Polyhedron 33 (2012) 107–113

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Metal complexes of an *N*-selenocarbamoyl benzamidine

Angela Bredenkamp, Xiaoqing Zeng, Fabian Mohr *

Fachbereich C, Anorganische Chemie, Bergische Universität Wuppertal, 42119 Wuppertal, Germany

ARTICLE INFO

Article history:
Received 28 October 2011
Accepted 9 November 2011
Available online 26 November 2011

Keywords:
Selenium ligands
Chelating ligands
X-ray crystal structure
NBO analysis

ABSTRACT

The *N*-selenocarbamoyl benzamidine 4-MeC_6H_4N(H)C(Ph)=NC(Se)NEt_2 (**HL**) was prepared from the reaction of the corresponding isoselenocyanate with Et_2NH. The reactivity of **HL** with various metal compounds including [Ni$(OAc)_2$], [PdCl_2(^{t}Bu$_2$bipy)], H[AuCl_4], [Au$Cl(SMe_2)$] as well as the cyclometallated species [Pd(OAc){κ*C*,*N*-C_6H_4N(Me)N=O}]$_2$ was studied. In the case of the Ni(II) and Pd(II) compounds, square planar bis(chelate) complexes were formed in which the deprotonated *N*-selenocarbamoyl benzamidine acts as a monoanionic [*Se*,*N*]$^-$ ligand. Reaction of the gold(III) precursor with two equivalents of **HL**, resulted in reduction and formation of the gold(I) complex [Au(HL)], in which the neutral *N*-selenocarbamoyl benzamidine coordinates to the metal only *via* the selenium atom. The same coordination mode of the *N*-selenocarbamoyl benzamidine is observed in the gold(I) salt [Au$(HL)_2$]Cl. Both these complexes are also accessible from the reaction of [Au$Cl(SMe_2)$] with one or two equivalents of **HL**. The electronic structure of the ligand was studied using computational methods.

1. Introduction

In 1984, the group of Beyer reported that the reaction of nickel(II) thioureato bis(chelates) react with $SOCl_2$ to give good yields of *N*-(amino-thiocarbonyl)benzimido chlorides, which can be further functionalised by reaction with primary amines to give the corresponding *N*-thiocarbamoyl benzamidines (Scheme 1) [1,2].

These *N*-thiocarbamoyl benzamidines react with various metal salts to give bis(chelate) complexes in which the deprotonated, monoanionic *N*-thiocarbamoyl benzamidine coordinates to the metal through the sulfur and nitrogen atoms forming M–S–C–N–C–N heterocycles (Scheme 2). Examples of bis(chelate) complexes containing *N*-thiocarbamoyl benzamidines have been reported with metals including Cu(II), Ni(II), Co(II), Pt(II) and Pd(II) [2–8]. Such compounds can therefore be considered nitrogen analogues of thioureas, which form M–S–C–N–C–O cycles (Scheme 2).

In marked contrast, the chemistry of their selenium counterparts, the *N*-selenocarbamoyl benzamidines, is virtually unexplored. Beyer reported that whilst the *N*-(aminoselenocarbonyl)benzimido chlorides are not accessible from the corresponding Ni(II) bis(selenoureato) complexes, they can however be prepared from the reaction of *N*-acyl selenoureas with thiophosgene (Scheme 3) [9].

The group of Heimgartner more recently reported an alternative synthesis procedure which leads directly to *N*-selenocarbamoyl benzamidines from the corresponding isoselenocyanates, which are readily accessible in two-steps from *N*-aryl benzamides (Scheme 4) [10].

In continuation of our exploration of the coordination chemistry of organoselenium compounds [11–19], we wished to study the reactivity of the *N*-selenocarbamoyl benzamidine 4-MeC_6H_4N(H)C(Ph)=NC(Se)NEt_2 (**HL**) with various transition metal compounds. Some results of this investigation are reported herein.

2. Results and discussion

Following the Heimgartner procedure [10], we prepared isoselenocyanate **A** in two steps from *N*-(*p*-tolyl)benzamide. The isoselenocyanate was subsequently reacted with Et_2NH to afford 4-MeC_6H_4N(H)C(Ph)=NC(Se)NEt_2 (**HL**) as a stable, orange-yellow solid in 76% yield (Scheme 5).

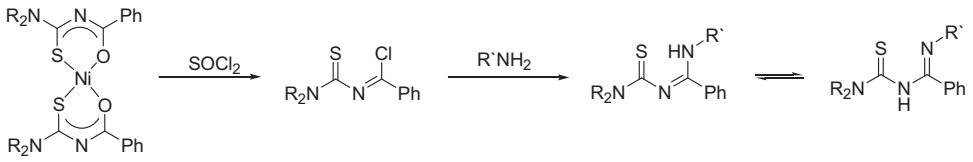
The identity of **HL** was confirmed by NMR spectroscopy (see Section 4) and also by single crystal X-ray diffraction (Fig. 1).

The solid-state structure of **HL** is very similar to that of the morpholino derivative reported by Heimgartner [10]. Here too, the NH proton is located on the nitrogen atom between the two aryl rings (N3) and not (as is the case in the selenoureas) on the nitrogen atom adjacent to the C–Se unit (N2). The C–N bond lengths along the N–C–N–C(Se)–NEt_2 backbone also clearly show the presence of a C=N double bond between C5 and N2. Within the asymmetric unit hydrogen bonding interactions between the selenium atom of one molecule and the N(3)–H proton of an adjacent molecule (Se···H–N distance of *ca.* 2.62 Å) can be observed. Such hydrogen bonding is also observed in the morpholino analogue (Se···H–N distance of *ca.* 2.64 Å).

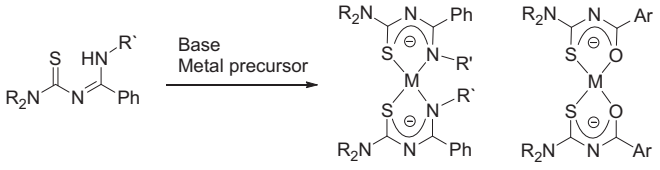
The reaction of **HL** with Ni$(OAc)_2$ gave a dark solution out of which a dark green solid precipitated in moderate yield (Scheme 6). The material was found to be insoluble or poorly soluble in

* Corresponding author.
E-mail address: fmohr@uni-wuppertal.de (F. Mohr).

