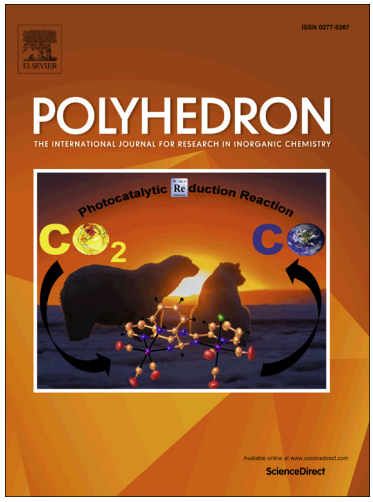

NMR Studies of Platinum *bis*phosphine complexes of phenylphosphonamido-diselenoate

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INDEX ENTRY

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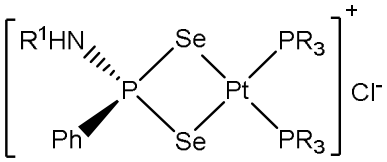

New Platinum complexes of the diselenophosphorus ligand show interesting multi-element NMR

NMR Studies of Platinum *bis*phosphine complexes of phenylphosphonamidodiselenoate.

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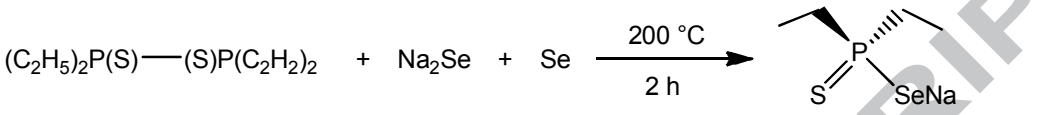
Abstract

A series of platinum (II) *bis*phosphine complexes **1**-**20** [Pt(R'NH(Ph)PSe_2)$(PR_3)_2$] (where R = Ph_3, Ph_2Me, Me_2Ph, PMe_3 and R' = ^{i}Pr, ^{n}Bu, ^{s}Bu, ^{t}Bu, Benz) have been prepared by reaction of *cis*-[Pt$(PR_3)_2Cl_2$)] and the alkyl ammonium salt of the ligand. The novel compounds were characterised by multinuclear NMR, and in one case X-Ray crystallography. The molecular structures of two ligand salts and [Pt(^{s}Bu'NH(Ph)PSe_2)$(PPh_3)_2$] are reported.

Keywords Selenium, phosphorus, platinum, complex, X-ray structure

The mixed chalcogen sodium diethylselenothiophosphinate[i] and sodium diethyldiselenophosphonate[1,2] have been known since the 1960's, when Kuchen and Knop synthesised the former by the reaction of sodium selenide with the 1,1,2,2-tetraethyldiphosphine 1,2-disulfide dimer (Eqn 1).



Eqn 1

Kuchen and Hertel[2,3] also studied the metal complexes of thiophosphinic and selenophosphinic acids including the chelating abilities of these ligand systems in discrete monomers and dimers, as well as some coordination polymers of zinc(II) and cadmium(II). Their results are based on IR studies performed by Coates and Mulcherjee,[4] which eg confirms the presence of the P-Se bonds by showing peaks between 400 and 500 cm^{-1}. In the late 1990's and early 2000's research on selenophosphorus ligands by Davies *et al.*,[5] with a view to investigating semiconducting metal selenides, led to the tris-(diselenophosphinato)indium complex.[6] As with all selenium chemistry reactions with metal containing compounds are much less common than those of their sulfur analogues. One similar reaction of Woollins' and Lawesson's Reagent is the reaction with sodium alkoxides to form sodium diselenophosphonate or sodium dithiophosphonates, which may then be reacted with metal salts to form a range of complexes.[7,8]

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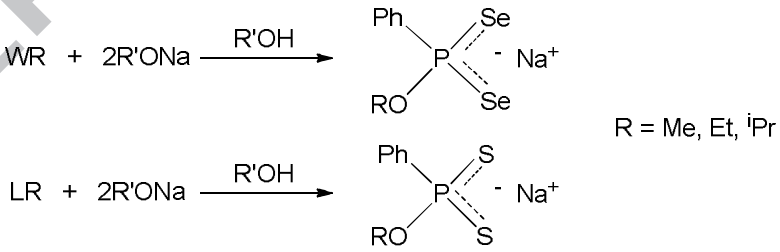


Eqn 2

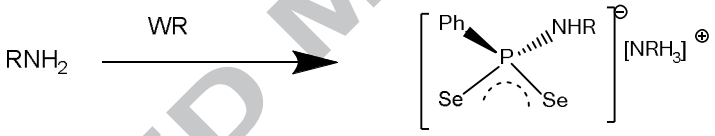
Whilst monomeric and dimeric species are the most common products of this type of reaction, several large clusters which contain diselenophosphate ligands have been synthesised, eg in 1998 Liu and co-workers[9] reported the first selenide-centred Cu^{I}_{8} cubic cluster incorporating dialkyl diselenophosphate ligands. Following the success of the above

synthesis, $Ag_8(\mu_8\text{-}Se)[Se_2P(O^iPr)_2]_6$ and $Ag_6[Se_2P(O^iPr)_2]_6$ were synthesised. The interstitial selenium atom has a body centred cubic array with the twelve silver atoms surrounding it.

In extension of the alkoxy systems, recent research carried out by our group has centred upon the synthesis of ammonium phenylphosphonamidodiselenoates and the first metal complex thereof.[10] Here we describe the generalisation of the synthesis of ammonium phenylphosphonamidodiselenoates and some investigations into this coordination chemistry of this system.

Results and Discussion

The direct reaction of Woollins' Reagent with amines, without solvent, produces ammonium phenylphosphonamidodiselenates. (eqn 3) in high yields. These compounds are air and light sensitive, changing colour from colourless or pale yellow to dark oranges and reds on exposure. The X-Ray structures of ^{n}BuAWR, and ^{s}BuAWR are shown below (Figure 1, Tables 1). The $^{31}P\{^1H\}$ NMR spectra of these compounds show singlets in the range 42.0 - 55.8 ppm with $^1J_{P\text{-}Se}$ in the range 613-634 Hz.



R = ^{n}Bu, ^{s}Bu, ^{t}Bu, Bz Eqn 3

Surprisingly we found that when isopropylamine was used in the synthesis, the counter ion of the product is the diisopropyl species. This is most likely formed from an impurity in the starting material (verified by ^{1}H NMR, the diisopropylamine impurity is generated during the purification process using CaH_2).

