Tertiary phosphine abstraction from a platinum(II) coordination complex with SeCN⁻: Crystal and molecular structures of Se=PTA and [Se=PTA-Me]I · CH₃OH

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Abstract

Reacting [PtCl(PTA)₃]Cl (PTA = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane) with KSeCN in aqueous or MeOH medium results in the abstraction of the PTA ligands to yield Se=PTA. The reaction also proceeds quantitatively by direct reaction of PTA and KSeCN in water or methanol. The methylated PTA ligand, [PTA-Me]I (1-methyl-1-azonia-3,5-diaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane iodide), reacts accordingly with KSeCN, albeit significantly slower. The crystal structure of Se=PTA, **1**, and [Se=PTA-Me]I · CH₃OH, **2**, revealed P=Se bond distances of 2.0991(19) and 2.100(2) Å, respectively. The first order phosphorous selenium coupling constants, $^{1}J_{P-Se}$ (D₂O), of 722 and 788 Hz for Se=PTA and [Se=PTA-Me]I, respectively, indicates the latter is significantly less electron rich.
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Keywords: PTA; Phosphine selenides; Crystal structures

1. Introduction

The air stable, water soluble phosphine ligand 1,3,5-triaza-7-phosphatricyclo [3.3.1.1^{3,7}]decane (PTA) has attracted much interest the last decade due to the fact that water soluble transition metal complexes can be prepared with relative ease. The groups of Darensbourg [1,2] and Joó [3] conducted extensive fundamental studies in this area and also illustrated preliminary applications in homogeneous catalysis. A comprehensive review on the coordination chemistry of this ligand was also published recently [4].

As part of a systematic study [5–8] on the co-ordination chemistry of the PTA phosphine ligand with the platinum group metals Se=PTA, **1**, was isolated after reaction of KSeCN and [PtCl(PTA)₃]Cl in methanol. Upon further investigation it was found that both PTA and the methylated version, [PTA-Me]I, reacts quantitatively with KSeCN, in both water and methanol, to yield the corresponding selenides. Crystal structures of both the latter compounds are reported in this paper.

The steric bulk and the electron donating ability of a phosphine ligand are difficult properties to separate and quantify since they are closely related. Several ways of evaluating the electronic properties of phosphine ligands are described in the literature. These include NMR measurements of first order Pt–P, P–BH₃ or Rh–P coupling constants [9–11], or by measuring the CO stretching frequencies in complexes such as [Ni(L)(CO)₃] or

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trans-[RhCl(CO)(L)$_2$] in solution [12–14]. Computational methods using density function theory and semi-empirical Hamiltonians, amongst others, to calculate the electronic properties of phosphine and other ligands are also emerging [15,16]. It is also known that the first order phosphorus selenium coupling constant, $^1J_{P–Se}$ is a fair measure of the basicity of the parent phosphine in phosphine selenide compounds, Se=PR$_3$, with a larger coupling constant corresponding to a less basic phosphine [17]. It is well established [18] that the coupling constant between two directly linked atoms is primarily governed by the Fermi-contact interactions between the respective s-orbitals. Electron withdrawing substituents results in an increase in the s-character of the phosphorous lone pair while electron donating substituents result in a decrease in s-character according to Bent's rule [19].

In this regard the preparation and characterisation of the selenide derivatives of PTA and [PTA-Me]I was used as a method to compare the electronic properties of these ligands with that of other well known phosphine ligands from the literature.

2. Experimental

^{31}P NMR spectra were recorded as D$_2$O and CD$_3$OD solutions on a Varian Unity spectrometer operating at 121.352 MHz; the spectra were calibrated relative to an external standard of 85% H$_3$PO$_4$ at 0 ppm. The ^{31}P NMR data for selected compounds are given in Table 1.

