43] J.M. German-Acacio, M. Reyes-Lezama, N. Zun iga-Villarreal, J. Organomet. Chem. 691 (2006) 3223–3231.
[44] N. Zuniga-Villarreal, J.M. German-Acacio, A.A. Lemus-Santana, M. Reyes-Lezama, R.A. Toscano, J. Organomet. Chem. 689 (2004) 2827–2832.
[45] R. Rossi, A. Marchi, L. Marvell, L. Magon, M. Peruzzini, U. Casellato, R. Graziani, J. Chem. Soc. Dalton Trans. (1993) 723–729.
[46] W.-H. Leung, K.-K. Lau, Q.-F. Zhang, W.-T. Wong, B. Tang, Organometallics 19 (2000) 2084–2089.
[47] 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.
[48] J. Parr, M.B. Smith, M.R.J. Elsegood, J. Organomet. Chem. 664 (2002) 85–93.
[49] J. Novosad, M. Necas, J. Marek, P. Veltsistas, Ch. Papadimitriou, I. Haiduc, M. Watanabe, J.D. Woollins, Inorg. Chim. Acta 290 (1999) 256–260.
[50] C. Papadimitriou, P. Veltsistas, J. Novosad, R. Cea-Olivares, A. Toscano, P. Garcıa y Garcia, M. Lopez-Cardoso, A.M.Z. Slawin, J.D. Woollins, Polyhedron 16 (1997) 2727–2729.
[51] H. Liu, N.A.G. Bandeira, M.J. Calhorda, M.G.B. Drew, V. Felix, J. Novosad, F. Fabrizi de Biani, P. Zanello, J. Organomet. Chem. 689 (2004) 2808–2819.
[52] S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, A. Silvestru, C. Silvestru, Inorg. Chim. Acta 347 (2003) 16–22.
[53] J.D.E.T. Wilton-Ely, A. Schier, H. Schmidbaur, J. Chem. Soc. Dalton Trans. (2001) 3647–3651.
[54] C.G. Pernin, J.A. Ibers, Inorg. Chem. 39 (2000) 1222–1226.
[55] M. Geissinger, J. Magull, Z. Anorg. Allg. Chem. 623 (1997) 755–761.
[56] P. Bhattacharyya, J. Novosad, J. Phillips, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1995) 1607–1613.
[57] E.D. Brady, T.P. Hanusa, M. Pink Jr., V.G. Young Jr., Inorg. Chem. 39 (2000) 6028–6037.
[58] T.K. Panda, C.G. Hrib, P.G. Jones, J. Jenter, P.W. Roesky, M. Tamm, Eur. J. Inorg. Chem. (2008) 4270–4279.
[59] M.F. Lappert, R. Pearce, J. Chem. Soc. Chem. Commun. (1973) 126–127.
[60] M. Sheldrick, SHELXS-97, Program of Crystal Structure Solution, University of Göttingen, Germany, 1997.
[61] G.M. . Sheldrick, SHELXL-97, Program of Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[62] T.P. Hanusa, in: R.H. Crabtree, M.P. Mingos (Eds.), Comprehensive Organometallic Chemistry III, vol. 2, Elsevier, Oxford, 2007, p. 67.
[63] (a) T.P. Hanusa, Organometallics 21 (2002) 2559–2571;
(b) T.P. Hanusa, Chem. Rev. 100 (2000) 1023–1036;
(c) T.P. Hanusa, Coord. Chem. Rev. 210 (2000) 329–367.
[64.] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984.