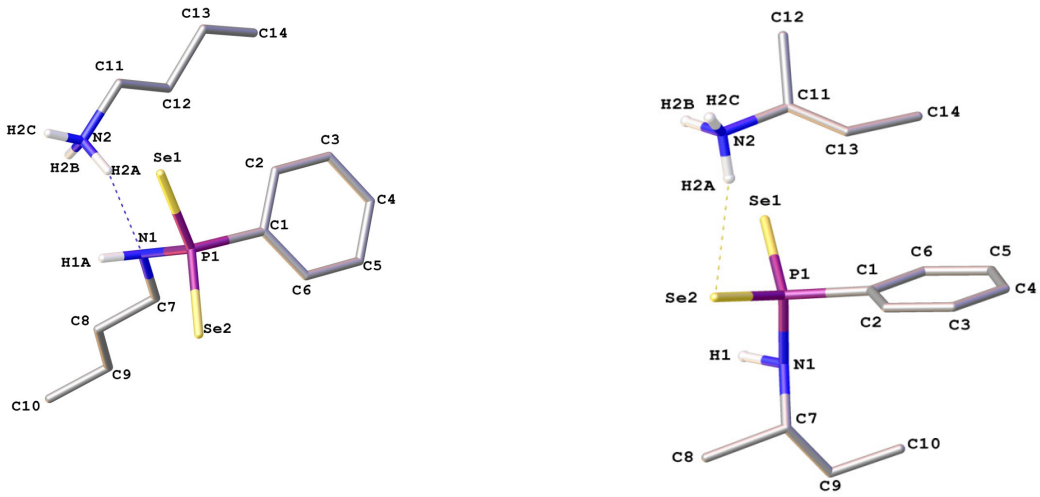


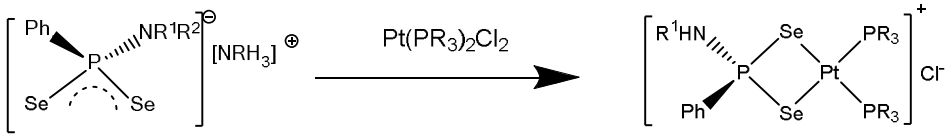
Figure 1. The X-ray crystal structures of ^{n}BuAWR, and ^{s}BuAWR,. C-H hydrogen atoms omitted for clarity.

.

	^{n}BuAWR	^{s}BuAWR		^{n}BuAWR	^{s}BuAWR
P(1)-Se(1)	2.1393(13)	2.152(2)	N(1)-P(1)-C(1)	101.94(12)	103.1(3)
P(1)-Se(2)	2.1613(9)	2.1669(18)	N(1)-P(1)-Se(1)	106.41(9)	105.6(2)
P(1)-N(1)	1.695(2)	1.683(6)	C(1)-P(1)-Se(1)	110.88(11)	110.8(2)
P(1)-C(1)	1.824(3)	1.821(7)	N(1)-P(1)-Se(2)	111.73(9)	113.5(2)
N(1)-C(7)	1.486(4)	1.504(10)	C(1)-P(1)-Se(2)	109.99(10)	107.1(2)
C(1)-C(2)	1.406(4)	1.397(10)	Se(1)-P(1)-Se(2)	115.06(3)	116.00(8)
C(1)-C(6)	1.392(4)	1.403(10)	C(7)-N(1-)P(1)	119.02(19)	120.4(5)
N(2)-C(11)	1.500(4)	1.515(9)	C(6)-C(1)-C(2)	119.0(2)	118.9(7)

Table 1 Selected bond lengths (Å) and angles (^{o}) for ^{n}BuAWR, and ^{s}BuAWR

^{i}PrAWR, ^{n}BuAWR, ^{s}BuAWR, ^{t}BuAWR and BenzAWR, were reacted with suitbale platinum phosphine chlorides synthesising twenty compounds **1**-**20,** Eqn 4



Eqn 4

	^{i}PrAWR	^{n}BuAWR	^{s}BuAWR	^{t}BuAWR	BenzAWR
PMe_3	(**1**)	(**5**)	(**9**)	(**13**)	(**17**)
PMe_2Ph	(**2**)	(**6**)	(**10**)	(**14**)	(**18**)
$PMePh_2$	(**3**)	(**7**)	(**11**)	(**15**)	(**19**)
PPh_3	(**4**)	(**8**)	(**12**)	(**16**)	(**20**)

Regardless of the size of the ligands, only one phenylphosphonamidodiselenoate ligand binds to the platinum centre in each case, coordinating in a bidentate manner, with an ammonium chloride salt being formed as a byproduct. No dimeric species or doubly substituted species are observed. The products are stable in air and to oxidation, although decompose if left in chlorinated solvents.

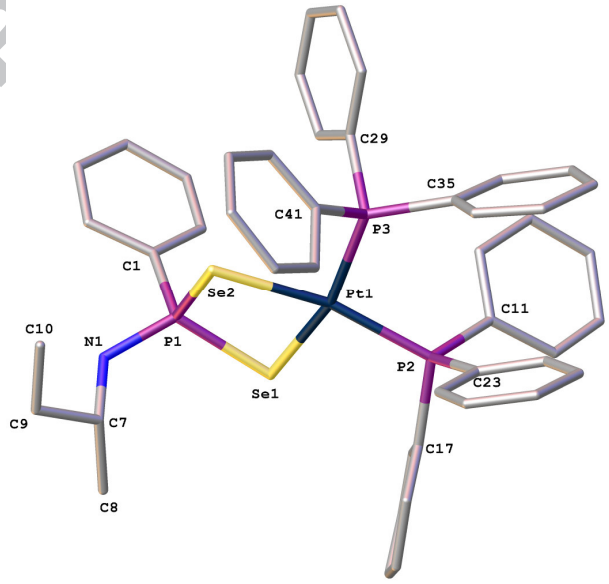


Figure 2 The X-ray crystal structure of **12**, H atoms and chloride counter ion omitted for clarity.

Typical of Pt(II) complexes **12** has a square planar geometry with the Pt-Se and Pt-P bond lengths being normal. The P(1)-Se(1) and P(1)-Se(2) bond lengths are is 2.4730(17) and 2.4772(14) Å respectively being, as expected, elongated compared to the free ligand, (2.152(2) Å and 2.1670(18) Å). The angles around the phenylphosphonamidodiselenoate phosphorus atom lie in the range of 97.4(2)° to 120.0(7)°, the smallest being the Se(1)-P(1)-Se(2) angle.