2.1. Preparations and chemicals

[PtCl(PTA)$_3$]Cl was prepared according to the procedure developed in our laboratories [5], KSeCN (Aldrich) were used as received. PTA, O=PTA and [PTA-Me]I were prepared according to the procedure of Daigle et al. [20]. S=PTA was prepared by refluxing PTA with sulphur in toluene under a nitrogen atmosphere to prevent oxidation of the PTA ligand [21]. [O=PTA-Me]I and [S=PTA-Me]I were prepared by the reaction of MeI with O=PTA and S=PTA, respectively [22].

Table 1
^{31}P NMR data for selected PTA derivatives, ($^1J_{P–Se}$/Hz)

	D$_2$O/ppm	CD$_3$OD/ppm
PTA	−98.4	−98.7
O=PTA	−2.9	−8.0
S=PTA	−17.9	[b]
Se=PTA	−31.9(722)	−34.3(753)
[PTA-Me]I	−85.6	−84.5
[O=PTA-Me]I	−1.3	[b]
[S=PTA-Me]I	−9.0	[b]
[Se=PTA-Me]I	−8.9(705)[a], −24.1(788)	−8.5(739)[a], −24.4(815)

[a] Intermediate, see text.
[b] Not obtained due to limited solubility.

2.1.1. [Se=PTA]

PTA (500 mg, 3.18 mmol) was dissolved in methanol (30 cm^3) and KSeCN (576 mg, 4 mmol) was added under a nitrogen atmosphere. The reaction mixture was stirred for 10 min at room temperature. After removal of the methanol under vacuum the solid residues were extracted with boiling dichloromethane. Filtration and evaporation of the dichloromethane fraction yielded the desired complex (698 mg, 93%). Compound **1** can be purified by recrystallization from water. Anal. Calc. for C$_6$H$_{12}$N$_3$PSe: C, 30.52; H, 5.12; N, 17.80. Found: C, 30.68; H, 5.22; N, 17.91.

2.1.2. [Se=PTA-Me]I

(a) [PTA-Me]I (250 mg, 0.84 mmol) was dissolved in methanol (20 cm^3) and KSeCN (288 mg, 2 mmol) was added under a nitrogen atmosphere followed by stirring at room temperature for 30 min. The methanol was reduced by half by passing a nitrogen stream over the solution followed by filtration to collect the desired product as a white precipitate (261 mg, 82%).

(b) [Se=PTA-Me]I was also prepared by refluxing [PTA-Me]I (250 mg, 0.84 mmol) and Se powder (118 mg, 1.5 mmol) in a 1:1 mixture of methanol and toluene for 5 h. The reaction mixture was transferred to a soxhlet extractor and extracted with methanol for 6 h. The methanol filtrate was evaporated to yield the desired complex (206 mg, 65%).

Crystals suitable for X-ray diffraction were obtained by recrystallization from methanol. Anal. Calc. for C$_8$H$_{19}$N$_3$OPSeI: C, 23.43; H, 4.67; N, 10.25. Found: C, 22.97.68; H, 4.84; N, 10.03.

2.2. Crystallography

The intensity data for the crystallography were collected at 293(2) K on a Siemens SMART CCD diffractometer using Mo Kα (0.71073 Å) radiation from a rotating anode source. Individual frames were collected using the ω-scan technique and the first 50 frames were recollected after completion to correct for decay, of which none was observed. All reflections were merged and integrated using SAINT [23] and corrected for Lorentz, polarisation and absorption effects using SADABS [24]. The structures were solved by the Patterson method and the positions of the non-H atoms determined from consecutive Fourier maps and refined through full-matrix least squares cycles using the SHELXS97 [25] and SHELXL97 [26] software package with $\Sigma(|F_o| - |F_c|)^2$ being minimised. The hydrogen atoms were calculated as riding on the parent C atoms (alkyl = 0.96 Å) and refined with an overall temperature factor; all non-H atoms were refined anisotropically. The graphics were done using the DIAMOND Visual Crystal Structure Information System software [27]. Details of the data collection and refinement parameters are given in Table 2. The

