Journal of Organometallic Chemistry, 56 (1973) 395–403

METAL COMPLEXES OF UNSATURATED PHENOLS AND BENZENETHIOLS

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(Received October 12th, 1972; in revised form December 4th, 1972)

SUMMARY

The preparation and properties of complexes of *o*-vinylbenzenethiol, *o*-allylbenzenethiol with palladium and platinum and of *o*-allylphenol with palladium, platinum and rhodium are reported. Their behaviour towards oxidation with bromine is also described.

INTRODUCTION

As an extension of previous studies on the chemical reactivity of metal complexes with unsaturated ligands[1], we turned to the synthesis of complexes of transition metals (namely Pd, Pt, Rh) with unsaturated phenols and thiophenols with the object of investigating their reactivity towards oxidising agents. Furthermore, while examples of replacement of protons on oxygen by Pt^{II} were known with ligands such as 2-pyridinemethanol[2] and diethanolamine[3] giving five membered rings with *trans* configuration, no examples of chelate complexes have been described for unsaturated alcohols in which the hydroxyl proton has been replaced. Complexes of palladium and platinum with aliphatic unsaturated sulphides[4] or with mercaptides[5] are known, but no examples of complexes involving unsaturated thiophenols have been previously reported.

In this note we describe the preparation and properties of complexes of palladium, platinum and rhodium with *o*-allylphenol, and of palladium and platinum with *o*-vinyl- and *o*-allylthiophenol, and we report the first results of the investigation on the reaction of these complexes with oxidants such as bromine.

RESULTS AND DISCUSSION

o-Allylphenol reacts with sodium chloroplatinite(II) in aqueous ethanol in the presence of a weak base, such as sodium hydrogen carbonate, to give a white product which is monomeric in chloroform and non-conducting in nitromethane, and which

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does not contain chlorine*. Its IR spectrum shows no band due to the free double bond (1639 cm^{-1} in the ligand alone) but includes a new band, at 1510 cm^{-1}, which is not present in the spectrum of the free ligand, and which can be assigned to the two coordinated double bonds. A new sharp band at 1573 cm^{-1}, which is present in the spectrum of *o*-allylphenol as a shoulder of a strong band at 1594 cm^{-1}, is more probably associated with a ring stretching modified by coordination. The spectrum of the complex differs markedly from that of the ligand in the 1000–900 cm^{-1} region, where the C–H bending out of the plane of the olefinic group is expected, which would be consistent with coordination of the double bonds to the metal (see Table 3).

The ^1H NMR spectrum of the bis(*o*-allylphenolato)platinum(II) complex shows that the proton resonances of the allylic group are shifted upfield with respect to those of the free ligand upon coordination to the metal (see Table 4). The greater shift of H_3 compared to H_2 may be due to the difference in the shielding field of the magnetic point dipole of the C=C bond felt by the two atoms which can arise from a situation in which the olefinic group is not quite perpendicular to the metal–olefin axis.

The observed increase in the $J(H\text{–}H)_{gem}$ (see Table 4) can be correlated to a decrease of the H–C–H angle of the methylene group due to the approach to the platinum metal atom[7,8]. We suggest formula (IV) for this complex, the *cis* configuration being supported by the dipole moment measurements in benzene at 25° (4.65 D)**. The coordinated double bonds in the complex can readily be replaced by other ligands. With pyridine it is possible to isolate two complexes with one or both of the double bonds replaced by the pyridine ligand (see Table 3). The mono- and di-pyridine derivatives are not very stable, and slowly lose pyridine in the solid state at room temperature and more readily when heated. In solution they are stable in the presence of a slight excess of the free ligand. After reaction with triphenylphosphine, the bis(*o*-allylphenolato)bis(triphenylphosphine)platinum(II), which shows only one band at 1639 cm^{-1} in its IR spectrum, was isolated. The NMR spectrum confirms that the two double bonds are not coordinated.

The reaction of $Pt(OA)_2(PPh_3)_2$*** with HCl in EtOH (1/2 molar ratio) gave *cis*-$[PtCl_2(PPh_3)_2]$, which was identified by means of a mixed melting point, analysis, and the far infrared spectrum. This result is consistent with the lower affinity of platinum for oxygen than for chlorine. The reaction of K_2PdCl_4 with *o*-allylphenol under the conditions used for platinum produced decomposition to palladium metal. Decomposition occurred also when $PdCl_2$ was treated with the sodium salt of *o*-allylphenol in a non polar medium, or when the pyridine was removed from the $Pd(OA)_2Py_2$ which was obtained from the reaction of $PdCl_2Py_2$ with sodium *o*-allylphenolate.