Bond	Length (Å)	Atoms	Angle (°)
Pt(1)-Se(1)	2.4730(17)	Se(1)-Pt(1)-Se(2)	84.06()
Pt(1)-Se(2)	2.4772(14)	Se(1)-Pt(1)-P(2)	91.64(7)
Pt(1)-P(2)	2.277(3)	Se(2)-Pt(1)-P(3)	85.63(8)
Pt(1)-P(3)	2.289(3)	P(2)-Pt(1)-P(3)	100.97(10)
Se(1)-P(1)	2.207(3)	Pt(1)-Se(1)-P(1)	87.35(8)
Se(2)-P(1)	2.192(3)	Pt(1)-Se(2)-P(1)	87.97(9)
P(1)-C(1)	1.796(10)	Se(1)-P(1)-Se(2)	97.75(11)
P(1)-N(1)	1.612(12)	Se(1)-P(1)-N(1)	117.2(4)
		Se(2)-P(1)-N(1)	113.4(4)

Table 2: Selected bond lengths (Å) and angles (°) in **12**

Figure 3 depicts a typical $^{31}P\{^{1}H\}$ NMR (**4**). All of the analogous complexes showed similar P NMR spectra. In the spectrum of **4** there are two resonances: one at ~31 ppm and the other at ~17 ppm due to the phenylphosphonamidodiselenoate phosphorus and phosphine phosphorus atoms respectively with the $^{3}J_{P\text{-}P}$ at ~ 7 Hz and $^{1}J_{P\text{-}Pt}$ of ca. 3000 Hz.

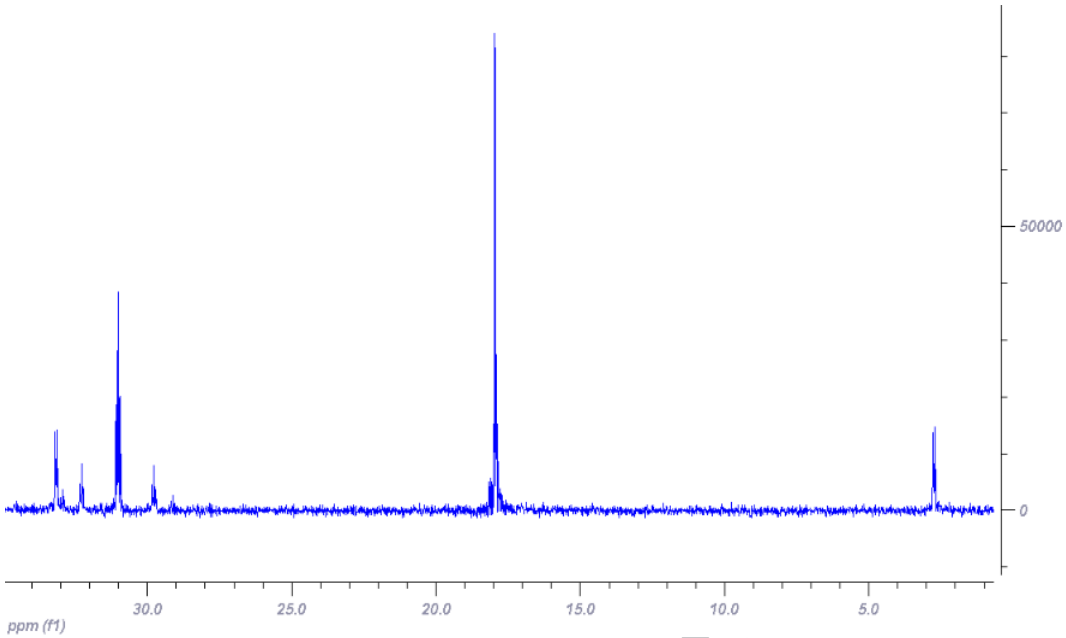


Figure 3 $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture from the preparation of *cis*-$[(PR_3)_2PtSe_2PPh(NHR)]Cl$ complex **4**.

The downfield peak due to the phenylphosphonamidodiselenoate moiety is most often observed as a series of triplets, (Figure 3) arising from the single phenylphosphonamidodiselenoate phosphorus atom coupling to the two equivalent phosphine P ($^{3}J_{P\text{-}P}$ ~ 7 Hz). The first set of satellites, the inner pair, arises from the $^{2}J_{P\text{-}Pt}$ coupling, of magnitude between 260 and 280 Hz. The second set of satellites, the smaller, outer satellites, are due to the $^{1}J_{P\text{-}Se}$ coupling of magnitude 420 – 430 Hz. Finally when suitably concentrated solutions were available we observed $^{1}J_{Pt\text{-}Se}$ values of around 275 Hz.

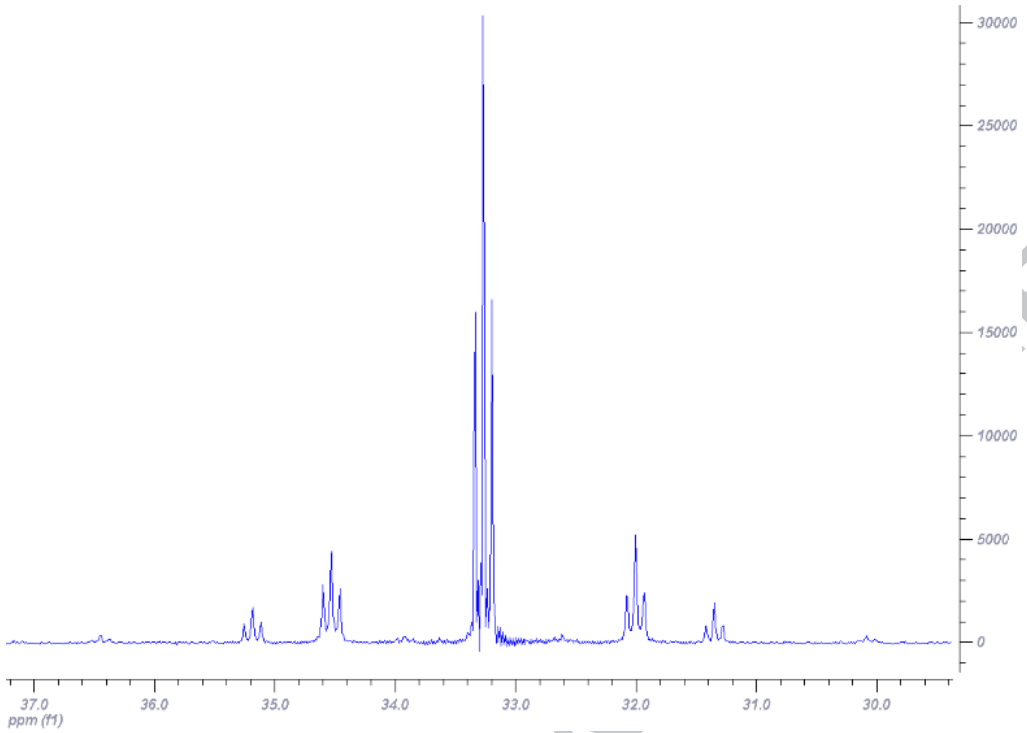


Figure 4. $^{31}P\{^{1}H\}$ NMR spectrum of a $[(PR_3)_2PtSe_2PPh(NHR)]Cl$ complex **4,** expanded to show the phenylphosphonamidodiselenoate region of the spectrum.