Table 2
Crystallographic data and refinement parameters

	1	2
Empirical formula	$C_6H_{12}N_3PSe$	$C_8H_{19}IN_3OPSe$
Formula weight	236.12	410.09
Crystal system	Hexagonal	Monoclinic
Space group	$R3m$	$P2_1/c$
a (Å)	9.4646(13)	9.5970(19)
b (Å)	9.4646(13)	12.457(3)
c (Å)	8.5047(17)	10.892(2)
α (°)	90	90
β (°)	90	90.38(3)
γ (°)	120	90
V (Å³)	659.77(18)	1302.1(5)
Z	3	4
D_c (g cm⁻³)	1.783	2.092
μ (mm⁻¹)	4.390	5.359
T_{max}/T_{min}	0.928/0.702	0.648/0.414
$F(000)$	354	792
Crystal size (mm)	$0.08 \times 0.04 \times 0.04$	$0.08 \times 0.07 \times 0.06$
θ Limit (°)	3.45–32.81	4.25–27.48
Index ranges	$-13 \leqslant h \leqslant 9$;	$-9 \leqslant h \leqslant 12$;
	$-13 \leqslant k \leqslant 13$;	$-16 \leqslant k \leqslant 16$;
	$-12 \leqslant l \leqslant 12$	$-14 \leqslant l \leqslant 14$
Reflections collected/unique	2353/551	11 269/2972
R_{int}	0.088	0.050
Observed reflections $[I > 2\sigma I]$	480	1905
Data/restraints/parameters	551/1/27	2972/2/149
Goodness-of-fit	1.047	1.104
R $(I > 2\sigma I)$		
R^a	0.0337	0.0586
wR^b	0.0802	0.1827
R (all data)		
R^a	0.0425	0.0931
wR^b	0.0865	0.2013
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å⁻³)	0.390; −0.624	1.519; −1.915

[a] $R = [(\Sigma\Delta F)/(\Sigma F_o)]$.
[b] $wR = \Sigma[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]^{1/2}$.

hydrogen atoms of the disordered methanol solvent molecule were omitted from the final refinement.

3. Results and discussion

Although the oxides and sulphides of PTA and the sulphide of its alkylated derivative [PTA-Me]I have been crystallographically investigated [28,29], the corresponding selenide derivatives have attracted a lot less interest. A single cursory reference to [Se=PTA] was obtained as part of a spectroscopic study on aminophosphines and related compounds [21], but to date no crystal structures or NMR data have been reported.

The reaction of KSeCN with arylphosphines in acetonitrile to yield the corresponding phosphine selenides has been reported [30]. An interesting crystal structure confirming Se abstraction from SeCN⁻ by the bidentate ligand $Ph_2PCH_2PPh_2$ (dppm) in a Pd(II) coordination sphere (from [Pd(SeCN)₂(dppm)]) is also known [31]. In this study after opening of the chelate, and selenation of one P atom, the resulting P=Se moiety re-attached to the Pd metal through the Se atom to incorporate the Se in the chelate to form [Pd(CN)(SeCN)(dppm = Se)]. This study represents the only prior example of phosphine abstraction from a metal coordination sphere by the Se originating from SeCN⁻.

We recently reported on the chemical behaviour of [MCl(PTA)₃]Cl (M = Pd and Pt) towards several halides and pseudo-halides in aqueous solutions. From the reactions of these complexes with SCN⁻ (Pd in acidic medium to prevent hydrolysis/decomposition) crystals with the composition trans-[Pd(SCN)₂(PTA-H)₂](SCN)₂ and {[Pt(NCS)(PTA)₃]SCN}₃ · 5H₂O were isolated, respectively [7,8]. The [Pt(NCS)(PTA)₃]⁺ complex was formed as the expected substitution product between [PtCl(PTA)₃]⁺ and NCS⁻ in an equilibrium process. In an attempt to prepare the analogous [Pt(SeCN)(PTA)₃]-SeCN complex KSeCN was added to an aqueous solution of [PtCl(PTA)₃]Cl. The original colourless solution immediately turned yellow and then began fading until it was colourless again. Upon slow evaporation of the solvent, crystals of 1 were obtained.