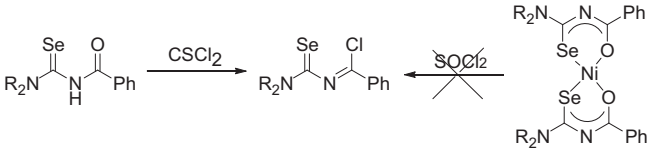
0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2011.11.008



Scheme 1.



Scheme 2.



Scheme 3.

common solvents including CH_2Cl_2, $CHCl_3$, MeOH, acetone, dmso and dmf.

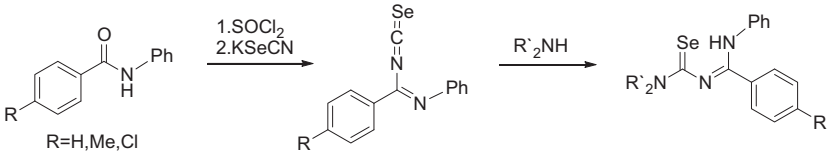
The ^1H NMR spectrum recorded in dmso was not very diagnostic. Apart from the disappearance of the NH signal, there was little change in position and multiplicity of the signals. In order to unambiguously identify the structure of the compound, an X-ray diffraction study was carried out (Fig. 2).

In complex **1** two deprotonated selenocarbamoyl benzamidine molecules coordinate to the nickel atom through the selenium atom and nitrogen atom (N3); the selenium atoms being *cis* to each other (Fig. 2). The coordination geometry about the nickel centre can be described as distorted square planar, with the six-membered rings adopting an almost boat-like conformation. These same structural features are also observed in the sulfur analogue $[Ni\{PhC(NPh)NC(S)NEt_2\}_2]$ [8]. At this point it is also appropriate to compare complex **1** with the structurally similar nickel(II) selenoureato bis(chelate) complex $[Ni\{PhC(O)NC(Se)NEt_2\}_2]$ [20]. In this compound the six-membered rings are, however, virtually planar, leading to an almost perfect square planar coordination environment around the metal. Possible reasons for these differences will be discussed below. In the selenoureato compound the selenium atoms are also *cis* to each other. The Ni–Se and Ni–N bond distances in complex **1** [2.2784(5) and 1.916(3) Å, respectively] are similar to those observed in $[Ni\{PhC(O)NC(Se)NEt_2\}_2]$ [Ni–Se = 2.244(1) Å] and $[Ni\{PhC(NPh)NC(S)NEt_2\}_2]$ [Ni–N = 1.90(1) Å], respectively.

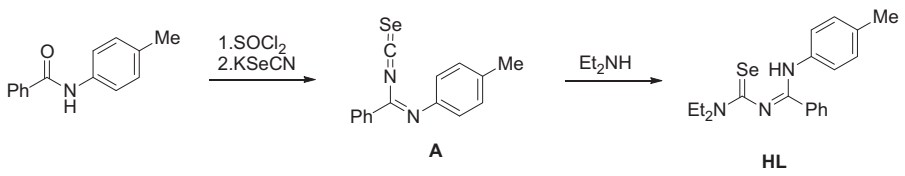
We subsequently examined the reactivity of **HL** with two palladium(II) species: **HL** reacts with $[PdCl_2(^tBu_2bipy)]$ in the presence of base to give the cationic species $[Pd(L)(^tBu_2bipy)]^+$ (**2**) which was isolated as the orange-brown PF_6 salt in good yield (Scheme 6). The proton NMR spectrum of **2** indicated that deprotonation of **HL** had occurred and doubling of all three signals from the $^tBu_2$-bipy protons was consistent with an asymmetric coordination environment about the metal. The high-resolution electrospray mass spectrum of the compound showed a strong signal corresponding to the molecular ion of the cation, whose observed isotopic distribution pattern perfectly agreed with the calculated one. Whilst we were unable to obtain X-ray quality crystals of **2**, the spectral data is consistent with the presence of a heteroleptic salt in which the deprotonated ligand is coordinated to the $^tBu_2$bipyPd unit *via* Se and N atoms. We have previously prepared and structurally characterised similar heteroleptic $^tBu_2$bipyPd(II) complexes with deprotonated thio- and selenoureas [18,21].

The cyclometallated acetato-bridged dimer $[Pd(OAc)\{\kappa C,N\text{-}C_6H_4N(Me)N{=}O\}]_2$ reacts with **HL** to give the yellow compound (**3**) in high yield (Scheme 6). No additional base is required since the acetate ions from the palladacycle are basic enough to deprotonate the ligand. The compound was fully characterised by NMR spectroscopy. The data showed again signals due to the presence of the deprotonated ligand as well as those of the cyclometallated nitrosamine. X-ray quality crystals were obtained, which allowed us to determine the solid-state structure of complex **3** (Fig. 3).

The molecule consists of the deprotonated selenocarbamoyl benzamidine coordinating to the Pd centre through the selenium and nitrogen atoms. The square planar geometry about the metal centre is completed by the nitrosamine ligand which coordinates through the arene carbon atom and the nitrogen atom of the



Scheme 4.



Scheme 5.

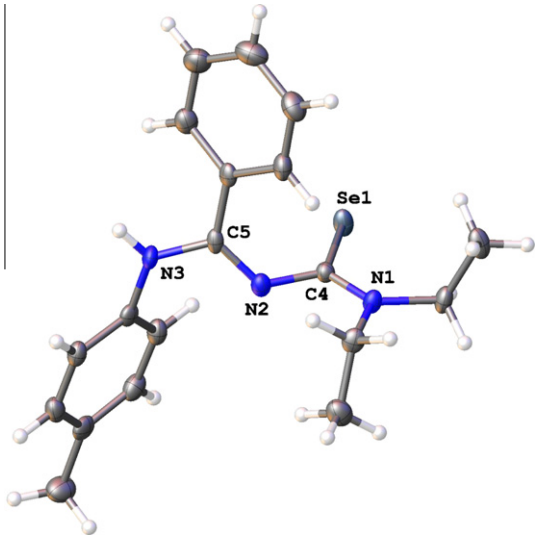


Fig. 1. Molecular structure of **HL**. Ellipsoids show 50% probability levels. Hydrogen atoms are shown as spheres with arbitrary radii. Selected bond lengths (Å): Se(1)–C(4) 1.873(3), N(1)–C(4) 1.330(4), N(2)–C(4) 1.346(4), N(2)–C(5) 1.294(4), C(5)–N(3) 1.353(4). Selected bond angles (°): N(1)–C(4)–Se(1) 123.6(2), C(4)–N(2)–C(5) 126.2(3), N(2)–C(5)–N(3) 118.9(3).