. The ^{195}Pt NMR spectra exhibit the expected doublet of triplets, we did not observe selenium-platinum coupling in the ^{195}Pt NMR spectra as the satellites are very weak and thus lost in the noise.

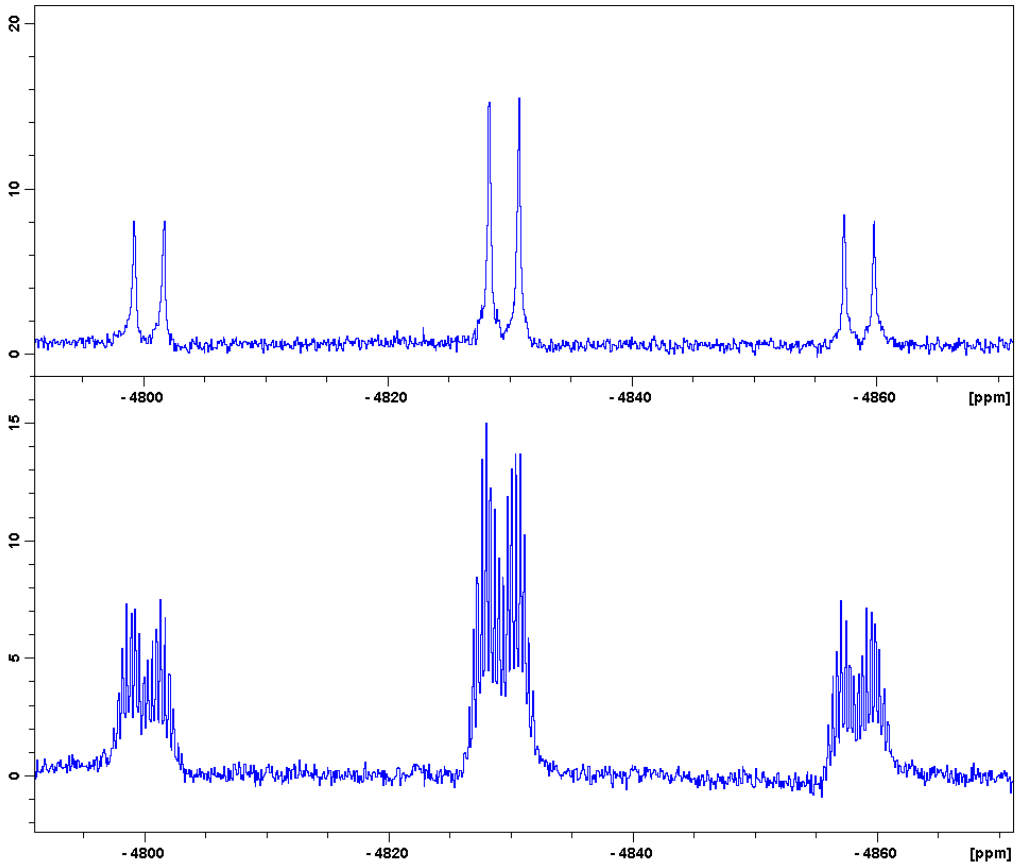


Figure 5 : Comparison of the ^{195}Pt NMR spectrum (below) with the ^{195}Pt{^{1}H} NMR spectrum (above) for compound **9**.

The most difficult to interpret of all the spectra is that of the ^{77}Se{^{1}H} NMR. Not only does selenium have the lowest natural abundance of the NMR active nuclei discussed herein, it also appears that both selenium atoms and the two phosphine phosphorus atoms are magnetically inequivalent in some complexes when rotation within the molecule is restricted due to bulky groups on the nitrogen atom. As such, between two and four resonances appear in the ^{77}Se{^{1}H} NMR spectra, often overlaying each other, giving complicated splitting patterns, and making the assignment of peaks and coupling constants very difficult. This is highlighted in Figure 6, which shows a selection of ^{77}Se{^{1}H} NMR spectra.

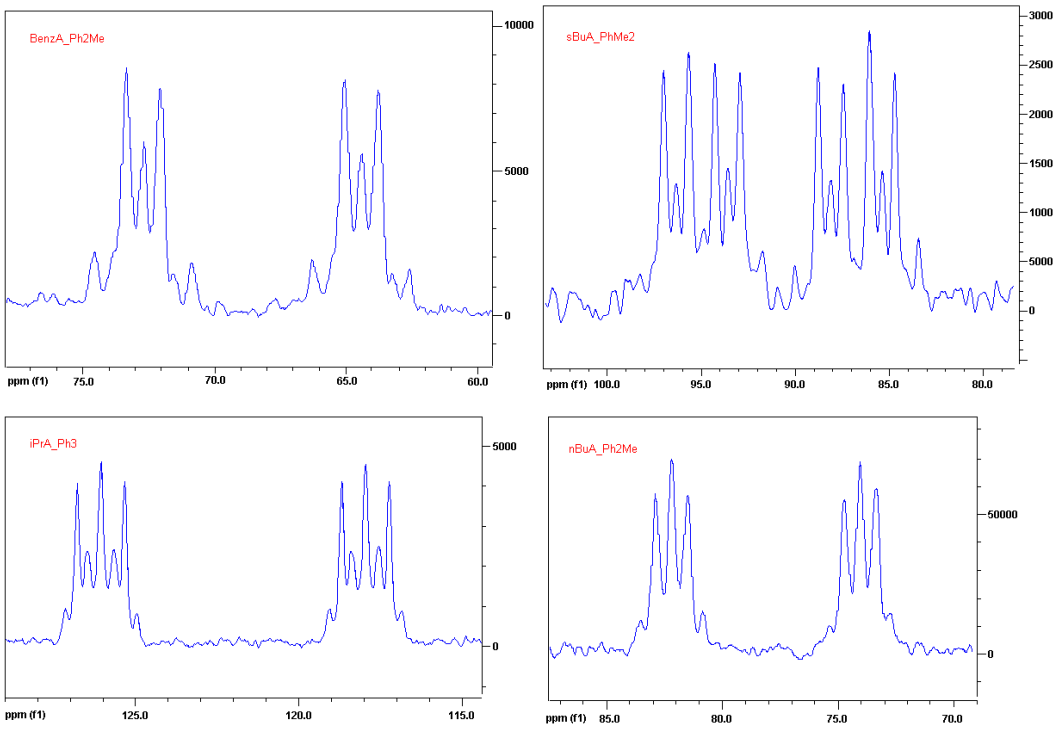


Figure 6 $^{77}Se\{^{1}H\}$ NMR spectra of: top left **19**, top right **10**, bottom left **4** and bottom right **7**