Direct reaction of PTA with KSeCN in D₂O and CD₃OD revealed a single rapid reaction converting PTA quantitatively to 1 as verified by ³¹P NMR. The reaction was completed within the time taken to process the first FID's, usually less than 3 min. The crystals of 1 decompose over a few weeks, with the first light pink signs of elemental Se appearing after about 3 days. It was furthermore found that the P(V) starting material used in the PTA synthesis, [P(CH₂OH)₄]Cl (³¹P D₂O: 26.2 ppm), reacts directly with KSeCN to yield the corresponding Se=P(CH₂OH)₃ (³¹P D₂O: 37.1 ppm $^1J_{P-Se} = 672$ Hz), complex; O=PTA and S=PTA does not however react with KSeCN. This observation emphasises the lability of the hydroxymethyl substituents in [P(CH₂OH)₄]Cl.

The preparation of [S=PTA-Me]I can be achieved either by reaction of [PTA-Me]I with sulphur in benzene as well as by the reaction of S=PTA with MeI [22]. In comparison the corresponding [O=PTA-Me]I cannot be prepared by oxidation of [PTA-Me]I with H₂O₂, however reaction of O=PTA with MeI does yield the desired compound [32,33]. In contrast to the behaviour of PTA that is quantitatively converted from PTA to Se=PTA by SeCN⁻, a ³¹P NMR study revealed that the methylated analogue, [PTA-Me]I, reacts significantly slower with KSeCN under similar conditions. Furthermore at least two different Se containing species were identified by ³¹P NMR see Table 1. Due to limited solubilities it could not be established which of the two respective signals corresponded with the intermediate and final products. In order to alleviate this problem a control experiment was performed where

[Se=PTA-Me]I was prepared by the action of Se powder on [PTA-Me]I in a refluxing methanol/toluene (1:1) solution and was identified as the resonance at −24 ppm. Currently the ^{31}P resonance at −8.5 ppm is postulated to be a [NCSe–PTA-Me] intermediate before liberation of CN$^-$ occurs. Poor solubility of the [X=PTA-Me]I (X = O, S, Se) complexes in all common solvents complicated the NMR investigation to such an extent that more detailed investigations were not possible.

The numbering scheme and thermal displacement ellipsoids for **1** and **2** are shown in Figs. 1 and 2, respectively, with selected geometrical parameters listed in Table 3.

Compound **1** crystallises on a threefold rotation axis (running through the Se and P atoms) in the hexagonal space group R3m. The PTA ligand retained its highly symmetrical rigid cage-like character with close to ideal tetrahedral angles observed around all atoms, see Table 3. All bond distances are within normal ranges for these kinds of compounds; see Table 4 for representative comparisons.

Compound **2** crystallises on a general position in the monoclinic space group P2$_1$/c as distinct anion–cation pairs with a closest contact of 2.963 Å (I–H1B). Each cation–anion pair is accompanied by a severely disordered MeOH solvent molecule. Due to the positive charge on the methylated N(1) atom all bond distances and angles towards this side of the molecule are significantly affected with all N(1)–C bonds appreciably longer

Fig. 2. Molecular diagram showing the numbering scheme and thermal displacement ellipsoids (30% probability level) of the cation in **2**, the I$^-$ anion and disordered methanol solvent molecule were omitted for clarity. Hydrogen atoms are of arbitrary size.