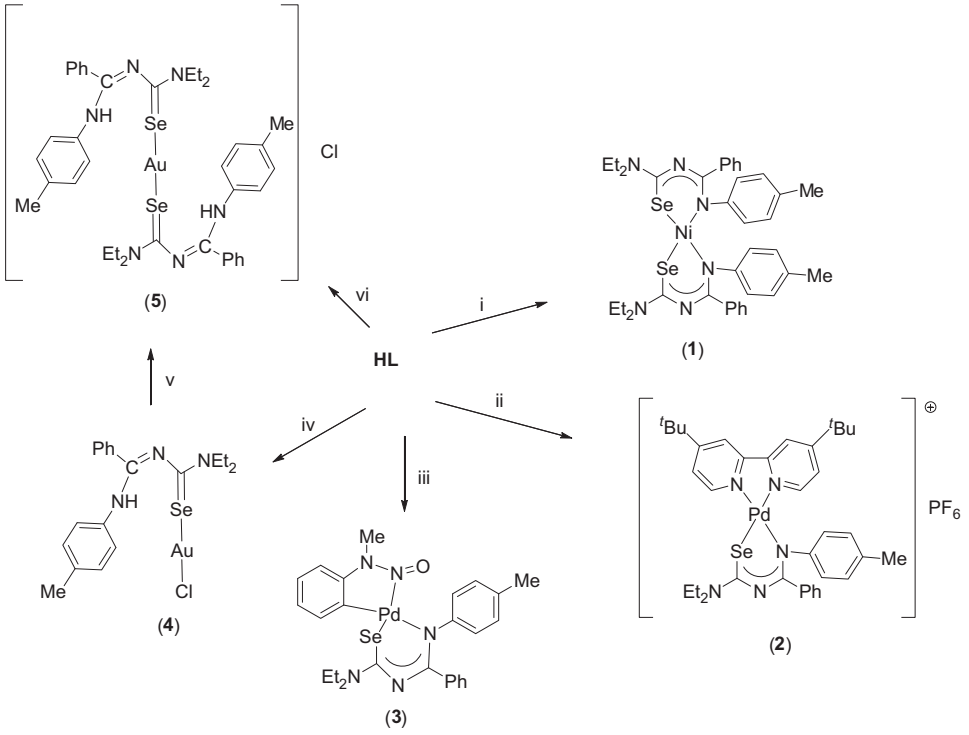
N═O group. The selenium is located *trans* to the nitrogen atom of the nitrosamine, an orientation which has previously been observed in a nitrosamine derived palladacycle containing a deprotonated selenourea ligand [15]. In this structure too, the deprotonated selenocarbamoyl benzamidine unit is not planar but adopts a boat-like conformation; the coordination geometry about the Pd centre is however square planar.

Two equivalents of **HL** react with H[$AuCl_4$] giving a yellow material (**4**) the ^{1}H NMR spectrum of which shows only the signals for neutral **HL**. A subsequent X-ray diffraction study revealed the compound to be a gold(I) chlorido complex containing the neutral selenocarbamoyl benzamidine acting as a Se-donor ligand (Fig. 4).

As expected for a gold(I) compound, the coordination geometry about the metal is linear [179.86(4)°] and the angle at the selenium atom is about 103°, typical for gold compounds containing selenium donor ligands [11]. The same is true for the gold-selenium distance which is typical for a gold(I) complex containing a neutral selenium donor ligand [11]. Complex **4** is generated by reduction of the gold(III) starting material by the selenocarbamoyl benzamidine which is itself thereby oxidised. The second equivalent of **HL** then coordinates to the $Au^{I}Cl$ unit. This behaviour of **HL** mimics that of structurally similar sulfur compounds [4]. In this case too, the thiocarbamoyl benzamidines reduce the H[$AuCl_4$] forming cyclic 1,2,4-thiadiazolium salts as oxidation products (Scheme 7). A subsequent paper reports the isolation and structural characterisation of these compounds as their $[AuCl_2]^-$ salts [22]. Analogous 1,2,4-selenadiazolium salts are known, however they are reported to be unstable and readily undergo a rearrangement reaction to give 2*H*-1,3,5-selenadiazines [23].

Upon standing in $CDCl_3$ for several days samples of **4** deposited crystals which appeared different than those of the batch used for the structure determination. An X-ray diffraction study allowed us to identify the compound as the gold(I) salt [$Au(HL)_2$]Cl in which two neutral selenocarbamoyl benzamidine ligands coordinate to the metal (Fig. 5).

Structurally salt **5** is rather similar to the neutral complex **4**. Two neutral selenocarbamoyl benzamidine ligands coordinate to the gold(I) centre in a linear fashion. The bond distances and angles are again typical for gold(I) salts containing neutral Se-donor ligands [11]. Unfortunately, there was not enough material for NMR spectroscopy; however the high-resolution electrospray mass spectrum showed a single peak whose isotopic distribution pattern corresponds to the molecular ion of the expected cation. The compound is probably formed by displacement of the chlorido ligand



Scheme 6. (i) $Ni(OAc)_2$. (ii) [$PdCl_2$(^{t}Bu$_2$bipy)], Et_3N, NH_4PF_6. (iii) [Pd(OAc){κ*C*,*N*-C_6H_4N(Me)N═O}]$_2$. (iv) 0.5 eq. H[$AuCl_4$] or [$AuCl(SMe_2)$]. (v) Standing in $CDCl_3$. (vi) 0.5 eq. [$AuCl(SMe_2)$].

