

*Dedicated to Professor Florin Dan Irimie on the
Occasion of His 65th Anniversary*

ESTERS OF DIPHENYLPHOSPHINOSELENOTHIOIC AND DIPHENYLPHOSPHINODISELENOIC ACIDS WITH POTENTIAL FOR RAFT POLYMERIZATION

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ABSTRACT. Compounds of type $\text{Ph}_2\text{P}(\text{E})\text{SeR}$ [$\text{E} = \text{S}$, $\text{R} = 2\text{-MeC}_6\text{H}_4$ (**1**), $2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4$ (**2**); $\text{E} = \text{Se}$, $\text{R} = 2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4$ (**3**)], were prepared and structurally characterized in solution by multinuclear NMR (^1H , ^{31}P , ^{77}Se). The attempts to obtain the derivative $\text{Ph}_2\text{P}(\text{S})\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMePr}^i)\text{-2}$ (**4**) resulted in a complex mixture. The attempts to separate the components resulted in further decomposition and hydrolysis and the isolated crystals were investigated by single-crystal X-ray diffraction when proved to be the ammonium salt $[\text{MePr}^i\text{BnNH}]^+[\text{Ph}_2\text{P}(\text{S})\text{O}]^-$ ($\text{Bn} = \text{benzyl}$) (**4a**).

Keywords: organophosphorus(V) compounds, organoselenium compounds; intramolecular coordination; solution behavior, solid state structure.

INTRODUCTION

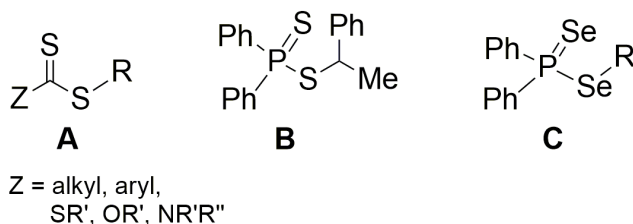
Radical polymerization is largely used in organic synthesis and different methods were employed during last years, e.g. reversible addition fragmentation transfers polymerization (RAFT) [1-3], nitroxide-mediated polymerization (NMP) [4,5], or atom transfer radical polymerization (ATRP) [6,7], in order to realize a better control of both the polymerization process and the characteristic properties of the obtained polymers. Among these methods, RAFT proved to be

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a very efficient one in living polymerization and it was observed that for best efficiency it is essential to design an appropriate RAFT agent. For this purpose esters of carboxydithioic [8] and phosphinodithioic [9,10] acids (Scheme 1, **A** and **B**) were used as RAFT agents. At a lesser extent esters of the phosphinodiselenoic acid (Scheme 1, **C**) were also investigated as RAFT agents for the polymerization of styrene [11,12].

Our research comprised in the last years several studies regarding organophosphorus [13,14] and organochalcogen [15,16] compounds bearing aromatic groups with pendant arms capable for intramolecular N→E (E = P, S, Se) intramolecular interactions. As a continuation of our work, we report here about several esters of the diphenylphosphinoselenothioic and the diphenylphosphinodiselenoic acids, namely compounds of type Ph₂P(E)SeR [E = S, R = 2-MeC₆H₄ (**1**), 2-(Me₂NCH₂)C₆H₄ (**2**); E = Se, R = 2-(Me₂NCH₂)C₆H₄ (**3**)], which might be used as RAFT agents. Our attempts to isolate in pure form the related ester Ph₂P(S)SeC₆H₄(CH₂NMePr)⁻² (**4**) were unsuccessful due to very fast decomposition in solution.