Table 3 NMR data for compounds **1- 20**

	δ_P (ppm)	$^1J_{P\text{-}Se}$ (Hz)	$^2J_{P\text{-}Pt}$ (Hz)	$^3J_{P\text{-}P}$ (Hz)	δ_P (ppm)	$^1J_{P\text{-}Pt}$ (Hz)	δ_{Se} (ppm)	δ_{Pt} (ppm)
(**1**)	35.3	429	261	-	-28.8	3112	60.6	-4829
(**2**)	28.8	373	237	7	-19.1	3130	152.9	-4849
(**3**)	32.2	418	275	7	-0.7	3208	97.3	-4900
(**4**)	30.3	418	277	7	18.0	3324	122.0	-4933
(**5**)	39.9	431	261	-	-30.1	3171	44.8	-4824
(**6**)	39.4	425	270	7	-18.1	3181	68.3	-4867
(**7**)	37.5	418	275	7	-0.7	3209	78.1	-4891
(**8**)	36.2	418	270	7	17.9	3324	96.8	-4925
(**9**)	35.7	429	261	-	-28.8	3126	66.6	-4832
(**10**)	35.2	425	270	7	-17.9	3181	91.2	-4874
(**11**)	33.3	420	275	7	-0.7	3211	98.8	-4900
(**12**)	30.3	425	270	7	17.5 17.3	3322	134.7 126.2	-4933
(**13**)	25.4	433	265	7	-28.3	3148	98.0	-4817
(**14**)	24.66	425	275	7	-17.75	3193	118.3	-4857
(**15**)	23.0	420	277	7	-0.7	3225	129.0	-4884
(**16**)	22.0	423	277	7	17.7	3342	160.2	-4916
(**17**)	41.4	433	268	-	-29.4	3084	135.6	-4816
(**18**)	40.9	427	270	7	-17.9	3179	67.6	-4856
(**19**)	40.8	429	264	7	-0.7	3229	129.8	-4903
(**20**)	37.0	418	270	7	18.3	3310	99.0	-4914

The general trends in the NMR spectra (Table 3) can be considered. The phenylphosphonamidodiselenoate phosphorus atom resonance chemical shift decreases with the increase in the number of phenyl groups on the phosphine ligands (associated with a decrease in electron density on the phosphine atoms). δ_P for the phosphine atoms follows the expected pattern: δ_P shows a steady increase from PMe_3 to PPh_3 concurrent with an increasing magnitude of $^1J_{P\text{-}Pt}$; the resonance for the PMe_3 ligand exhibits the greatest upfield shift due to the methyl groups being most electron donating, whilst the PPh_3 species has the most positive chemical shift as the rings are slightly electron withdrawing. The coupling constants increase from PMe_3 to PPh_3 indicates an increase in s-character in the P-Pt bond from PMe_3 to PPh_3. In the $^{77}Se\{^1H\}$ NMR spectra, δ_{Se} increases with an increase in the number of phenyl groups in the phosphine ligands. The platinum chemical shift becomes more negative with an increase in steric bulk of the groups of the phosphine ligands, following the observations of Pregosin and Green *et al.*.[11,12] As is to be expected, the chemical shift of the phosphine P atom stay fairly stable with the variation of the R group on the phenylphosphonamidodiselenoate phosphorus atom. It appears that, in the sequence ^{n}Bu to ^{s}Bu to ^{t}Bu, the chemical shifts become less negative (-30.1, -28.8 and -28.3 ppm respectively), a trend we see for all phosphine R groups. We note a decrease in δ_P for the phenylphosphonamidodiselenoate phosphorus atom from ^{n}Bu to ^{s}Bu to ^{t}Bu because there is an increase in electron donation from ^{n}Bu to ^{t}Bu. δ_{Pt} appears to be insensitive to the size of the amine moiety on the ligand.

This paper has demonstrated the synthesis of a range of platinum complexes of the type $[(PR_3)_2PtSe_2PPh(NHR)]Cl$. The multielement NMR data is convincing proof of their existence and the analysis of general trends in the chemical shifts and couple constants

Experimental

All experiments were carried out using standard Schlenk line techniques under an inert and dry nitrogen atmosphere, unless otherwise stated. Subsequent work up, such as chromatography, was performed in air unless otherwise indicated. Toluene, THF, hexane, dichloromethane, and diethyl ether were dried, degassed and purified using an MBraun Solvent Drying System. All other solvents used were distilled using standard techniques. All

glassware was oven dried before use. All chemicals were obtained from Acros, Sigma Aldrich and Alfa Aesar and used as received.

NMR experiments were performed on a Jeol GSX 270 MHz spectrometer with δ(H) and δ(C) referenced to tetramethylsilane, δ(P) referenced to 85% H_3PO_4 and δ(Se) referenced to dimethyl selenide as external standards at 270, 68, 109 and 52 MHz respectively, unless otherwise indicated. All experiments were performed at room temperature, unless otherwise stated. Some NMR experiments were carried out on a Bruker Avance 300 MHz spectrometer and a Bruker Avance II 400 MHz spectrometer, which is highlighted in individual syntheses.

The Ligand salts were prepared according to literature method[10]

Crystal Structure Analyses

X-ray crystal structures for ^{n}BuAWR, and ^{s}BuAWR were collected at −180(1) °C using a Rigaku MM007 high brilliance RA generator (Mo Kα radiation, confocal optic) and Mercury CCD system whilst data for **12** was collected using the St Andrews robotic system (STANDARD).[13] All data had intensities corrected for Lorentz, polarization, and absorption. Data for **L** were collected at −148(1) °C on a Rigaku SCX Mini instrument with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The data was collected and processed using CrystalClear (Rigaku).[14] The structures were solved by Patterson or direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using CrystalStructure[15] and SHELXL-97.[16] The chloride counterion in the structure of **12** was disordered over three sites which were refined with occupancies of 60/20/20. The major site is hydrogen bonded [N(1)..Cl(1) 3.124(7), H(1)…Cl(1) 2.244(9) Å, N(1)-H(1)..Cl(1) 148.8(1)^{o}].