Treatment of $PdCl_2(PPh_3)_2$ with the sodium salt of *o*-allylphenol in benzene gave an orange complex of formula $Pd(OA)_2(PPh_3)$ (V). It is monomeric in benzene and non-conducting in nitromethane. Its IR spectrum displays bands at 1638 and 1520 cm^{-1} ($\Delta\nu = 119$ cm^{-1}) due to the uncoordinated and the coordinated double

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* The course of this reaction is sensitive to the temperature and to the base used. In the presence of sodium acetate and above room temperature, isomerization of the allyl group to the propenyl group has been detected.

** This result is only approximate because of the limited solubility of the complex in benzene.

*** OA = *o*-allylphenolato.

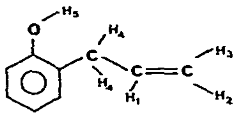
TABLE 1

PHYSICAL PROPERTIES OF COMPLEXES

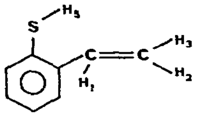
Complex	*Colour*	*m.p.* (°C)	*Molecular weight*[a] *found* (*calcd.*)	*Molar conductivity* ($\Omega^{-1}\cdot cm^2\cdot mole^{-1}$)
$Pt(OA)_2$	White	137(dec.)	495(461)	1.8 (nitromethane)
$Pt(OA)_2Py$	Cream	104(dec.)	[b]	
$Pt(OA)_2Py_2$	Cream	89(dec.)	[b]	
$Pt(OA)_2(PPh_3)_2$	White	127–128	1003(986)	2.1(nitromethane)
$[Pt(SV)_2]_n$	Yellow	Above 240	[c]	[c]
$Pt(SV)_2(PPh_3)_2$	Yellow	164–165	1048(1018)	1.8 (nitromethane)
$[Pt(SA)_2]_6$	Yellow	Above 270	3020(2958)	1.4 (nitrobenzene)
$Pt(SA)_2(PPh_3)_2$	Yellow	172–174	1030(990)	0.7 (nitromethane)
$[Pd(SV)_2]_n$	Orange	Above 260	[c]	[c]
$Pd(SV)_2(PPh_3)_2$	Orange	138	938(901)	1.2 (nitromethane)
$[Pd(SA)_2]_6$	Orange	241	2390(2430)	1.9 (nitromethane)
$Pd(SA)_2(PPh_3)_2$	Orange	156	926(929)	0.8 (nitromethane)
$Pd(OA)_2(PPh_3)$	Red	126(dec.)	[b]	1.4[g] (nitromethane)
$[Rh(OA)(C_8H_{12})]_2$	Pale Yellow	188	450[f](688) 515[e] 598[d]	0.8[d] (nitromethane)

[a] Measured osmometrically in $CHCl_3$ [b] Decomposes. [c] Insufficiently soluble. [d] 1.13×10^{-2} *M*. [e] 5.93×10^{-3} *M*. [f] 2.74×10^{-3} *M*. [g] Measured in an inert gas atmosphere.

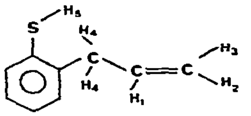
bond, respectively. The NMR spectrum of the complex shows signals due to the coordinated and the free double bonds. The solid complex is stable for a considerable time towards atmospheric oxygen, but it decomposes readily in solution. It reacts with chloroform to give a green chlorine-containing compound, the stoichiometry of which has not yet been determined.



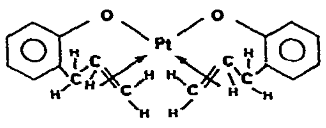
(I) AOH



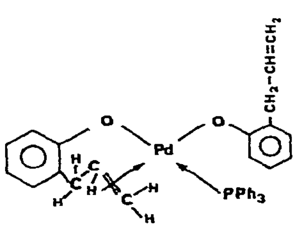
(II) VSH



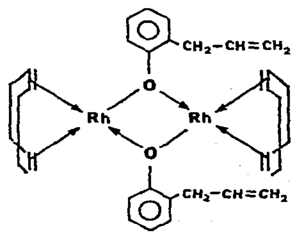
(III) ASH



(IV) $Pt(OA)_2$



(V) $Pd(OA)_2(PPh_3)$



(VI) $[(C_8H_{12})Rh(OA)]_2$

The complex $[(1,5\text{-COD})RhCl]_2$ reacts with *o*-allylphenol in alcohol/water solution in the presence of $NaHCO_3$, or with sodium *o*-allylphenolate in THF to give a complex which does not contain chlorine. Mol.wt. determinations in $CHCl_3$ show it to be a dimer, which dissociates in solution as the concentration is reduced (see Table 1). A bridged structure is postulated, with oxygen atoms linking the rhodium atoms (VI). Its IR spectrum shows a sharp band at 1638 cm^{-1} due to the uncoordinated allylic double bond, and supports the proposed formulation. Further evidence for the oxygen-bridged structure comes from the analysis of the NMR spectrum of the complex in $CDCl_3$, which shows that both the double bonds of the COD are still coordinated, while the allylic double bonds are uncoordinated (see Table 4). We can thus exclude attack by the phenoxy group on the double bonds of the COD, as has been observed in the reaction of $PtCl_2COD$ with alkoxy groups[9].

