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REGULAR ARTICLE

Transformation of 1,3-imidazolidine-2-thione ($SC_3H_6N_2$) into ($SC_3H_4N_2$–O–$N_2C_3H_4S$)$^{2-}$ dianion chelated in [Pd{κ^3–S, O, S–($SC_3H_4N_2$–O–$N_2C_3H_4S$)}(PPh_3)]·CH_3CN

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Abstract. Reaction of [$PdCl_2(PPh_3)_2$] with imidazolidine-2-thione {$SC_3H_4(NH)_2$}in the presence of triethylamine involved activation of N–H bonds and formed an unusual oxo-bridged dianion, ($SC_3H_4N_2$–O–$N_2C_3H_4S$)$^{2-}$ coordinated to Pd^{II} in Pd{κ^3–S, O, S–($SC_3H_4N_2$–O–$N_2C_3H_4S$)}(PPh_3)]·CH_3CN **1**, which has been studied using elemental analysis, IR, NMR, X-ray crystallography and ESI-mass studies.

Keywords. Imidazolidine-2-thione; palladium; triphenylphosphine; oxygen atom insertion; oxo-bridged dianion.

1. Introduction

Heterocyclic thioamides bearing functional groups such as, −N(H)−C(=S)− or −N(H)−C(=S)−N(H)−, in their reactions with metal ions have shown interesting coordination variability which has resulted in the formation of a diverse range of coordination compounds: mononuclear, dinuclear, oligomers and polymers.[1–12] The thio-ligands have shown coordination versatility in neutral or anionic forms and have shown κ^1–S, μ–S, μ_3–S, κ^2–N,S (chelating), μ–N,S, *etc*., bonding modes.[1–12]

Coordination chemistry of palladium(II) with pyridine-2-thione (pySH), 1-methyl-imidazoline-2-thione (mimzSH), pyrimidine-2-thione (pymSH), purine-6-thione ($purSH_2$) and quinoline-2-thione (qnSH) has been reported and complexes are generally mononuclear or dinuclear with nearly square planar geometry around each metal center.[2,4–7,13–18] A few examples are presented below to provide a glimpse of complexes reported with palladium(II), namely, [Pd^{II}(κ^1–S–mimzSH)$_4$]Cl_2·$2H_2O$,[13] [Pd(κ^1: S–pymS)$_2$(PPh_3)$_2$],[14] [PdCl(κ^2:N,S–pyS)(PPh_3)],[15] [Pd_2^{II}(μ–κ^2:N,S–pyS)$_4$],[16,17] and [Pd_2(μ–κ^2: N,S–pyS)(μ–κ^2:S–pyS)(κ^1:S–pyS)$_2$(μ–P,P–dppm)] (dppm = Ph_2P–CH_2–PPh_2).[18] The thio-ligand, 1-methyl-imidazoline-2-thiolate has formed a N,S-bridged heterobimetallic Pd–Sn complex.[19] In continuation of our interest in palladium-heterocyclic thioamide chemistry, this paper reports a reaction of 1,3-imidazolidine-2-thione having two imino (–NH–) groups and the resulting novel complex has been characterized using elemental analysis, IR NMR spectroscopy, x-ray crystallography and ESI-mass studies.

2. Experimental

2.1 *Materials and techniques*

Palladium chloride ($PdCl_2$), triphenyl phosphine and imidazolidine-2-thione were procured from Aldrich Sigma Ltd. Trans-$PdCl_2(PPh_3)_2$ was prepared by reacting a solution of $PdCl_2$ in acetonitrile with 2 moles of PPh_3, by a method analogous to literature method.[20] C, H and N analyses were obtained with a Thermoelectron FLASHEA1112 CHNS analyzer. Infrared spectra were recorded using KBr pellets in the range 4000–200 cm^{-1}on a Pye–Unicam SP-3-300 spectrophotometer. Melting point was determined with an electrically heated Gallenkamp apparatus. ^1H NMR spectra were recorded on a JEOL AL-300 FT spectrometer operating at a frequency of 300 MHz using $CDCl_3$ as the solvent with TMS as the internal standard. ^{31}P NMR spectra were recorded on a Bruker ACP-300 spectrometer operating at a frequency of 121.5 MHz with H_3PO_4 as the external standard with $\delta = 0$.