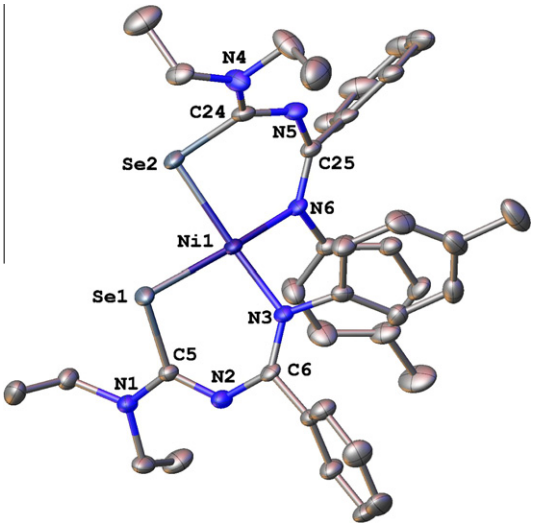


Fig. 2. Molecular structure of compound **1**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ni(1)–Se(1) 2.2784(5), Ni(1)–N(3) 1.916(3), Ni(1)–Se(2) 2.2934(5), Ni(1)–N(6) 1.915(3), Se(1)–C(5) 1.921(3), N(3)–C(6) 1.310(4), N(2)–C(6) 1.344(4), N(2)–C(5) 1.312(4), C(5)–N(1) 1.341(4). Selected bond angles (°): Ni(1)–Se(1)–C(5) 94.71(10), Se(1)–Ni(1)–Se(2) 85.139(19), Se(1)–Ni(1)–N(6) 162.27(8), Se(1)–Ni(1)–N(3) 93.18(8), Se(1)–C(5)–N(2) 124.1(2), C(5)–N(2)–C(6) 125.0(3), N(2)–C(6)–N(3) 125.9(3).

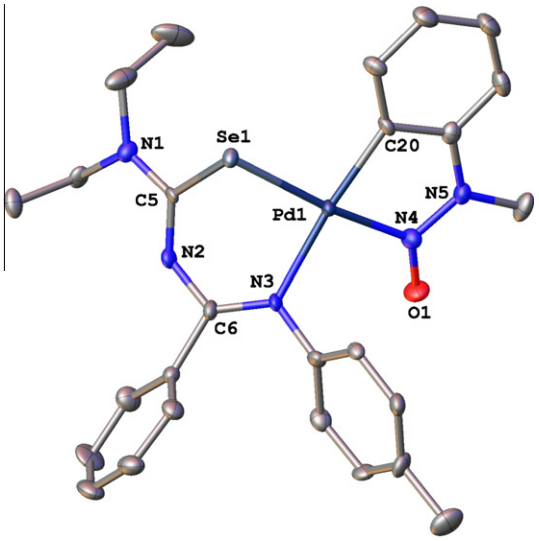


Fig. 3. Molecular structure of compound **3**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Pd(1)–Se(1) 2.3804(7), Pd(1)–N(3) 2.115(4), Pd(1)–C(20) 1.979(5), Pd(1)–N(4) 2.040(5), Se(1)–C(5) 1.929(6), C(5)–N(2) 1.295(7), N(2)–C(6) 1.369(7), C(6)–N(3) 1.301(7). Selected bond angles (°): Se(1)–Pd(1)–N(4) 170.72(15), Se(1)–Pd(1)–C(20) 94.35(16), Se(1)–Pd(1)–N(3) 88.53(13), N(4)–Pd(1)–N(3) 96.73(19), Pd(1)–Se(1)–C(5) 91.42(17), Se(1)–C(5)–N(2) 125.8(4), C(5)–N(2)–C(6) 126.0(5), N(2)–C(6)–N(3) 123.4(6), C(6)–N(3)–Pd(1) 125.9(4).

by free selenocarbamoyl benzamidine in solution. Both complexes **4** and **5** can also be prepared by the direct reaction of **HL** with one or two equivalents of the gold(I) compound [AuCl(SMe$_2$)] (Scheme 6). Spectroscopic data for complex **4** prepared by this method is identical to that for the product obtained using the Au(III) precursor. As would be expected, the proton NMR spectrum of salt **5** shows the same sets of resonances (including a broad NH signal) as that of complex **4**. We were however able to obtain a ^{77}Se NMR spectrum of **5**: the observed chemical shift of 348 ppm occurs within the same range as those of structurally similar Au(I) selenoureato complexes [24].

As mentioned in the structural discussions above, the coordinated selenocarbamoyl benzamidine ligand is not planar. Given this marked difference to the selenoureas, which form planar chelate rings, we studied possible reasons for this difference by computational methods. Using the coordinates from the X-ray structures of complex **1** and the selenoureato nickel complex [Ni{PhC(O)NC(Se)NEt$_2$}$_2$] [20], we carried out an NBO calculation using GAUSSIAN 03 [25].

Both the Wiberg bond indices and the atomic charges (Fig. 6) show that in complex **1**, the delocalisation is less pronounced when compared to the selenourea derivative. This is manifested by Wiberg bond indices indicating delocalised bonding between the carbon, nitrogen and oxygen atoms in the backbone of the selenourea. In contrast, in the selenocarbamoyl benzamidine bonding in the C–N–C–N unit alternates between single and delocalised. The same trend can be observed in the C–N bond distances. One of the C–N bonds in complex **1** is with 1.344 Å significantly longer than the other two (1.310 Å). As a consequence of this reduced delocalisation, the ring does not need to be planar resulting in the observed puckered structure.

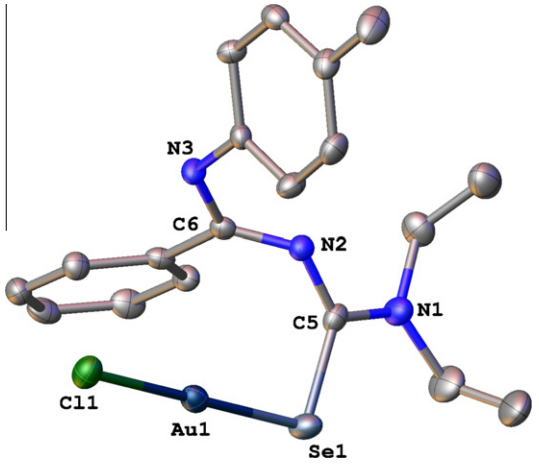


Fig. 4. Molecular structure of compound **4**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au(1)–Se(1) 2.3672(5), Au(1)–Cl(1) 2.2952(12), Se(1)–C(5) 1.904(5), C(5)–N(2) 1.342(6), N(2)–C(6) 1.294(6), C(6)–N(3) 1.349(5). Selected bond angles (°): Cl(1)–Au(1)–Se(1) 179.86(4), Au(1)–Se(1)–C(5) 102.99(13), Se(1)–C(5)–N(2) 122.4(3), C(5)–N(2)–C(6) 126.9(4), N(2)–C(6)–N(3) 120.2(4).