Table 3
Selected geometrical parameters for **1** and **2**

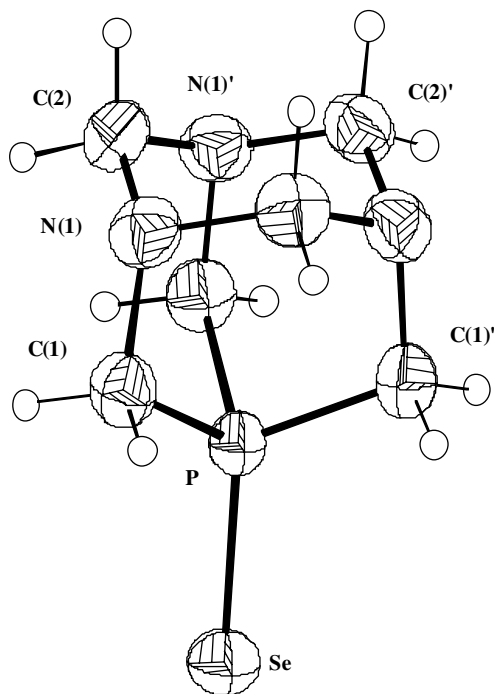| Bond/angle	1/Å/°	2/Å/°
P–Se	2.0991(19)	2.100(2)
P–C(1)	1.823(4)	1.846(8)
P–C(2)		1.827(8)
P–C(3)		1.824(8)
N(1)–C(1)	1.478(7)	1.483(10)
N(1)–C(2)	1.469(3)	
N(1)–C(4)		1.525(10)
N(1)–C(5)		1.545(10)
N(1)–C(7)		1.495(10)
N(2)–C(2)		1.452(10)
N(2)–C(4)		1.431(9)
N(2)–C(6)		1.461(10)
N(3)–C(3)		1.474(10)
N(3)–C(5)		1.433(10)
N(3)–C(6)		1.455(10)
Se–P–C(1)	117.78(17)	113.3(3)
Se–P–C(2)		119.9(3)
Se–P–C(3)		120.3(3)
C(1)–P–C(1)′	100.0(2)	
C(1)–P–C(2)		99.2(4)
C(1)–P–C(3)		100.4(4)
C(2)–P–C(3)		100.1(4)
N–C(1)–P	110.7(3)	
[N–C–P]avg		109.7(5)
C(1)–P–C(2)		
[C–N–C]avg	109.7(5)	110.7(8)
N–C(2)–N	114.8(4)	
[N–C–N]avg		112.1(6)

Fig. 1. Molecular diagram of **1** showing the numbering scheme and thermal displacement ellipsoids (30% probability level). Hydrogen atoms are of arbitrary size.
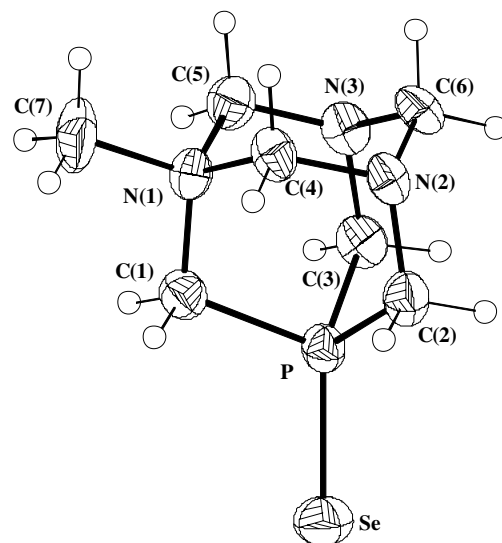
than the corresponding bonds towards N(2) and N(3), see Table 3.

Selected geometrical parameters for PTA and representative X=PTA complexes (substituted on the P atom) are listed in Table 4.

Table 4
Comparison of geometrical parameters for PTA and derivatives

No.	Ligand	P–X/Å	[P–C]avg/Å	[C–P–C]avg/°	Ref.
1	PTA		1.857(3)	96.1(1)	[34]
2	O=PTA	1.476(2)	1.816(2)	100.3(1)	[28]
3	S=PTA	1.9572(4)	1.834(2)	100.3(1)	[28]
4	Se=PTA	2.0991(19)	1.823(4)	100.0(2)	[TW]
5	[Me-PTA]BF$_4$[a]	1.772(2)	1.811(2)	102.2(1)	[35]
6	[O=PTA-Me]BPh$_4$	1.478(13)	1.814(23)	100.51(1)	[29]
7	[Se=PTA-Me]I · MeOH	2.100(2)	1.832(8)	99.9(4)	[TW]

TW = This work.
[a] "Me-PTA" refers to methylation on P, while "PTA-Me" refers to methylation on N.