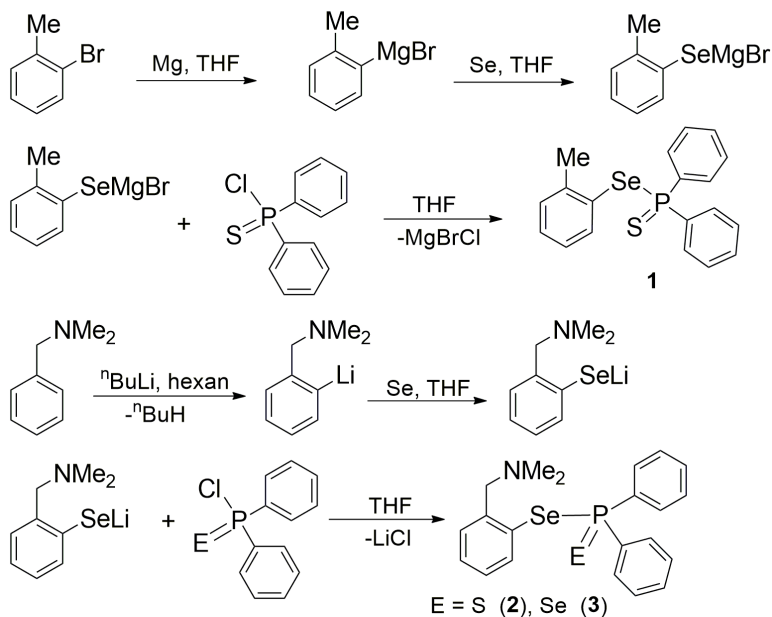
Scheme 1

RESULTS AND DISCUSSION

Synthesis and solution behavior

The new compounds were obtained by a succession of reactions, as depicted in Scheme 2, based on the *in situ* prepared organomagnesium (for compound **1**) or organolithium (for compounds **2** and **3**) reagents, subsequent selenium insertion in the new formed metal-carbon bond and further metal halide elimination between the as formed metal organoselenolate and the appropriate thio- or selenophosphinyl halide.

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Scheme 2

The reaction between the lithium organoselenolate 2-(MePrⁱNCH₂)C₆H₄SeLi and Ph₂P(S)Cl resulted in a complex mixture and our attempts to separate the ester Ph₂P(S)SeC₆H₄(CH₂NMePrⁱ)-2 (**4**) only allowed to isolate the ammonium salt [MePrⁱBnNH]⁺[Ph₂P(S)O]⁻ (Bn = benzyl) (**4a**), formed by hydrolysis/decomposition processes.

Compound **1** was isolated as a slightly brown oil, while compounds **2** and **3** as yellowish solids, soluble in organic solvents. The new species were investigated in solution by multinuclear NMR (¹H, ³¹P and ⁷⁷Se). The ¹H NMR spectra show the expected resonances for the aliphatic and the aromatic organic groups, with multiplicities due to ¹H-¹H and ³¹P-¹H couplings. The room temperature ¹H NMR spectra of compounds **2** and **3**, which contain a 2-Me₂NCH₂C₆H₄ group attached to selenium, show no evidence for an intramolecular N→Se interaction. In the aliphatic region they show singlet resonances for the CH₂N and the N(CH₃)₂ protons of the pendant arm. For all these three compounds the ³¹P{¹H} NMR resonances appear as singlets, accompanied by satellites due to ³¹P-⁷⁷Se coupling, as shown in Figure 1 for **2** and **3**. One pair of satellites due to the coupling with the single bonded Se atom was observed for **2**, while couplings with both single and double bonded Se atoms in **3** resulted in two pairs of satellites.

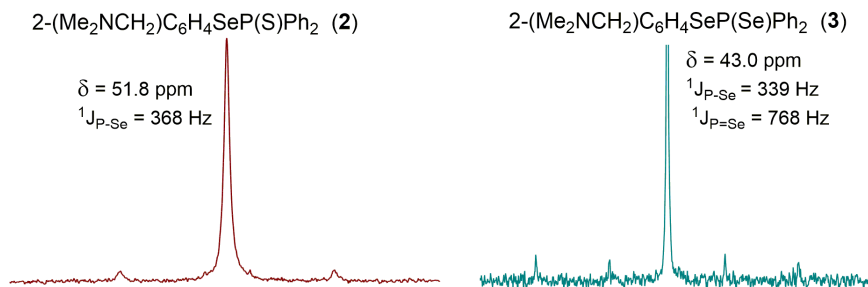


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ resonances for compounds **2** and **3**