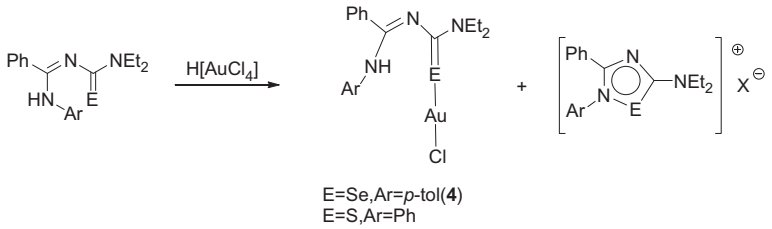
3. Conclusions

In conclusion, we have prepared a selenocarbamoyl benzamidine and have explored its coordination chemistry with various transition metal species. Like the selenoureas the selenocarbamoyl benzamidine can form both homoleptic and heteroleptic complexes with divalent metals in which the ligand coordinates as monoanionic [*N*,*Se*]$^-$ donor. In contrast to the selenoureato complexes, the metallacycles containing selenocarbamoyl benzamidine are not planar but form boat-like rings. Furthermore, the compound may also act as neutral Se-donor in gold(I) complexes. Electronic structure calculations show that the ligand backbone is not completely delocalised, thus giving rise to non-planar rings. We are currently further developing the coordination chemistry of this new class of ligands with other transition and main-group metals.

4. Experimental

4.1. General

^{1}H, ^{13}C{^{1}H} and ^{77}Se NMR spectra were recorded on a 400 or 600 MHz Bruker Avance spectrometer. Chemical shifts are quoted



Scheme 7.

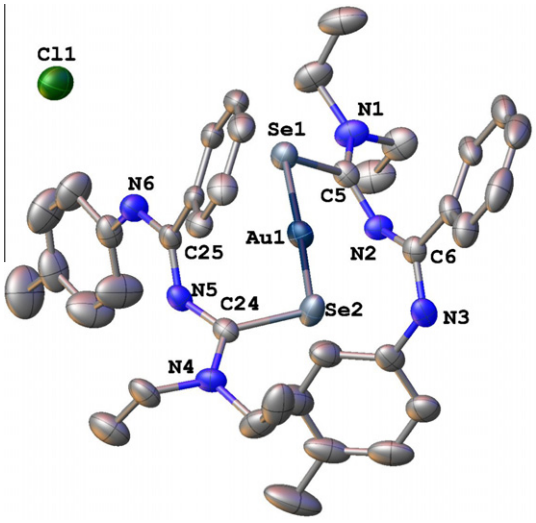


Fig. 5. Molecular structure of compound **5**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au(1)–Se(1) 2.3843(6), Au(1)–Se(2) 2.3932(6), Se(1)–C(5) 1.903(5), Se(1)–C(24) 1.901(5), C(5)–N(2) 1.328(7), N(2)–C(6) 1.305(6), C(6)–N(3) 1.344(7). Selected bond angles (°): Se(1)–Au(1)–Se(2) 176.66(2), Au(1)–Se(1)–C(5) 104.32(16), Au(1)–Se(2)–C(24) 100.40(16), Se(1)–C(5)–N(2) 122.7(4), C(5)–N(2)–C(6) 127.2(5), N(2)–C(6)–N(3) 118.7(5).

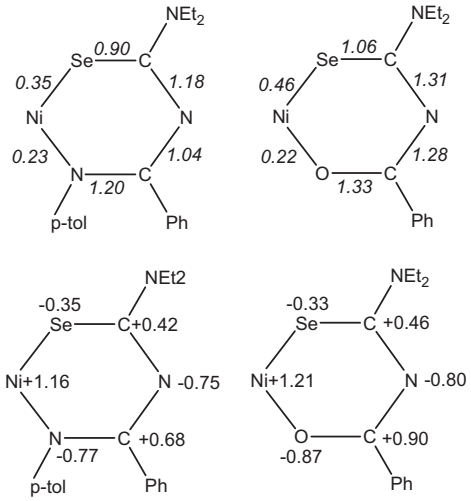


Fig. 6. Computed Wiberg bond indices (top) and atomic charges (bottom) for complex **1** and [Ni{PhC(O)NC(Se)NEt$_2$}$_2$].

relative to external SiMe$_4$ (^{1}H, ^{13}C) or Me$_2$Se (^{77}Se). Elemental analyses were performed by staff of the microanalytical laboratory of the University of Wuppertal. High-resolution electrospray mass spectra were recorded on a Bruker Daltonics MicroTOF instrument in positive ion mode using MeCN solutions of the samples. All reactions were carried out under aerobic conditions unless stated otherwise. Isoselenocyanate **A** [10] as well as the metal precursors [PdCl$_2$(^{t}Bu$_2$bipy)] [26] [Pd(OAc){κ*C*,*N*-C$_6$H$_4$N(Me)N=O}]$_2$ [15] and [AuCl(SMe$_2$)] [27] were prepared as described in the literature. All other chemicals and solvents (HPLC grade) were sourced commercially and used as received.

4.2. *HL*

To a solution of isoselenocyanate **A** (2.0 g, 6.7 mmol) in acetone (20 mL) was added Et$_2$NH (0.8 mL, 7.4 mmol). After stirring for 30 min the orange brown solution was filtered into water (100 mL), causing an orange-yellow solid to precipitate. The material was subsequently isolated by filtration, washed with water and dried in air. The compound was obtained in 84% yield (2.1 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.27 (t, J = 7.1 Hz, 3 H, C*H*$_3$CH$_2$N), 1.34 (t, J = 7.1 Hz, 3 H, C*H*$_3$CH$_2$N), 2.26 (s, 3 H, Me), 3.86 (q, J = 7.1 Hz, 2 H, C*H*$_2$N), 4.07 (q, J = 7.1 Hz, 2 H, C*H*$_2$N), 6.82 (d, J = 8.3 Hz, 2 H, *p*-tol), 6.98 (d, J = 8.3 Hz, 2 H, *p*-tol), 7.27–7.32 (m, 2 H, *m*-Ph), 7.36-7.41 (m, 1 H, *p*-Ph), 7.57–7.51 (m, 2 H, *o*-Ph), 11.29 (br. s, 1 H, NH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 12.31, 13.31 (*C*H$_3$CH$_2$N), 20.80 (Me), 45.26, 48.43 (CH$_2$N), 122.81 (*p*-tol), 128.13 (*m*-Ph), 129.30 (*o*-Ph), 129.47 (*p*-tol), 130.56 (*p*-Ph), 134.39 (*ipso p*-tol), 135.30 (*ipso* Ph), 136.17 (*p*-tol), 157.37 (C=N), 183.27 (C=Se). ^{77}Se NMR (76 MHz, CDCl$_3$): δ 322. *Anal.* Calc. for C$_{19}$H$_{23}$N$_3$Se (372.27): C, 61.28; H, 6.23; N, 11.28. Found: C, 61.34; H, 6.11; N, 11.07%. X-ray quality crystals were obtained from recrystallisation of the compound from EtOH.