Table 4 Crystallographic data for ligand **L** and compounds ^{n}BuAWR, and ^{s}BuAWR **12**

	^{n}BuAWR	^{s}BuAWR	**12**
Empirical Formula	$C_{14}H_{27}N_2PSe_2$	$C_{14}H_{27}N_2PSe_2$	$C_{42}H_{44}Cl\ NP_3PtSe_2$
Formula Weight	412.27	412.27	1044.20
Crystal Colour, Habit	colourless, prism	colourless, rod	yellow, chip
Crystal Dimensions (mm^3)	0.10 x 0.10 x 0.10	0.18 x 0.03 x 0.03	0.12 x 0.09 x 0.03
Crystal System	monclinic	triclinic	triclinic
Lattice Parameters	a = 21.737(11) Å	a = 7.740(3) Å	a = 11.168(5) Å
	b = 7.6822(19) Å	b = 10.214(4) Å	b = 14.421(8) Å
	c = 22.049(6) Å	c = 11.867(5) Å	c = 14.998(7) Å
	α = 90°	α = 84.00(2) °	α = 103.400(9) °
	β = 99.048(6) °	β = 83.06(2) °	β = 93.744(7)°
	γ = 90°	γ = 82.97(2) °	γ = 109.184(13)°
Volume ($Å^3$)	3636(2)	920.5(6)	2192.8(19)
Space Group	*I*2/*a*	*P*-1	*P*-1
Z Value	8	2	2
Dcalc (g/cm^3)	1.506	1.487	1.653
F000	1664	416	1074
μ(MoKα) (mm^{-1})	4.147	4.095	5.050
No. of Reflections Measured	10969	5913	16719
Rint	0.0509	0.0492	0.0719
Min and Max Transmissions	0.802 – 1.00	0.643-1.000	0.548-0.860
Observed Independent Reflection	2928	2457	7017
Residuals: R1 (I>2.00σ(I))	0.0338	0.0609	0.0650
Residuals: R (All Reflections)	0.0400	0.0809	0.0736
Residuals: wR_2 (All Reflections)	0.0760	0.1736	0.2138
Goodness of Fit Indicator	1.048	1.057	1.053
Maximum peak in Final Diff.	0.509 e-/$Å^3$	1.880 e-/$Å^3$	2.47 e-/$Å^3$
Minimum peak in Final Diff. Map	-0.601 e-/$Å^3$	-0.828 e-/$Å^3$	-1.78 e⁻/$Å^3$

Synthesis of Platinum Complexes

For simplicity and to prevent repetition, the generic term *cis*-$Pt(PR_3)_2Cl_2$ is employed in each synthesis description. The amount used in grams and moles is entered at the beginning of the NMR characterisation data for each compound.

Compounds **1-4** Using ^{i}PrAWR

cis-$Pt(PR_3)_2Cl_2$ was dissolved in DCM (20 mL) and stirred at room temperature. To this, ^{i}PrAWR was added. The mixture was left to stir overnight, during which a colour change from off-white to orange-light brown occurred. The resulting mixture was washed with distilled water (2 x 20 mL), dried over $MgSO_4$ and purified by column chromatography with

an eluent of 95% toluene: 5% ethyl acetate. Once all the side products were washed through, the desired product was purged from the column with MeOH and the fractions evaporated to dryness under reduced pressure. The products were obtained as dark orange to brown oils.

1 R_3 = Me_3, 0.15 g, 0.36 mmol. ^{i}PrAWR: 0.16 g, 0.38 mmol. Yield: 0.144 g, 60%.$^{31}P\{^{1}H\}$ NMR: (162.0 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 35.3 ($^{1}J_{P\text{-}Se}$ = 429 Hz, $^{2}J_{P\text{-}Pt}$ = 261 Hz) and -28.8 ($^{1}J_{P\text{-}Pt}$ = 3112 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^{1}H\}$ NMR: (76.3 MHz, $CDCl_3$) (ppm) δ_{Se} = 60.6 (d, $^{1}J_{Se\text{-}P}$ = 432 Hz). $^{195}Pt\{^{1}H\}$ NMR: (107.5 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4830 (dt, $^{1}J_{Pt\text{-}P}$ = 3115 Hz, $^{2}J_{Pt\text{-}P}$ = 261 Hz).

2 R_3 = Me_2Ph, 0.15 g, 0.27 mmol. ^{i}PrAWR: 0.12 g, 0.28 mmol. Yield: 0.11 g, 48%. $^{31}P\{^{1}H\}$ NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 28.8 ($^{1}J_{P\text{-}Se}$ = 373 Hz, $^{2}J_{P\text{-}Pt}$ = 237 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and -19.1 ($^{1}J_{P\text{-}Pt}$ = 3130 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^{1}H\}$ NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 152.9 (d, $^{1}J_{Se\text{-}P}$ = 372 Hz). $^{195}Pt\{^{1}H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4849 (dt, $^{1}J_{Pt\text{-}P}$ = 3133 Hz, $^{2}J_{Pt\text{-}P}$ = 237 Hz).

3 R_3 = $MePh_2$, 0.15 g, 0.23 mmol. ^{i}PrAWR: 0.10 g, 0.24 mmol. Yield: 0.15 g, 69 %. $^{31}P\{^{1}H\}$ NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 32.2 ($^{1}J_{P\text{-}Se}$ = 418 Hz, $^{2}J_{P\text{-}Pt}$ = 275 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and -0.73 ($^{1}J_{P\text{-}Pt}$ = 3208 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz).$^{77}Se\{^{1}H\}$ NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 97.3 (d, $^{1}J_{Se\text{-}P}$ = 417 Hz). $^{195}Pt\{^{1}H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4900 (dt, $^{1}J_{Pt\text{-}P}$ = 3200 Hz, $^{2}J_{Pt\text{-}P}$ = 267 Hz). Mass TOF MS ES^{+}: *m/z* = 919.56 (M^{+}).

4 R_3 = Ph_3, 0.18 g, 0.23 mmol. ^{i}PrAWR: 0.10 g, 0.24 mmol. Yield: 0.16 g, 65 %.$^{31}P\{^{1}H\}$ NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 30.3 ($^{1}J_{P\text{-}Se}$ = 418 Hz, $^{2}J_{P\text{-}Pt}$ = 277 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and 18.0 ($^{1}J_{P\text{-}Pt}$ = 3324 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^{1}H\}$ NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 122.0 (d, $^{1}J_{Se\text{-}P}$ = 418 Hz). $^{195}Pt\{^{1}H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4933 (dt, $^{1}J_{Pt\text{-}P}$ = 3316 Hz, $^{2}J_{Pt\text{-}P}$ = 273 Hz).

Compounds **5 – 8** Using ^{n}BuAWR

5 R_3 = Me_3, 0.14 g, 0.335 mmol. ^{n}BuAWR: 0.15 g, 0.36 mmol. Yield: 0.10 g, 45%. $^{31}P\{^{1}H\}$ NMR: (121.5 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 39.9 ($^{1}J_{P\text{-}Se}$ = 431 Hz, $^{2}J_{P\text{-}Pt}$ = 261 Hz) and -30.1 ($^{1}J_{P\text{-}Pt}$ = 3170 Hz). $^{77}Se\{^{1}H\}$ NMR: (76.3 MHz, $CDCl_3$) (ppm) δ_{Se} = 44.8 (d, $^{1}J_{Se\text{-}P}$ = 429 Hz). $^{195}Pt\{^{1}H\}$ NMR: (107.5 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4824 (dt, $^{1}J_{Pt\text{-}P}$ = 3165 Hz, $^{2}J_{Pt\text{-}P}$ = 259 Hz).