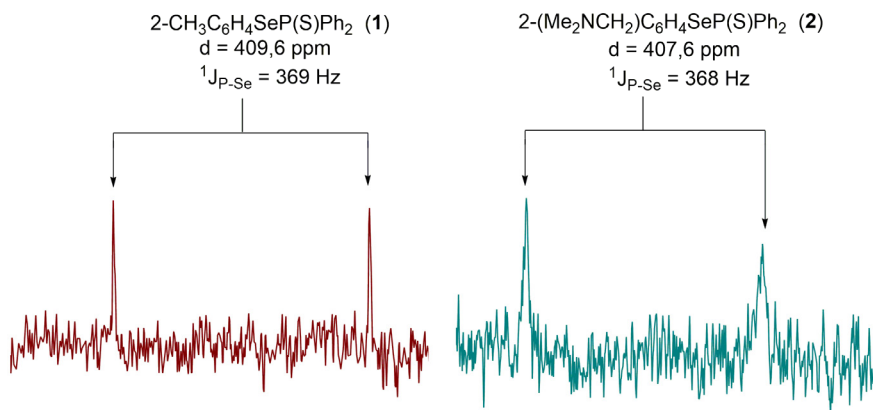


Figure 2. $^{77}\text{Se}\{^1\text{H}\}$ resonances for compounds **1** and **2**.

The $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra of compounds **1** and **2** exhibit doublet resonances due to ^{31}P - ^{77}Se couplings, as shown in Figure 2. For compound **3** the $^{77}\text{Se}\{^1\text{H}\}$ resonances could not be observed.

Single-crystal X-ray diffraction studies

The ORTEP-like diagram of **4a** with the atom numbering scheme is depicted in Figure 3, while selected interatomic distances and angles are given in Table 1.

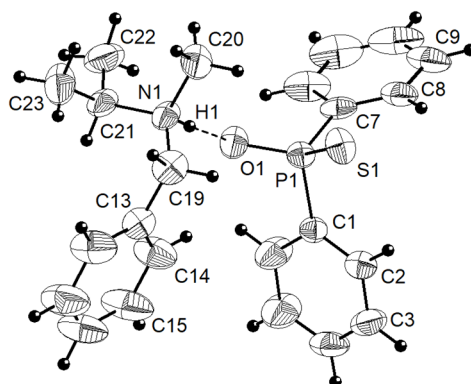


Figure 3. ORTEP-like diagram at 30% probability ellipsoids for **4a**.

The coordination geometries about phosphorus and nitrogen are distorted tetrahedral, with angles in the range 102.5(2)–118.1(2)° and 106.4–114.1(5)°, respectively. The phosphorus-oxygen and phosphorus-sulfur interatomic distances are characteristic for single P–O and double P=S bonds, close to the values found in the diphenylphosphinomonothioic acid [P–O 1.582(2) Å, and P=S 1.956(1) Å] [17].

Table 1. Selected interatomic distances [Å] and angles [°] in **4a**

P1–C1	1.805(7)	C1–P1–C7	102.5(2)
P1–C7	1.818(6)	C1–P1–S1	110.0(2)
P1–S1	1.967(2)	C7–P1–S1	110.0(2)
P1–O1	1.507(4)	C1–P1–O1	107.2(2)
N1–C19	1.484(8)	S1–P1–O1	118.1(2)
N1–C20	1.501(7)	C7–P1–O1	107.9(3)
N1–C21	1.504(8)	C19–N1–C20	109.6(5)
N1–H1	0.980	C19–N1–C21	114.1(5)
H1…O1	1.650	C20–N1–C21	113.4(5)
N1…O1	2.624(6)	C19–N1–H1	106.4
N1–H1…O1	176	C20–N1–H1	106.4
P1–O1…H1	125	C21–N1–H1	106.4

The ammonium cation and the diorganophosphinomonothioato anion are connected in the crystal through hydrogen bonding: N1–H1 0.980 Å, H1…O1 1.650 Å, N1…O1 2.624(6) Å [cf $\Sigma r_{vdW}(O,H)$ 2.60 Å; $\Sigma r_{vdW}(N,O)$ 2.94 Å] [18].