The *o*-vinyl- and *o*-allylbenzenethiol ligands [(II) and (III)] are air sensitive, and readily undergo ring closure reactions between the olefinic chain and the thiol group. It is well known that thiols are very reactive towards activated olefins and that oxygen can cause peroxidation under very mild conditions[10].

In an attempt to prepare the complex $Pt(SV)_2$ [$SV = o\text{-}CH_2{=}CH{-}C_6H_4{-}S{-}$] by treating sodium chloroplatinite (II) with *o*-vinylbenzenethiol and $NaHCO_3$ in aqueous ethanol in the absence of oxygen, the only products isolated were *cis*- and *trans*-dichlorobis(dihydrothianaphthene)platinum(II), showing that a ring closure had taken place. The same products were obtained by the direct reaction of the ligand itself[12] with Na_2PtCl_4 in aqueous alcohol[11]. When the sodium salt of *o*-vinylbenzenethiol is treated with Na_2PtCl_4 in H_2O/EtOH solution, the isolated product has the

TABLE 2

ANALYTICAL DATA

Compound	*Found (calcd.)* (%)				
	C	*H*	*P*	*S*	*M*
V-SH	70.4(70.6)	5.88(5.92)			
A-SH	71.8(71.95)	6.56(6.71)			
$Pb(SV)_2$	40.3(40.2)	3.08(2.96)			
$Pb(SA)_2$	42.5(42.8)	3.81(3.59)			
$Pt(OA)_2$	47.4(46.9)	4.38(3.93)			42.2(42.28)
$Pt(OA)_2Py$	51.43(51.11)	4.30(4.29)	[a]		35.7(36.09)
$Pt(OA)_2Py_2$	54.55(54.27)	4.39(4.55)	[b]		31.00(31.49)
$Pt(OA)_2(PPh_3)_2$	66.0(65.78)	5.33(4.91)	6.30(6.28)		19.70(19.78)
$[Pt(SV)_2]_n$	40.99(41.28)	3.31(3.03)		14.00(13.77)	42.0(41.91)
$Pt(SV)_2(PPh_3)_2$	62.76(63.1)	4.45(4.46)	6.48(6.26)	6.61(6.48)	19.88(19.7)
$[Pt(SA)_2]_6$	44.23(43.8)	3.92(3.68)		12.78(13.0)	39.1(39.5)
$Pt(SA)_2(PPh_3)_2$	63.86(63.7)	4.81(4.75)	6.08(6.09)	6.07(6.3)	19.1(19.15)
$[Pd(SV)_2]_n$	50.90(51.0)	3.70(3.74)		17.0(17.3)	27.0(27.7)
$Pd(SV)_2(PPh_3)_2$	69.55(69.3)	5.09(4.92)	6.93(6.87)	7.20(7.11)	12.03(11.81)
$[Pd(SA)_2]_6$	53.21(53.4)	4.45(4.48)		15.67(15.86)	26.12(26.3)
$Pd(SA)_2(PPh_3)_2$	69.7(69.78)	5.15(5.21)	6.79(6.66)	6.88(6.9)	11.1(11.46)
$Pd(OA)_2(PPh_3)$	67.83(68.09)	5.07(5.23)	4.82(4.87)		16.52(16.75)
$[Rh(OA)(C_8H_{12})]_2$	59.26(59.3)	6.14(6.12)			29.3(29.9)

[a] Found: N, 2.51. $Pt(OA)_2Py$ calcd.; N, 2.59%. [b] Found: N, 4.48. $Pt(OA)_2Py_2$ calcd.: N, 4.52%.

TABLE 3

INFRARED DATA[a]