6 R_3 = Me_2Ph, 0.18 g, 0.33 mmol. ^{n}BuAWR: 0.15 g, 0.36 mmol. Yield: 0.15 g, 53%. $^{31}P\{^{1}H\}$ NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 39.4 ($^{1}J_{P\text{-}Se}$ = 425 Hz, $^{2}J_{P\text{-}Pt}$ = 270 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and -18.1 ($^{1}J_{P\text{-}Pt}$ = 3181 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^{1}H\}$ NMR: (51.5 MHz, $CDCl_3$)

(ppm) δ_{Se} = 68.3 (d, $^{1}J_{Se\text{-}P}$ = 424 Hz). ^{195}Pt{^{1}H} NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4867 (dt, $^{1}J_{Pt\text{-}P}$ = 3200 Hz, $^{2}J_{Pt\text{-}P}$ = 273 Hz).

7 R_3 = $MePh_2$, 0.15 g, 0.23 mmol. ^{n}BuAWR: 0.10 g, 0.24 mmol. Yield: 0.13 g, 62%. ^{31}P{^{1}H} NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 37.5 ($^{1}J_{P\text{-}Se}$ = 418 Hz, $^{2}J_{P\text{-}Pt}$ = 275 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and -0.74 ($^{1}J_{P\text{-}Pt}$ = 3209 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). ^{77}Se{^{1}H} NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 78.1 (d, $^{1}J_{Se\text{-}P}$ = 417 Hz). ^{195}Pt{^{1}H} NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4891 (dt, $^{1}J_{Pt\text{-}P}$ = 3206 Hz, $^{2}J_{Pt\text{-}P}$ = 273 Hz). Mass TOF MS ES$^+$: M = 933.63 (M^+).

8 R_3 = Ph_3, 0.18 g, 0.23 mmol. ^{n}BuAWR: 0.10 g, 0.24 mmol. Yield: 0.13 g, 54%. ^{31}P{^{1}H} NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 36.2 ($^{1}J_{P\text{-}Se}$ = 418 Hz, $^{2}J_{P\text{-}Pt}$ = 270 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and 17.9 ($^{1}J_{P\text{-}Pt}$ = 3324 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). ^{77}Se{^{1}H} NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 96.9 (d, $^{1}J_{Se\text{-}P}$ = 422 Hz). ^{195}Pt{^{1}H} NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4925 (dt, $^{1}J_{Pt\text{-}P}$ = 3328 Hz, $^{2}J_{Pt\text{-}P}$ = 261 Hz). Mass TOF MS ES$^+$: M = 1057.4 (M^+).

Compounds **9-12** Using ^{s}BuAWR

9 R_3 = Me_3, 0.14 g, 0.34 mmol. ^{s}BuAWR: 0.14 g, 0.34 mmol. Yield: 0.14 g, 61%. ^{31}P{^{1}H} NMR: (162.0 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 35.7 ($^{1}J_{P\text{-}Se}$ = 429 Hz, $^{2}J_{P\text{-}Pt}$ = 263 Hz) and -28.83($^{1}J_{P\text{-}Pt}$ = 3125 Hz). ^{77}Se{^{1}H} NMR: (76.3 MHz, $CDCl_3$) (ppm) δ_{Se} = 66.6 (d, $^{1}J_{Se\text{-}P}$ = 430 Hz). ^{195}Pt{^{1}H} NMR: (107.5 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4832 (dt, $^{1}J_{Pt\text{-}P}$ = 3128 Hz, $^{2}J_{Pt\text{-}P}$ = 259 Hz).

10 R_3 = Me_2Ph, 0.16 g, 0.30 mmol. ^{s}BuAWR: 0.13 g, 0.32 mmol. Yield: 0.19 g, 72%. ^{31}P{^{1}H} NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 35.2 ($^{1}J_{P\text{-}Se}$ = 425 Hz, $^{2}J_{P\text{-}Pt}$ = 270 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and -17.9 ($^{1}J_{P\text{-}Pt}$ = 3181 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). ^{77}Se{^{1}H} NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 91.2 (d, $^{1}J_{Se\text{-}P}$ = 424 Hz). ^{195}Pt{^{1}H} NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4874 (dt, $^{1}J_{Pt\text{-}P}$ = 3183 Hz, $^{2}J_{Pt\text{-}P}$ = 268 Hz).

11 R_3 = $MePh_2$, 0.17 g, 0.26 mmol. ^{s}BuAWR: 0.11 g, 0.27 mmol. Yield: 0.13 g, 54%.^{31}P{^{1}H} NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 33.4 ($^{1}J_{P\text{-}Se}$ = 420 Hz, $^{2}J_{P\text{-}Pt}$ = 275 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and -0.72 ($^{1}J_{P\text{-}Pt}$ = 3211 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). ^{77}Se{^{1}H} NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 98.8 (d, $^{1}J_{Se\text{-}P}$ = 420 Hz). ^{195}Pt{^{1}H} NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4900 (dt, $^{1}J_{Pt\text{-}P}$ = 3212 Hz, $^{2}J_{Pt\text{-}P}$ = 267 Hz).

12 R_3 = Ph_3, 0.20 g, 0.25 mmol. ^{s}BuAWR: 0.11 g, 0.27 mmol. Yield: 0.20 g, 75%. ^{31}P{^{1}H} NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 30.33 ($^{1}J_{P\text{-}Se}$ = 425 Hz, $^{2}J_{P\text{-}Pt}$ = 270, $^{3}J_{P\text{-}P}$ = 7.04 Hz), 17.55 ($^{1}J_{P\text{-}Pt}$ = 3322 Hz, $^{3}J_{P\text{-}P}$ = 7.74 Hz) and 17.35 ($^{1}J_{P\text{-}Pt}$ = 3322 Hz, $^{3}J_{P\text{-}P}$ = 6.77 Hz). ^{77}Se{^{1}H} NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 134.7 (d, $^{1}J_{Se\text{-}P}$ = 417 Hz) and 126.2 (d,

$^{1}J_{Se\text{-}P}$ = 415 Hz). $^{195}Pt\{^{1}H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4933 (dt, $^{1}J_{Pt\text{-}P}$ = 3320 Hz, $^{2}J_{Pt\text{-}P}$ = 281 Hz). Mass TOF MS ES^{+}: M = 1057.63 (M^{+}).

Compounds **13 – 16** Using ^{t}BuAWR

13 R_3 = Me_3, 0.15 g, 0.35 mmol. ^{t}BuAWR: 0.15 g, 0.36 mmol. Yield: 0.12 g, 51%. $^{31}P\{^{1}H\}$ NMR: (202.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 25.4 ($^{1}J_{P\text{-}Se}$ = 433 Hz, $^{2}J_{P\text{-}Pt}$ = 265 Hz) and -28.3 ($^{1}J_{P\text{-}Pt}$ = 3148 Hz). $^{77}Se\{^{1}H\}$ NMR: (95.4 MHz, $CDCl_3$) (ppm) δ_{Se} = 98.0 (d, $^{1}J_{Se\text{-}P}$ = 435.0 Hz). $^{195}Pt\{^{1}H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4817 (dt, $^{1}J_{Pt\text{-}P}$ = 3138 Hz, $^{2}J_{Pt\text{-}P}$ = 264 Hz).