4.3. *[Ni(L)$_2$] (**1**)*

To a solution of [Ni(OAc)$_2$]·4H$_2$O (0.068 g, 0.275 mmol) in warm EtOH (10 mL) was added a solution of **HL** (0.205 g, 0.55 mmol) in EtOH (10 mL). After 30 min the dark precipitate was isolated by filtration, washed with H$_2$O, EtOH and dried in air. Yield: 0.084 g (40%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.32–1.47 (br. m, 12 H, C*H*$_3$CH$_2$N), 2.25 (s, 6 H, Me), 3.63, 4.14 (br. m, 8 H, NCH$_2$), 6.79–6.86 (m, 8 H, *p*-tol, Ph), 6.93–7.06 (m, 6 H, Ph), 7.52 (d, J = 7.9 Hz, 4 H, *p*-tol). *Anal.* Calc. for C$_{38}$H$_{44}$N$_6$Se$_2$Ni (801.41): C, 56.95; H, 5.53; N, 10.49. Found: C, 57.03; H, 5.59; N, 10.65%. X-ray quality crystals were grown by slow evaporation of the mother liquor.

4.4. *[Pd(L)(^{t}Bu$_2$bipy)]PF$_6$ (**2**)*

To a suspension of [PdCl$_2$(^{t}Bu$_2$bipy)] (0.050 g, 0.108 mmol) in MeOH (5 mL) containing NH$_4$PF$_6$ (0.023 g, 0.141 mmol) was added **HL** (0.042 g, 0.113 mmol) and Et$_3$N (1 mL). The mixture was heated to reflux for 15 min by which time an orange-red solution had formed. The solution was filtered and the solvent removed in vacuum. The resulting residue was washed with water and Et$_2$O, filtered and dried to give the product as a red-brown solid. Yield: 0.87 g (91%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.26–1.34 (m, 6 H,

CH_3CH_2N), 1.39 (s, 9 H, ^{t}Bu), 1.46 (s, 9 H, ^{t}Bu), 2.21 (s, 3 H, Me), 3.76 (q, J = 7.0 Hz, 2 H, CH_2N), 3.90 (q, J = 7.0 Hz, 2 H, CH_2N), 6.95 (d, J = 8.1 Hz, 2 H, *p*-tol), 7.19–7.24 (m, 5 H, Ph), 7.36 (d, J = 8.3 Hz, 2 H, *p*-tol), 7.42 (dd, J = 6.0, 1.9 Hz, 1 H, H5-bipy), 7.61 (dd, J = 6.1, 2.0 Hz, 1 H, H5-bipy), 7.97 (d, J = 6.0 Hz, 1 H, H6-bipy), 8.05 (d, J = 1.7 Hz, 1 H, H3-bipy), 8.10 (d, J = 1.9 Hz, 1 H, H3-bipy), 9.05 (d, J = 6.1 Hz, 1 H, H6-bipy). $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 12.98, 14.46 (CH_3CH_2N), 20.88 (Me), 30.05, 30.08 (^{t}Bu), 45.00, 48.93 (CH_2N), 119.70, 120.49 (C3-bipy), 124.25, 124.57 (C5-bipy), 127.31 (Ph), 127.83 (*p*-tol), 128.95 (Ph), 129.18 (*p*-Ph), 129.41 (*p*-tol), 136.07 (quart. *p*-tol), 136.09 (*ipso* Ph), 144.86 (*ipso p*-tol), 148.07, 151.99 (C6-bipy), 154.25, 156.52 (C2-bipy), 158.85 (CSe), 165.93, 166.30 (C4-bipy), 172.22 (NCN). ^{77}Se NMR ($CDCl_3$, 114 MHz): δ = 233.7. HR-ESMS (*m/z*): 746.1962 $[M]^+$. *Anal.* Calc. for $C_{37}H_{46}N_5PSeF_6Pd$ (891.14): C, 49.87; H, 5.20; N, 7.86. Found: C, 50.01; H, 5.33; N, 7.66%.

4.5. [Pd(L){κC,N-$C_6H_4N(Me)N{=}O$}] (**3**)

To a solution of $[Pd(OAc)\{\kappa C,N\text{-}C_6H_4N(Me)N{=}O\}]_2$ (0.049 g, 0.082 mmol) in MeOH (10 mL) was added a solution of **HL** (0.061 g, 0.164 mmol) in the same solvent (10 mL). A yellow solid deposited almost instantly upon mixing the two solutions. The precipitate was isolated by filtration, washed with MeOH and dried in air. The product was obtained as a yellow solid. Yield: 0.060 g (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 1.40 (m, 6 H, CH_3CH_2N), 2.24 (s, 3 H, Me), 3.34 (s, 3 H, NMe), 3.69 (br. m, 2 H, CH_2N), 3.96 (br. m, 2 H, CH_2N), 6.84–6.93 (m, 3 H, *p*-tol, H6-CM ring), 7.05–7.15 (m, 6 H, H5 CM ring, Ph), 7.17–7.24 (m, 3 H, *p*-tol, H4 CM ring), 7.83 (dd, J = 7.5, 1.1 Hz, 1 H, H3 CM ring). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 13.01, 14.37 (CH_3CH_2N), 20.96 (Me), 30.16 (NMe), 44.41, 47.43 (CH_2N), 112.71 (C6 CM ring), 125.28 (C4 CM ring), 125.48 (C5 CM ring), 126.58 (*o*-Ph), 127.17 (*m*-Ph), 127.49 (*p*-Ph), 128.03 (*p*-tol), 129.12 (*p*-tol), 133.12 (quart. *p*-tol), 136.76 (C3 CM ring), 139.46 (*ipso* Ph), 140.64 (C-Pd), 144.10 (C2 CM ring), 148.17 (*ipso p*-tol), 158.15 (CSe), 165.26 (NCN). ^{77}Se NMR ($CDCl_3$, 114 MHz): δ = 147.6. *Anal.* Calc. for $C_{26}H_{29}N_5OSePd$ (612.92): C, 50.95; H, 4.77; N, 11.43. Found: C, 51.22; H, 5.04; N, 11.39%. X-ray quality crystals were grown by slow evaporation of the mother liquor.