2.2 *Synthesis of [Pd{κ^3–S, O, S–($SC_3H_4N_2$–O–$N_2C_3H_4S$)}(PPh_3)]·CH_3CN(**1**)*

$PdCl_2(PPh_3)_2$ (0.050 g, 0.071 mmol) was added to imidazolidine-2-thione (0.0146 g, 0.142 mmol) in acetonitrile followed by the addition of triethyl amine base

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*For correspondence

Table 1. Crystal data for compound **1.**

T(K)	**1** 295(2) K		
Empirical formula	$C_{24}H_{23}N_5OPPdS_2{\cdot}C_2H_3N$	V(Å^3)	2663.4(4)
M	626.01	Z	4
λ(Å)	0.71073	D_{calcd}(g cm^{-3})	1.561
Crystal system	Monoclinic	μ(mm^{-1})	0.943
Space group	$P2_1/n$	F(000)	1272
Unit cell dimensions		Reflections collected	5280
a(Å)	9.078(1)	Unique reflns	4951($R_{int} = 0.0209$)
b(Å)	18.418(2)	Data/restraints/ parameters	4951/0/325
c(Å)	15.941(1)	Reflns.with [I>2σ(I)]	3283
α(°)	90	R Indices R_1 wR_2	0.0374 0 0.0984
β(°)	92.204(8)	R indices (all data) R_1 wR$_2$	0.0636 0.1146
γ(°)	90	Largest diff. Peak and hole	0.418, –1.384 e.Å^{-3}

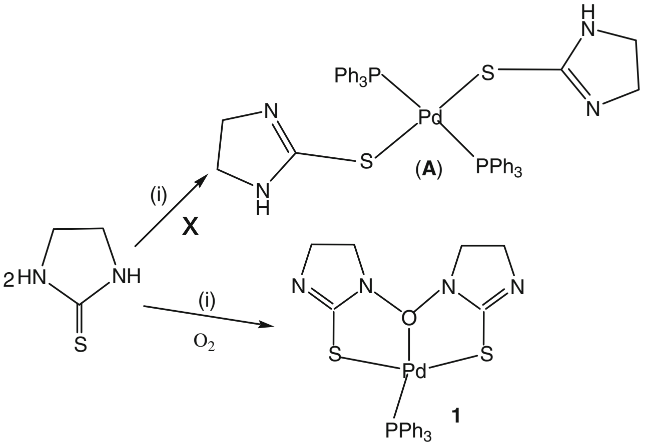
(0.5 mL). The clear orange solution was refluxed for 5 h and solvent removed with a rotary evaporator. The solid obtained was treated with acetone which dissolved complex leaving behind $Et_3NH^+Cl^-$ salt. The acetone extract was placed in a culture tube layered with a mixture of dichloromethane – methanol, and crystals were formed over a period of one month. M.p.: 220–230°C, Yield: 0.025 g, 52%. C, H, N, analysis for $C_{26}H_{26}N_5OPPdS_2$: C, 49.84; H, 4.15; N, 11.12%; Found: C, 50.01; H, 4.65; N, 11.34%. IR data (KBr, cm^{-1}): 3072 (w, C–H), 3048 (m, C–H), 2953 (w, C–H), 2929 (m, C–H), 2852 (w, C–H); 2358m, 2331w (C–N); 1085 (s, P–C_{Ph}); 746 (s. C–S). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.46–7.67m (P–C_6H_5), 3.67s (–CH_2); ^{31}P NMR data ($CDCl_3$, δ ppm), 30.0, 48.7, $\Delta\delta$, 34.7, 44.0 [Free ligand NMR values: δ 6.40s (2H + NH), 3.59s (CH_2-CH_2)].[15,16]

2.3 *X-ray crystallography*

A single crystal was mounted on a glass fiber and used for data collection with a Bruker Apex (II) CCD diffractometer (296(2) K) equipped with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å). The data recorded for compounds were processed with Bruker APEX II CCD. The structure was solved by direct methods using the program SIR-92[21] refined by full-matrix least-squares techniques against F^2 using SHELXL-97 and molecular graphics from SHELXTL.[22] The data were corrected for absorption using SADABS. The crystal data are placed in Table 1.