Within the range of P(V) complexes (2–7 in Table 4) most of the bond distances and angles are very similar but differ significantly from those found in the parent P(III) PTA molecule. Most notably of these include the slightly shorter P–C bond distances and the larger C–P–C angles for the P(V) complexes compared to those in PTA. The major geometrical parameters for X=PTA and [X=PTA-Me]$^+$ (2 and 4 compared to 6 and 7 in Table 4) were found to be very similar; these include the X=P and P–C bonds and the C–P–C angles.

It is generally accepted that first order coupling constants are primarily composed of the s-orbital contribution to the bond in question. A decrease in the P=Se bond distance, resulting in more effective s-orbital overlap should therefore correspond with an increase in the first order coupling constant. In an earlier study [43] it has been claimed that there is indeed a linear correlation between P–Se bond distances and $^1J_{P-Se}$ in some selected phosphine selenides even though the P=Se bond distances are very similar. Furthermore it was found that very large phosphines did not form phosphine selenide compounds under even the most extreme conditions. If the steric demand of the phosphine did permit the corresponding selenide to form it obeyed the above mentioned linear relationship between bond length and coupling constant indicating that the electronic property of the phosphine can in fact be isolated from the steric properties of the phosphine. However, the data in Table 5 does not lend support to a linear correlation over a wider selection of phosphine selenides. Although the P=Se bond distances are very similar for most complexes ($\Delta d = 0.030(5)$ Å) listed in Table 5, the first order coupling constants differ considerably ($\Delta J_{P-Se} = 139$ Hz), but not systematically with distance. The differences in coupling constants most likely reflect differences in electronic properties of the different phosphines ligands as indicated by a general trend in the carbonyl stretching frequencies of the corresponding [Ni(L)(CO)$_3$] [12] complexes (P(NMe$_2$)$_3$ being one definite outlier).

Even though PTA is generally accepted to be a water soluble oxygen stable analogue of PMe$_3$, from the data presented in Table 5 it is clear that PTA is significantly less electron rich. Furthermore it is also evident that [PTA-Me]$^+$ is in turn less electron rich than PTA, which is most probably due to electron density withdrawn from the phosphorous atom towards the positively charged nitrogen atom.

4. Supplementary material

Full crystallographic details for [Se=PTA] and [Se=PTAMe]I · CH$_3$OH have been deposited with the Cambridge Crystallographic Data Centre, CCDC 271787 and CCDC 271786, respectively.

Table 5
P=Se bond distances and $^1J_{P-Se}$ coupling constants for selected phosphines and CO stretching frequencies in their corresponding [Ni(L)(CO)$_3$] complexes

Phosphine	P–Se/Å	$^1J_{P-Se}$/Hz/CDCl$_3$	υNi/cm^{-1}	Ref.
PCy$_3$	2.108(1)	676	2056.4	[36]
P(2,6-C$_6$H$_3$(OMe)$_2$)$_3$	2.136(2)	717	∼2058	[37]
P(NMe$_2$)$_3$	2.120(1)	797	2061.9	[38]
PMe$_3$	2.111(3)	684	2064.1	[39]
P(2-C$_6$H$_3$(Me))$_3$	2.116(5)	708	2066.6	[40]
P(3-C$_6$H$_3$(Me))$_3$	2.109(5)	736	2067.2	[41]
PPh$_3$	2.106(1)	733	2068.9	[42]
PTA	2.0991(19)	753[a]		[TW]
PTA-Me	2.100(2)	815[a]		[TW]

[a] CD$_3$OD.

Acknowledgements

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