4.6. [AuCl(HL)] (**4**) from $H[AuCl_4]$

To a solution of $H[AuCl_4]$ (0.050 g, 0.133 mmol) in EtOH (10 mL) was added a solution of **HL** (0.099 g, 0.0266 mmol) in the same solvent (10 mL). The mixture was heated to reflux for *ca.* 10 min. The resulting brownish solution was taken to dryness and the residue was extracted into CH_2Cl_2. The solution was subsequently passed through celite to remove some metallic gold. Concentration of the filtrate in vacuum and addition of hexanes gave yellow crystals of the product (0.078 g, 97% yield) after several days. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (br. m, 3 H, CH_3CH_2N), 1.33 (br. m, 3 H, CH_3CH_2N), 2.39 (s, 3 H, Me), 3.61 (br. m, 2 H, CH_2N), 3.81 (br. m, 2 H, CH_2N), 7.13 (d, J = 8.0 Hz, 2 H, *p*-tol), 7.18 (d, J = 8.0 Hz, 2 H, *p*-tol), 7.31–7.51 (m, 5 H, Ph), 8.80 (br. s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 12.91 (CH_3CH_2N), 20.61 (Me), 46.70, 49.06 (CH_2N), 126.76 (*p*-tol), 128.56 (Ph), 130.61 (*p*-tol), 130.96 (Ph), 132.16 (Ph), 134.41 (*ipso* Ph), 140.46 (quart. *p*-tol), 158.63 (*ipso p*-tol), 166.41(NCN), 179.79 (CSe). *Anal.* Calc. for $C_{19}H_{23}N_3SeAuCl$ (604.79): C, 37.73; H, 3.83; N, 6.95. Found: C, 37.64; H, 4.01; N, 6.93%. X-ray quality crystals were picked from the bulk sample. Crystals of $[Au(HL)_2]Cl$ (**5**) deposited from the $CDCl_3$ NMR sample solution after several days. Whilst there were insufficient crystals of **5** to obtain any NMR spectra, the HR mass spectrum showed the molecular ion peak $[M]^+$ for the cation at *m/z* 943.1789 (calculated for $C_{38}H_{46}N_6Se_2Au$: 943.1780).

4.7. [AuCl(HL)] (**4**) from [$AuCl(SMe_2)$]

To a solution of $[AuCl(SMe_2)]$ (0.050 g, 0.169 mmol) in CH_2Cl_2 (10 mL) was added **HL** (0.063 g, 0.169 mmol). The mixture was stirred at room temperature for *ca.* 2 h. The resulting brownish solution was passed through celite to remove some metallic gold. Concentration of the filtrate in vacuum and addition of hexanes gave the product (0.048 g, 47% yield) as yellow solid. Spectral data for this material was identical to that given above.

4.8. $[Au(HL)_2]Cl$ (**5**)

This was prepared as described above using $[AuCl(SMe_2)]$ (0.050 g, 0.169 mmol) and **HL** (0.126 g, 0.338 mmol). The product

Table 1
Crystallographic and refinement details for compounds **HL**, **1**, **3**, **4** and **5**.

	HL	**1**	**3**	**4**	**5**
Empirical formula	$C_{19}H_{23}SeN_3$	$C_{38}H_{44}N_6Se_2Ni$	$C_{26}H_{29}ON_5SePd$	$C_{19}H_{23}AuClN_3Se$	$C_{38}H_{46}AuClN_6Se_2$
Colour	yellow	reddish-brown	orange	yellow	yellow
M_r (g mol^{-1})	372.36	801,42	612.90	604.78	977.14
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.4692(3)	11.2134(6)	7.0460(4)	9.2191(4)	10.0780(3)
b (Å)	19.6150(9)	18.4090(10)	21.1674(13)	10.8783(4)	11.7138(4)
c (Å)	10.0270(4)	18.1157(11)	17.1503(15)	11.1442(5)	18.5026(7)
α (°)	90.0	90.0	90.0	64.067(5)	89.112(3)
β (°)	96.264(4)	95.449(5)	92.664(8)	80.580(4)	87.691(3)
γ (°)	90.0	90.0	90.0	86.032(3)	70.839(3)
V (Å^3)	1851.29(12)	3722.7(4)	2555.1(3)	991.54(8)	2061.57(12)
Z	4	4	4	2	2
D_{calc} (g cm^{-3})	1.336	1.430	1.593	2.026	1.574
μ (mm^{-1})	2.031	2.511	2.179	9.395	5.431
$F(000)$	768	1640	1232	576	960
θ Range	3.00–28.73°	2.98–29.43°	3.04–29.30°	3.05–29.42°	3.12–29.31°
Reflections collected	10251	22457	12776	6282	12077
Independent reflections	3920	8784	6692	4432	9510
Parameters	211	430	312	229	439
Goodness-of-fit (GOF)	1.098	1.036	1.012	1.033	1.070
R_1 [I > 2σ(I)]	0.0450	0.0503	0.0522	0.0319	0.0443
wR_2 (all data)	0.1003	0.1335	0.1340	0.0609	0.1109
Largest difference peak/hole (e Å^{-3})	0.875/−0.467	1.404/−1.053	1.983/−1.618	1.027/−1.034	2.269/−1.299

was obtained as yellow solid in 82% yield (0.136 g). ^{1}H NMR (400 MHz, dmso-d_6): δ 1.14 (br. m, 12 H, CH_3CH_2N), 2.31 (s, 3 H, Me), 3.62 (br m, 8 H, CH_2N), 7.07–7.20 (m, 4 H, *p*-tol), 7.37–7.65 (m, 14 H, *p*-tol, Ph), 10.91 (br. s, 1 H, NH). $^{13}C\{^{1}H\}$ NMR (dmso-d_6, 100 MHz): δ = 12.16, 12.61 (CH_3CH_2N), 20.61 (Me), 46.31, 48.87 (CH_2N), 122.35 (*p*-tol), 128.53, 128.81 (Ph), 129.51 (*p*-tol), 130.40 (Ph), 131.96 (*ipso* Ph), 132.60 (Ph), 134.98, 135.39 (quart. *p*-tol), 158.13 (NCN), 173.59 (CSe). ^{77}Se NMR (dmso-d_6, 114 MHz): δ = 348.5. HR-ESMS (*m/z*): 943.1783 $[M]^+$. *Anal.* Calc. for $C_{38}H_{46}N_6Se_2AuCl$ (977.15): C, 46.71; H, 4.74; N, 8.60. Found: C, 46.68; H, 4.80; N, 8.43%.