3. Results and Discussion

Reaction of $[PdCl_2(PPh_3)_2]$ with imidazolidine-2-thione$\{SC_3H_4(NH)_2\}$in presence of triethylamine base did not form a simple anticipated square planar complex, $[Pd(\kappa^1\text{–S–}SC_3H_4(NH)(N))_2(PPh_3)_2]$ (product **A**, Scheme 1), similar to other known complexes.[2–7] The analytical data revealed composition of the product as ($C_{26}H_{26}N_5OPPdS_2$) (**B**) and its single crystal x-ray crystallography revealed that this product is not a simple compound **A**, rather it involves unusual bonding properties having tridentate S, O, S donor set with a fourth site occupied by P atom in the resulting product: $[Pd\{\kappa^3\text{–S, O, S–}(SC_3H_4N_2\text{–O–}N_2C_3H_4S)\}(PPh_3)]{\cdot}CH_3CN$ **1** (Figure 1). There is *in situ* transformation of two imidazolidine-2-thione rings into $(SC_3H_4N_2\text{–O–}N_2C_3H_4S)^{2-}$ dianion, which subsequently binds to Pd^{II} forming compound **1**. The trans S1–Pd–S2, 169.60(4), and O1–Pd–P1, 177.58(11) angles deviate significantly from linearity. Likewise, other angles around Pd metal center are either obtuse {S1−Pd−P1, 95.81(4), S2−Pd−P1 94.14(4)°}, or acute {O1−Pd−S1 85.12(12), O1–Pd–S2 85.06(12)°}, and thus the geometry is severely distorted from a square planar arrangement. The Pd−P and Pd−S distances are comparable to the literature trends.[12]



Scheme 1. (i) $PdCl_2(PPh_3)_2$, Et_3N.

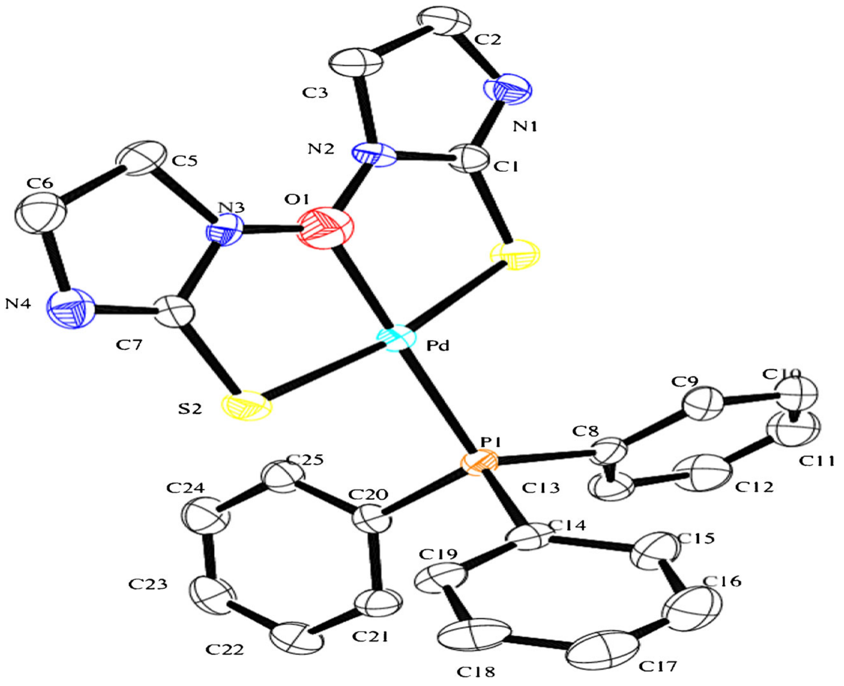


Figure 1. ORTEP diagram for complex **1** at 30% probability. Hydrogens and the solvent molecule have been removed for clarity. Selected bond lengths/Å and angles/°: P1–Pd, 2.3393(10); S1–Pd, 2.2866(12); S2–Pd, 2.3018(12); Pd–O1, 2.016(4); N2–O1, 1.344(5); N3–O1, 1.346(5); C1–S1, 1.739(4), C7–S2, 1.739(4); S1–Pd–S2, 169.60(4); O1–Pd–P1, 177.58(11); S1–Pd–P1, 95.81(4); S2–Pd–P1, 94.14(4); O1–Pd–S1, 85.12(12); O1–Pd–S2, 85.06(12).