EXPERIMENTAL SECTION

Starting materials were prepared according to literature procedures: $\text{Ph}_2\text{P}(\text{S})\text{Cl}$, $\text{Ph}_2\text{P}(\text{Se})\text{Cl}$ [19], $\text{MePr}^i\text{NCH}_2\text{C}_6\text{H}_5$ [20] or were commercially available and used as purchased. Solvents were dried and distilled under argon prior to use. Elemental analysis was performed on a Flash EA 1112 analyzer and melting points were measured on an Electrothermal 9200 apparatus. ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra were recorded on a BRUKER Avance 400 instrument in CDCl_3 solutions. The chemical shifts are reported in δ units (ppm) relative to TMS (ref. CHCl_3 : ^1H 7.26 ppm), H_3PO_4 85% and Me_2Se_2 , respectively. The NMR data were processed using the MestReNova software [21].

Synthesis of 2-MeC₆H₄SeP(S)Ph₂ (1)

Selenium powder (2.303 g, 29.16 mmol) was added at 0 °C to a THF solution of a Grignard reagent *in situ* prepared from 2-bromotoluene (3.6 mL, 4.988 g, 29.16 mmol) and magnesium span (0.815 g, 29.16 mmol). The reaction mixture was stirred for 30 min until all selenium was reacted. Subsequently, $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ (7.37 g, 29.16 mmol) was added and stirring continued for other two hours. THF was removed under reduced pressure and the desired product was extracted in CH_2Cl_2 . After removing the solvent and washing with 3 x 10 mL of n-hexane, the title compound resulted as a slightly brown oil. Yield: 5.86 g (52%). ^1H NMR: δ 1.73 (s, 3H, CH_3), 6.52 (t, 1H, C_6H_4 , $^3\text{J}_{\text{HH}}$ 7.9 Hz), 6.63-6.79 (m, 2H, C_6H_4), 6.90-7.04 (m, 6H, C_6H_5 -*meta+para* + 1H, C_6H_4), 7.40 (ddd, 4H, C_6H_5 -*ortho*, $^3\text{J}_{\text{HH}}$ 7.4, $^4\text{J}_{\text{HH}}$ 1.5, $^3\text{J}_{\text{PH}}$ 14.3 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 53.14 (s, $^1\text{J}_{\text{PSe}}$ = 368 Hz, $^1\text{J}_{\text{PC}}$ 75.4 Hz). $^{77}\text{Se}\{^1\text{H}\}$ NMR: δ 409.6 (d, $^1\text{J}_{\text{PSe}}$ = 369 Hz).

Synthesis of [2-(Me₂NCH₂)C₆H₄]SeP(S)Ph₂ (2)

Selenium powder (0.547g, 6.93 mmol) was added under stirring to a solution of [2-(Me₂NCH₂)C₆H₄]Li (0.978 g, 6.93 mmol) in 20 mL THF. After two hours a solution of $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ (1.75 g, 6.93 mmol) in 20 mL THF was added dropwise and stirring continued for other two hours. THF was removed under reduced pressure and the reaction mixture was worked up with toluene (40 mL). From the clear toluene solution, after removing the solvent and washing with n-hexane (3 x 10 mL), the title compound was obtained as a yellowish solid. Yield: 2.98 g (50%). M.p. 66 °C. ^1H NMR: δ 2.15 (s, 6H, NCH_3), 3.35 (s, 2H, CH_2N), 7.04 (t, 1H, C_6H_4 , $^3\text{J}_{\text{HH}}$ 6.9 Hz), 7.22-7.37 (m, 3H, C_6H_4), 7.40-7.57 (m, 6H, C_6H_5 -*meta+para*), 7.96 (dd, 4H, C_6H_5 -*ortho*, $^3\text{J}_{\text{HH}}$ 6.4, $^3\text{J}_{\text{PH}}$ 14.1 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 51.78 (s, $^1\text{J}_{\text{PSe}}$ = 367 Hz). $^{77}\text{Se}\{^1\text{H}\}$ NMR: δ 407.6 (d, $^1\text{J}_{\text{PSe}}$ = 368 Hz).