4.9. Computational details

Single point natural bond order (NBO) analyses [28] were performed for the two complexes using the Hartree–Fock (HF) method based using X-ray structure data. The double-ζ basis set LANL2DZ with Hay and Wadt effective core potential (ECP) [29,30] for the heavy atoms (Ni and Se) and the 6-31G* basis set for the remaining atoms (H, C, N, and O) were used. The NBO analyses were performed with the NBO 3.1 program incorporated in the GAUSSIAN 03 package [25].

4.10. X-ray crystallography

Diffraction data were collected at 150 K using an Oxford Diffraction Gemini E Ultra diffractometer, equipped with an EOS CCD area detector and a four-circle kappa goniometer. For the data collection the Mo source emitting graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used. Data integration, scaling and empirical absorption correction was carried out using the CRYSALISPRO program package.[31] The structure was solved using Direct Methods and refined by Full-Matrix-Least-Squares against F^2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealised positions and refined using the riding model. All calculations were carried out using the program OLEX2.[32] Important crystallographic data and refinement details are summarised in Table 1. The dataset of compound **3** showed signs of twinning. The data was therefore processed using the twin integration module in CRYSALIS. After refinement convergence of the data for complex **5** there remained two high (*ca.* 2 e Å^{-3}) electron density peaks within 1 Å of the chlorine atom, for which we could not find a plausible model.

Acknowledgments

We wish to thank RETORTE GmbH for a generous donation of selenium metal as well as the DFG for a grant to purchase the diffractometer.

Appendix A. Supplementary data

CCDC 848199, 831978, 831979, 831980 and 831981 contain the supplementary crystallographic data for **HL** and compounds **1**, **3**, **4** and **5**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] L. Beyer, J. Hartung, R. Widera, Tetrahedron 40 (1984) 405.
[2] J. Hartung, G. Weber, L. Beyer, R. Kirmse, J. Stach, J. Prakt. Chem. 332 (1990) 359.
[3] E. Guillon, I. Déchamps-Olivier, A. Mohamadou, J.P. Barbirt, Inorg. Chim. Acta 268 (1998) 13.
[4] R. Richter, U. Schröder, M. Kampf, J. Hartung, L. Beyer, Z. Anorg. Allg. Chem. 623 (1997) 1021.
[5] R. del Campo, J.J. Criado, E. García, M.R. Hermosa, A. Jiménez-Sánchez, J.L. Manzano, E. Monte, E. Rodríguez-Fernández, F. Sanz, J. Inorg. Biochem. 89 (2002) 74.
[6] U. Schröder, R. Richter, L. Beyer, J. Angulo-Cornejo, M. Lino-Pacheco, A. Guillen, Z. Anorg. Allg. Chem. 629 (2003) 1051.
[7] W. Hernández, E. Spodine, R. Richter, K.H. Hallmeier, U. Schröder, L. Beyer, Z. Anorg. Allg. Chem. 629 (2003) 2559.
[8] J. Sieler, R. Richter, L. Beyer, O. Lindqvist, L. Andersen, Z. Anorg. Allg. Chem. 515 (1984) 41.
[9] G. Weber, J. Hartung, L. Beyer, Tetrahedron Lett. 29 (1988) 3475.
[10] Y. Zhou, A. Linden, H. Heimgartner, Helv. Chim. Acta 83 (2000) 1576.
[11] A. Molter, F. Mohr, Coord. Chem. Rev. 254 (2010) 19.
[12] P. Bippus, A. Molter, D. Müller, F. Mohr, J. Organomet. Chem. 695 (2010) 1657.
[13] M. Ben Dahman Andaloussi, F. Mohr, J. Organomet. Chem. 695 (2010) 1276.
[14] D. Gallenkamp, T. Porsch, A. Molter, E.R.T. Tiekink, F. Mohr, J. Organomet. Chem. 694 (2009) 2380.
[15] F. Fuge, C. Lehmann, F. Mohr, J. Organomet. Chem. 694 (2009) 2395.
[16] D. Gallenkamp, E.R.T. Tiekink, F. Mohr, Phosphorus Sulfur Silicon 183 (2008) 1050.
[17] A. Molter, F. Mohr, Dalton Trans. 40 (2011) 3754.
[18] A. Molter, J. Rust, C.W. Lehmann, F. Mohr, ARKIVOC VI (2011) 10.
[19] A. Molter, J. Rust, C.W. Lehmann, G. Deepa, P. Chiba, F. Mohr, Dalton Trans. 40 (2011) 9810.
[20] W. Bensch, M. Schuster, Z. Anorg. Allg. Chem. 620 (1994) 177.
[21] S. Pisiewicz, J. Rust, C.W. Lehmann, F. Mohr, Polyhedron 29 (2010) 1968.
[22] U. Schröder, R. Richter, J. Hartung, U. Abram, L. Beyer, Z. Naturforsch. 52b (1997) 620.
[23] R.N. Butler, A. Fox, J. Chem. Soc., Perkin Trans. 1 (2001) 394.
[24] A. Molter, Ph.D. Thesis, University of Wuppertal, 2011.
[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Yengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision D.01, Gaussian Inc., Wallingford CT, 2004.
[26] F.R. Hartley, Organomet. Chem. Rev. A 6 (1970) 119.
[27] A. Tamaki, J.K. Kochi, J. Organomet. Chem. 64 (1974) 411.
[28] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
[29] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
[30] W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284.
[31] CRYSALISPRO 171.33.49, Oxford Diffraction Ltd., 2009.
[32] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Cryst. 42 (2009) 339.