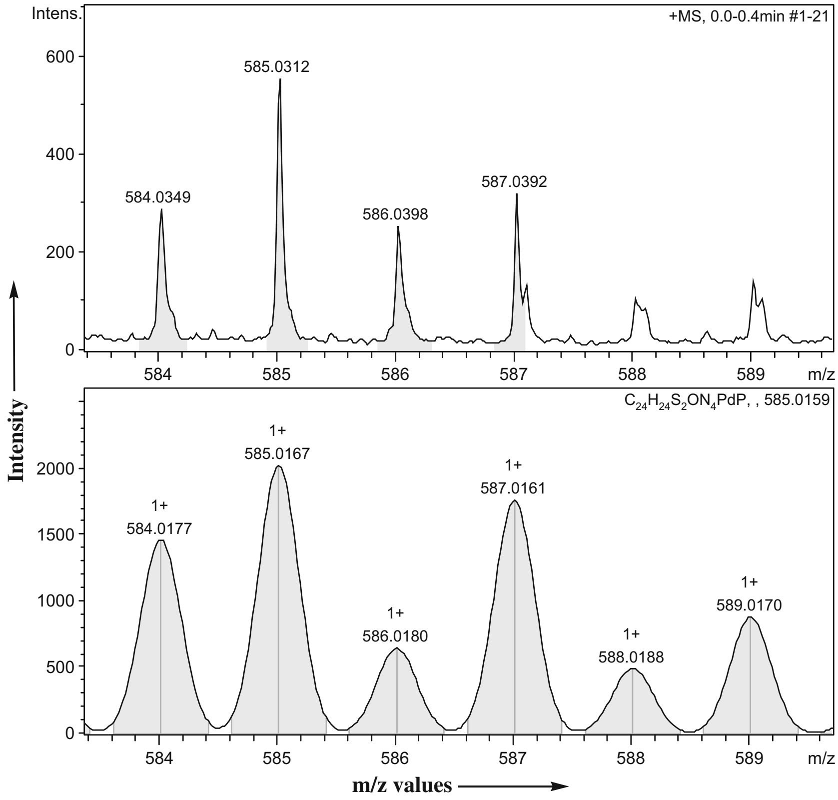
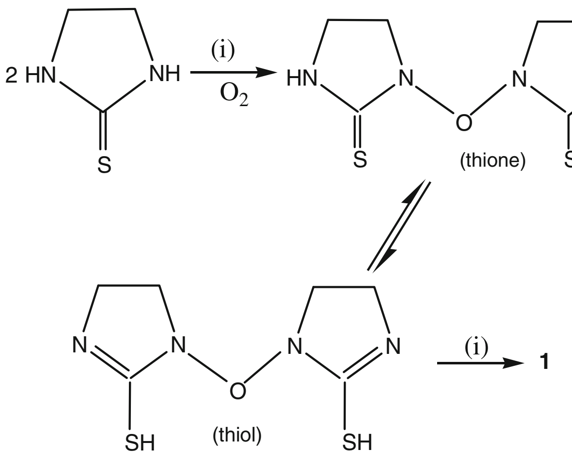


Figure 2. Isotopic pattern of molecular species, $[M+H]^+$: (above) observed, m/z = 585.03, (below) calcd. 585.02).



Scheme 2. (i) $PdCl_2(PPh_3)_2$, Et_3N.

Proton NMR spectrum of compound **1** in $CDCl_3$ did not show –NH signal (*cf*: ligand, NH signal, δ = 6.40 ppm) and it confirmed deprotonation of NH protons. The $-CH_2-$ protons showed a broad signal at δ, 3.67 ppm, a lower field relative to the free ligand at 3.59 ppm. The P–Ph protons showed a multiplet in the range, 7.46–7.67 ppm. The presence of CH_3CN was confirmed as a characteristic signal occurring at 2.18 ppm. Further, the ^{31}P NMR spectrum showed a signal at δ, 30.0 ppm with coordination shift ($\delta_{\text{complex}} - \delta_{\text{ligand}}$) of 34.7 ppm.