Synthesis of [2-(Me₂NCH₂)C₆H₄]SeP(Se)Ph₂ (3)

Compound **3** was prepared similarly with compound **2**, from [2-(Me₂NCH₂)C₆H₄]Li (0.524 g, 3.71 mmol), selenium powder (0.293 g, 3.71 mmol) and Ph₂P(Se)Cl (1.11 g, 3.71 mmol), as a yellowish solid. Yield: 0.91 g (51%). M.p. 75 °C. ¹H NMR: δ 2.75 (s, 6H, NCH₃), 4.41 (s, 2H, CH₂N), 7.04 (t, 1H, C₆H₄, ³J_{HH} 6.9 Hz), 7.22-7.37 (m, 6H, C₆H₅-*meta*+*para* + 1H C₆H₄), 7.42-7.54 (m, 2H, C₆H₄), 7.84 (dd, 4H, C₆H₅-*ortho*, ³J_{HH} 7.4, ⁴J_{HH} 1.8, ³J_{PH} 13.7 Hz), 7.97 (d, 1H C₆H₄). ³¹P{¹H} NMR: δ 42.93 (s, ¹J_{P-Se} 339, ¹J_{P=Se} 768 Hz).

Formation of [MePrⁱBnNH]⁺[Ph₂P(S)O]⁻ (4a)

The lithium organoselenolate [2-(MePrⁱNCH₂)C₆H₄]SeLi was prepared *in situ* from a 1.6 M solution of ⁿBuLi in hexane (4.1 mL, 5.91 mmol) and *N,N*-methylisopropylbenzylamine (0.97 g, 5.91 mmol) in hexane (20 mL). Selenium powder (0.47 g, 5.91 mmol) was inserted in the C–Li bond and the synthesis continued as described for compound **2**. The obtained oil was layered with hexane and left overnight at –20 °C, when a beige powder was formed. Yield: 1.72 g (64%). ¹H and ³¹P{¹H} NMR suggested a complex mixture. Further attempts to separate the components by recrystallization resulted in the hydrolysis title product, as a colorless solid. M.p. 112-114 °C. ¹H NMR: δ 1.31 [s, br., 3H, NCH(CH₃)₂], 1.40 (s, br., 3H, NCH(CH₃)₂), 2.55 (s, 3H, NCH₃), 3.69 [m, br, 1H, NCH(CH₃)₂], 4.20 (s, br, 2H, CH₂N), 7.25-7.30 (m, 1H, C₆H₄), 7.32-7.39 (m, 6H, C₆H₅-*meta*+*para* + 2H, C₆H₄), 7.63 (d, 1H, C₆H₄, ³J_{HH} 7.4 Hz), 7.99 (ddd, 4H, C₆H₅-*ortho*, ³J_{HH} = 7.3, ⁴J_{HH} = 2.3, ³J_{PH} = 12.6 Hz). ³¹P{¹H} NMR: δ 56.8 (s).

X-ray structure determination

The details of the crystal structure determination and refinement for **4a** are given in Table 2. Data were collected on a Bruker SMART APEX diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals were attached with paraton/N oil on cryoloops and the data were collected at room temperature (293 K). The structure was refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used [22]. The drawings were created with the Diamond program [23].

Table 2. Crystallographic data for **4a**

4a	
Empirical formula	C ₂₃ H ₂₈ NOPS
Formula weight	397.49
Temperature (K)	293(2) K
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	P21/c
<i>a</i> (Å)	9.0645(17)
<i>b</i> (Å)	19.403(4)
<i>c</i> (Å)	13.339(2)
α (°)	90
β (°)	106.335(4)
γ (°)	90
Volume, (Å ³)	2251.4(7)
<i>Z</i>	4
Density (calculated) (g/cm ³)	1.173
Absorption coefficient (mm ⁻¹)	0.227
F(000)	848
Crystal size, mm	0.25 x 0.32 x 0.40
θ range for data collections, °	1.91 to 25.00
Reflections collected	21394
Independent reflections	3963 [R(int) = 0.099]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	3963 / 0 / 247
Goodness-of-fit on <i>F</i> ²	1.144
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.1114, wR2 = 0.2330
<i>R</i> indices (all data)	R1 = 0.1745, wR2 = 0.2648
Largest diff. peak and hole, eÅ ⁻³	0.30 and -0.35