14 R_3 = Me_2Ph, 0.15 g, 0.27 mmol. ^{t}BuAWR: 0.12 g, 0.29 mmol. Yield: 0.12 g, 52%. $^{31}P\{^{1}H\}$ NMR: (121.5 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 24.7 ($^{1}J_{P\text{-}Se}$ = 425 Hz, $^{2}J_{P\text{-}Pt}$ = 275 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and -17.8 ($^{1}J_{P\text{-}Pt}$ = 3193 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^{1}H\}$ NMR: (95.4 MHz, $CDCl_3$) (ppm) δ_{Se} = 118.4 (d, $^{1}J_{Se\text{-}P}$ = 425 Hz). $^{195}Pt\{^{1}H\}$ NMR: (107.5 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4857 (dt, $^{1}J_{Pt\text{-}P}$ = 3194 Hz, $^{2}J_{Pt\text{-}P}$ = 272 Hz).

15 R_3 = $MePh_2$, 0.23 g, 0.34 mmol. ^{t}BuAWR: 0.15 g, 0.36 mmol. Yield: 0.12 g, 38%. $^{31}P\{^{1}H\}$ NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 23.0 ($^{1}J_{P\text{-}Se}$ = 420 Hz, $^{2}J_{P\text{-}Pt}$ = 277 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and -0.70 ($^{1}J_{P\text{-}Pt}$ = 3223 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^{1}H\}$ NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 129.0 (d, $^{1}J_{Se\text{-}P}$ = 420 Hz). $^{195}Pt\{^{1}H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4884 (dt, $^{1}J_{Pt\text{-}P}$ = 3225 Hz, $^{2}J_{Pt\text{-}P}$ = 273 Hz).

16 R_3 = Ph_3, 0.18 g, 0.23 mmol. ^{t}BuAWR: 0.10 g, 0.24 mmol. Yield: 0.11 g, 44%. $^{31}P\{^{1}H\}$ NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 22.0 ($^{1}J_{P\text{-}Se}$ = 423 Hz, $^{2}J_{P\text{-}Pt}$ = 277 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and 17.7 ($^{1}J_{P\text{-}Pt}$ = 3342 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^{1}H\}$ NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 160.2 (d, $^{1}J_{Se\text{-}P}$ = 418 Hz). $^{195}Pt\{^{1}H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4916 (dt, $^{1}J_{Pt\text{-}P}$ = 3337 Hz, $^{2}J_{Pt\text{-}P}$ = 273 Hz).

Compounds **17 – 20** Using BenzAWr

17 R_3 = Me_3, 0.11 g, 0.26 mmol. BenzAWR: 0.14 g, 0.29 mmol. Yield: 0.12 g, 67%. $^{31}P\{^{1}H\}$ NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 41.4 ($^{1}J_{P\text{-}Se}$ = 433 Hz, $^{2}J_{P\text{-}Pt}$ = 268 Hz) and -29.4 ($^{1}J_{P\text{-}Pt}$ = 3084 Hz). $^{77}Se\{^{1}H\}$ NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 135.6 (d, $^{1}J_{Se\text{-}P}$ = 411 Hz). $^{195}Pt\{^{1}H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4816 (dt, $^{1}J_{Pt\text{-}P}$ = 3091 Hz, $^{2}J_{Pt\text{-}P}$ = 233 Hz).

18 R_3 = Me_2Ph, 0.14 g, 0.26 mmol. BenzAWR: 0.13 g, 0.27 mmol. Yield: 0.13 g, 56%. $^{31}P\{^{1}H\}$ NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 40.9 ($^{1}J_{P\text{-}Se}$ = 427 Hz, $^{2}J_{P\text{-}Pt}$ = 270 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz) and -17.9 ($^{1}J_{P\text{-}Pt}$ = 3179 Hz, $^{3}J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^{1}H\}$ NMR: (51.5

MHz, $CDCl_3$) (ppm) δ_{Se} = 67.6 (d, $^1J_{Se\text{-}P}$ = 427 Hz). $^{195}Pt\{^1H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4856 (dt, $^1J_{Pt\text{-}P}$ = 3180 Hz, $^2J_{Pt\text{-}P}$ = 272 Hz).

19 R_3 = $MePh_2$, 0.16 g, 0.24 mmol. BenzAWR: 0.12 g, 0.25 mmol. Yield: 0.14 g, 62%. $^{31}P\{^1H\}$ NMR: (162.0 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 40.8 ($^1J_{P\text{-}Se}$ = 429 Hz, $^2J_{P\text{-}Pt}$ = 264 Hz, $^3J_{P\text{-}P}$ = 7.04 Hz) and -0.72 ($^1J_{P\text{-}Pt}$ = 3209 Hz, $^3J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^1H\}$ NMR: (76.3 MHz, $CDCl_3$) (ppm) δ_{Se} = 129.8 (d, $^1J_{Se\text{-}P}$ = 426 Hz). $^{195}Pt\{^1H\}$ NMR: (107.5 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4903 (dt, $^1J_{Pt\text{-}P}$ = 3204 Hz, $^2J_{Pt\text{-}P}$ = 261 Hz).

20 R_3 = Ph_3, 0.15 g, 0.20 mmol. BenzAWR: 0.10 g, 0.21 mmol. Yield: 0.14 g, 64%. $^{31}P\{^1H\}$ NMR: (109.4 MHz, $CDCl_3$, H_3PO_4) (ppm) δ_P = 37.0 ($^1J_{P\text{-}Se}$ = 418 Hz, $^2J_{P\text{-}Pt}$ = 270 Hz, $^3J_{P\text{-}P}$ = 7.04 Hz) and 18.3 ($^1J_{P\text{-}Pt}$ = 3310 Hz, $^3J_{P\text{-}P}$ = 7.04 Hz). $^{77}Se\{^1H\}$ NMR: (51.5 MHz, $CDCl_3$) (ppm) δ_{Se} = 99.0 (d, $^1J_{Se\text{-}P}$ = 417 Hz). $^{195}Pt\{^1H\}$ NMR: (58.1 MHz, $CDCl_3$) (ppm) δ_{Pt} = -4914 (dt, $^1J_{Pt\text{-}P}$ = 3316 Hz, $^2J_{Pt\text{-}P}$ = 267 Hz).

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Supporting Information

CCDC 1045404-1045406 contain the supplementary crystallographic data for. 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

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