The ESI-mass spectrum of compound **1** has shown a signal at m/z = 585.03 (calcd m/z = 585.02) which supports the formation of molecular species, $[Pd\{\eta^3\text{–S, O, S–}(SC_3H_4N_2\text{–O–}N_2C_3H_4S)\}(PPh_3)+H]^+$, chemical formula $C_{24}H_{24}N_4OPPdS_2$, (Figure 2). The isotopic pattern, observed and calculated, confirm the formation of molecular ion species. Scheme 2 depicts the probable pathway for the formation of compound **1.**

4. Conclusions

Complex $[Pd\{\kappa^3\text{–S, O, S–}(SC_3H_4N_2\text{–O–}N_2C_3H_4S)\}(PPh_3)]\cdot CH_3CN$ **1** emerged from *in situ* transformation of 1,3-imidazolidine-2-thione into a new thiolate dianion, $(SC_3H_4N_2\text{–O–}N_2C_3H_4S)^{2-}$. This is an unusual reaction in synthetic inorganic chemistry, and may play an important role in the heterocyclic chemistry by easily combining imino groups.

Supplementary Information (SI)

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC number: 784651 or **1** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.cam.ac.uk).

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References

1. Raper E S 1996 Complexes of heterocyclic thionates.1. Complexes of monodentate and chelating ligands *Coord. Chem. Rev.* **153** 199
2. Raper E S 1997 Complexes of heterocyclic thionates. Part 2. Complexes of bridging ligands *Coord. Chem. Rev.* **165** 475
3. Garcia-Vazquez J A, Romero J and Sousa A 1999 Electrochemical synthesis of metallic complexes of bidentate thiolates containing nitrogen as an additional donor atom *Coord. Chem. Rev.* **193–195** 691
4. Nakatsu Y, Nakamura Y, Matsumoto K and Ooi S 1992 Synthesis and solution behavior of mononuclear palladium(II) and platinum(II) complexes containing pyridine-2-thiolate as a ligand. Crystal structure of chloro (pyridine-2thiolato)(triphenylphosphine)palladium(II) *Inorg. Chim. Acta* **196** 81
5. Lobana T S, Verma R, Hundal G and Castineiras A 2000 Metal-heterocyclic thione interactions-12. Heterocyclic-2-thiolates platinum(II)/palladium(II): The crystal structures of first examples of cis-$[M(\eta^1\text{-S-pyridine-2-thiolato})_2(L\text{–}L)]$ {M = Pt, Pd, L–L = 1, 2-bis(diphenyl phosphino)ethane, M = Pt, L–L = 1,2-bis(diphenylphosphino)ethene}complexes containing pendant pyridyl groups *Polyhedron* **19** 899
6. Galan R F, Manzano B R, Otero A, Poujaud N and Kubicki M 1999 Synthesis and characterization of new allyl palladium complexes with thionate ligands; X-ray molecular structures of $[Pd_3(\eta^3\text{–}C_4H_7)_3\{pm(Me)_2S\}_2](CF_3SO_3)$ and $[Pd\{pm(Me)_2S\}_2]$, $\eta^3\text{–}C_4H_7 = \eta^3\text{–2–Me}C_3H_4$, $pm(Me)_2S$ = Pyridine-4,6-dimethyl-2-thionate *J. Organomet. Chem.* **579** 321
7. Padilla E M, Yamamoto J W and Jensen C M 1990 Isolation of palladium(II) quinoline-2-thione (HqnS) and quinoline-2-thiolate (qnS) complexes: Crystal structures of $Pd(HqnS)(PMe_3)Cl_2$, $[Pd(HqnS)_2(PMe_3)Cl][Cl]$ and vic-$Pd_2(\mu, N\text{–}S\eta^2\text{–qnS})_2(\eta^1\text{–qnS})_2(PMe_3)_2$ *Inorg. Chim. Acta* **174** 209
8. Lobana T S, Sultana R, Hundal G and Castineiras A 2009 Synthesis and crystal structures of polynuclear complexes of Cu^I with 1-methyl-1, 3-imidazoline-2-thione *Polyhedron* **28** 1573
9. Lobana T S, Kaur P J, Castineiras A, Turner P and Failes T W 2008 Synthesis, crystal and molecular structures of isomorphic N, S-bridged $[Cu_2(\mu_2\text{–I})_2(PPh_3)_2(\mu_2\text{–N,S–pymSH})]$ dimer and S-bonded $[CuX(\eta^1\text{–S–pymSH})(PPh_3)_2]$ monomers (X = Cl, Br) *Struct. Chem.* **19** 727