CONCLUSIONS

The reactions between 2-MeC₆H₄SeMgBr or 2-(Me₂NCH₂)C₆H₄SeLi with diphenylthio- or diphenylselenophosphinyl chloride allowed the isolation of stable esters **1** - **3**, while the reaction between 2-(MePr^{*i*}NCH₂)C₆H₄SeLi and Ph₂P(S)Cl resulted in a complex mixture of products, from which the ammonium salt [MePr^{*i*}BnNH]⁺[Ph₂P(S)O]⁻ (Bn = benzyl) (**4a**), formed during a hydrolysis/decomposition process, could be isolated and structurally characterized. The ¹H NMR spectra for compounds **2** and **3**, which contain

the 2-(Me₂NCH₂)C₆H₄ group attached to selenium, brought no evidence for the intramolecular N→Se interaction in solution at room temperature. This observation might be consistent with the absence of any intramolecular interaction or it might suggest a dynamic behavior involving de-coordination, inversion at nitrogen and re-coordination, too fast at room temperature to be observed at the NMR time scale.

ACKNOWLEDGMENTS

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SUPPLEMENTARY DATA

CCDC 1902133 contain the supplementary crystallographic data for **4a**. 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. X. Tian, J. Ding, B. Zhang, F. Qiu, X. Zhuang, Y. Chen, *Polymers*, **2018**, *10*, 318.
2. C. Barner-Kowollik, T.P. Davis, J.P. A. Heuts, M.H. Stenzel, P. Vana, M. Whittaker, *J. Polym. Sci., Part A: Polym. Chem.*, **2003**, *41*, 365.
3. D.J. Keddie, G. Moad, E. Rizzardo, S.H. Thang, *Macromolecules*, **2012**, *45*, 5321.
4. C. Konn, F. Morel, D.L. Beyou, P. Chaumont, E. Bourgeat-Lami, *Macromolecules*, **2007**, *40*, 7464.
5. J. Nicolas, Y. Guillaneuf, C. Lefay, D. Bertin, D. Gigmes, B. Charleux, *Prog. Polym. Sci.*, **2013**, *38*, 63.
6. N.V. Tsarevsky, K. Matyjaszewski, *Chem. Rev.*, **2007**, *107*, 2270.
7. J. Ran, L. Wu, Z. Zhang, T. Xu, *Prog. Polym. Sci.*, **2014**, *39*, 124.
8. A. Alberti, M. Benaglia, M. Laus, K. Sparnacci, *J. Org. Chem.*, **2002**, *67*, 7911.
9. D. Gigmes, D. Bertin, S. Marque, O. Guerret, P. Tordo, *Tetrahedron Lett.*, **2003**, *44*, 1227.
10. J.L. Hodgson, K.A. Green, M.L Coote, *Org. Lett.*, **2005**, *7*, 4581.
11. J. Moon, H. Nam, S. Kim, J. Ryu, C. Han, C. Lee, S. Lee, *Tetrahedron Lett.*, **2008**, *49*, 5137.

12. T. Kimura, T. Murai, *J. Org. Chem.*, **2005**, *70*, 952.
13. R. Şuteu, S. Shova, A. Silvestru, *Inorg. Chim. Acta*, **2018**, *475*, 105.
14. A. Covaci, R. Mitea, I. Hosu, A. Silvestru, *Polyhedron*, **2014**, *72*, 157.
15. A. Pop, A. Silvestru, E.J. Juárez-Pérez, M. Arca, V. Lippolis, C. Silvestru, *Dalton Trans.*, **2014**, *43*, 2221.
16. R.A. Popa, E. Licarete, M. Banciu, A. Silvestru, *Appl. Organomet. Chem.*, **2018**, *32*, e4252.
17. R. Mattes, D. Rühl, *Acta Crystallogr., Sect. C: Struct. Chem.*, **1984**, *C40*, 106.
18. J. Emsley, "Die Elemente", Walter de Gruyter, Berlin, **1994**.
19. M.W. Schmidt, P.H. Truong, M.S. Gordon, *J. Am. Chem. Soc.*, **1987**, *109*, 5217.
20. H. Ahlbrecht, J. Harbach, R.W. Hoffmann, T. Ruhland, *Liebigs Ann.*, **1995**, 211.
21. *MestReC and MestReNova*, Mestrelab Research S.L., Feliciano Barrera 9B, Bajo, 15706 Santiago de Compostela, Spain, **2015**.
22. G.M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **2008**, *A64*, 112.
23. *DIAMOND*, Visual Crystal Structure Information System, Crystal Impact, Postfach 1251, 53002 Bonn, Germany, **2015**.