10. Lobana T S, Renu Sharma, Hunda G and Butcher R J 2006 Synthesis of 1D $\{Cu_6(\mu_3\text{–}SC_3H_6N_2)_4(\mu\text{–}SC_3H_6N_2)_2(\mu\text{–}I)_2I_4\}_n$ and 3D $\{Cu_2(\mu\text{–}SC_3H_6N_2)_2(\mu\text{–}SCN)_2\}_n$ polymers with 1, 3-imidazolidine-2-thione: Bond isomerism in polymers *Inorg. Chem.* **45** 9402
11. Lobana T S, Rohit Sharma and Butcher R J 2008 Pyridine-2-thione (pySH) derivatives of silver(I): Synthesis and crystal structures of dinuclear $[Ag_2X_2(\mu\text{–S–pySH})_2(PPh_3)_2]$ complexes (X = Cl, Br) *Polyhedron* **27** 1375
12. Lobana T S and Castineiras A 2002 Metal-heterocyclic thione interactions. 13. Pyridine-2-thione derivatives of copper(I): Crystal structure of dinuclear [bromo (pyridine-2-thione)(tri-p-tolylphosphine)copper(I)]$_2$complex *Polyhedron* **21** 1603
13. Butler L M, Creighton J R, Oughtred R E and Raper E S 1983 Preparation, characterisation and crystal structure of dichloro tetrakis-(1-methylimidazoline-2(3H)-thione)palladium(II) dehydrate *Inorg. Chim. Acta* **75** 149
14. Lobana T S, Kaur P J, Hundal G, Butcher R J and Castineiras A 2008 Variable bonding modes of pyrimidine-2-thione in Pd^{II}/Pt^{II} complexes $[M(\eta^2\text{–N, S–pymS})(\eta^1\text{–S–pymS})(PPh_3)]$ and $[M(\eta^1\text{–S–pymS})^2(L\text{–}L)]$ (L–L = dppm, dppe) *Z. Anorg. Allg. Chem.* **634** 747
15. Nakatsu Y, Nakamura Y, Matsumoto K and Ooi S 1992 Synthesis and solution behavior of mononuclear palladium(II) and platinum(II) complexes containing pyridine-2-thiolate as a ligand. Crystal structure of chloro (pyridine-2-thiolato)-(triphenylphosphine)palladium(II) *Inorg. Chim. Acta* **196** 81
16. Umakoshi K, Kinoshita I and Ooi S 1987 Dinuclear palladium(II) complex of pyridine-2-thiol *Inorg. Chim. Acta* **127** L41
17. Umakoshi K, Ichimura A, Kinoshita I and Ooi S 1990 The dinuclear palladium(II) complex of pyridine-2-thiol. Synthesis, structure, and electrochemistry *Inorg. Chem.* **29** 4005
18. Mendia A, Cerrada E, Arnaiz F J and Languna M 2006 Pyridine-2-thionate as a versatile ligand in Pd(II) and Pt(II) chemistry: The presence of three different coordination modes in $[Pd_2(\mu_2\text{–}S, N\text{–}C_5H_4SN)(\kappa^2\text{–}\mu_2\text{–}S\text{–}C_5H_4SN)(\kappa^2\text{–dppm})(S\text{–}C_5H_4SN)_2]$ *Dalton Trans.* 609
19. Brendler E, Wachtler E, Heine T, Zhechkov L, Langer T, Pottgen R, Hill A F and Wagler J 2011 Stannlyene or metallastanna(IV)octane: A matter of formalism *Angew Chem. Int. Eng. Ed.* **50** 4696
20. Pons J, García-Antón J, Solans X, Font-Bardia M and Ros J 2008 Trans-dichloridobis(triphenylphosphine) palladium(II) *Acta Cryst. E* **64** m621
21. Altomare A, Cascarano G, Giacovazzo C and Guagliardi A 1993 Completion and refinement of crsytal structures with SIR 92 *J. Appl. Crystallogr.* **26** 343
22. Sheldrick G M 2008 A short history of SHELX *Acta Cryst. A* **64** 112