Compound	*ν(C=C) olefinic*	*δ(C–H) olefinic out-of-plane deformation*
A–OH[b]	1639m	955ms, 915(br)
V–SH[b]	1618m	983m, 912ms
A–SH[b]	1638m	990m, 917s
$Pt(OA)_2$	1510w[c]	982w, 968vw, 951m, 936ms, 918m
$Pt(OA)_2Py$	1638w, 1506w[c]	985w, 956w, 948w, 931m, 917m
$Pt(OA)_2Py_2$	1638m	997m, 947w, 914m
$Pt(OA)_2(PPh_3)_2$	1638m	998m, 918s, 908m
$[Pt(SV)_2]_n$	1618m	912m, 980m
$Pt(SV)_2(PPh_3)_2$	1618m	900m, 907m, 986m
$[Pt(SA)_2]_6$	1638m	995m, 912s
$Pt(SA)_2(PPh_3)_2$	1638m	997m, 909m
$[Pd(SV)_2]_n$	1618m	980m, 908ms
$Pd(SV)_2(PPh_3)_2$	1618m	982m, 910m
$[Pd(SA)_2]_6$	1638m	995m, 911m
$Pd(SA)_2(PPh_3)_2$	1638m	997m, 908m
$Pd(OA)_2(PPh_3)$	1638m, 1520m[c]	998m, 970m, 935w, 912m
$[Rh(OA)(C_8H_{12})]_2$	1638m	998s, 963m, 932w, 910m, 900s

[a] In Nujol unless otherwise stated; vs very strong; s strong; ms medium strong; m medium; w weak; vw very weak; (br) broad. [b] Liquid film. [c] In hexachlorobutadiene.

formula $[Pt(SV)_2]_n$, is insoluble in water and common organic solvents, and is polymeric. An analogous complex is obtained with Na_2PdCl_4. An open chain structure is postulated for these complexes. The R–S⁻ group is still a powerful bridging agent for Pt and Pd, in spite of the presence of the vinyl group which could coordinate to the metal. For both the Pt and the Pd complex the IR spectrum shows a sharp band at ca. 1620 cm^{-1} due to the uncoordinated double bonds. The sulphur bridges can be split by ligands such as triphenylphosphine to form complexes of the type $M(SV)_2(PPh_3)_2$, in which the double bonds are still uncoordinated. A *cis* structure is proposed for these complexes on the basis of the far IR spectra, since all of them show two bands attributable to ν(M–P) stretching at ca. 450 m and 425 m cm^{-1}*.

In addition to small amounts of insoluble materials, the reaction of the sodium salt of the *o*-allylbenzenethiol and sodium chloroplatinite or palladite yields complexes of formula $[M(SA)_2]_n$**, which were found to be hexamers in $CHCl_3$ solution. These complexes may have a structure similar to that of $(PtCl_2)_6$, in which an octahedral arrangement of metal atoms is bridged by sulphur atoms along the edges, but are more likely to have a hexagonal structure similar to that of $[Ni(SEt)_2]_6$[13] and $[Pd(SC_3H_7)_2]_6$[5]. In both the cases the metal is in a square planar environment and

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* Attempts to remove the coordinated phosphine by treatment with $AgClO_4$ in benzene instead gave $Pt(SV)_2(PPh_3)_2 \cdot AgClO_4$. This is a 1/1 electrolyte in acetone ($\Lambda = 131\ \Omega^{-1} \cdot cm^2 \cdot mole^{-1}$), and the IR spectrum contains two bands at 1620 and 1560 cm^{-1}: the latter can be assigned to a double bond coordinated to a silver atom[6]. We tentatively propose a formula in which the silver atom is coordinated through the sulphur atoms and one of the two double bonds.

** SA = *o*-allylbenzenethiolato.

TABLE 4

PROTON NMR DATA FOR THE LIGANDS AND THEIR COMPLEXES

Compound	Chemical shifts^{a} (ppm)					Spin-spin coupling constants (Hz)			
	H_1^{b}	H_2	H_3	H_4	H_5	J_{12}	J_{13}	J_{14}	J_{23}
A–OH	3.95(1)^{c}	4.91(1)	4.95(1)	6.63(2)	^{d}	10.3	14.1	6.3	2.0
$Pt(OA)_2$	5.05(1)	6.15(1)	7.28(1)	6.94(2)		8.3	13.5	6.2	3.5
$Pt(OA)_2(PPh_3)_2$	3.60(1)	5.10(1)^{e}	5.10(1)^{e}	6.59(2)		9.5	14.5	6.0	
$[Rh(OA)(C_8H_{12})]_2$	3.70(1)	4.79(1)^{e}	4.79(1)^{e}	6.72(2)^{g}				6.0	
V–SH	^{f}	4.70(1)	4.39(1)		6.83(1)	11.0	17.1		1.7
$Pt(SV)_2(PPh_3)_2$	^{f}	4.61(1)	4.25(1)			9.5	16.3		1.7
A–SH	4.2(1)	4.97(1)	5.05(1)	6.62(2)	6.85(1)	10.2	15.8	6.3	1.8
$[Pt(SA)_2]_6$	3.7(1)	4.78(1)^{e}	4.78(1)^{e}	6.51(2)					
$Pt(SA)_2(PPh_3)_2$	3.48(1)	5.23(1)	5.27(1)	6.83(2)		9.9	16.2	6.6	1.9

[a] Chemical shifts values (τ) relative to TMS as the internal standard in $CDCl_3$. [b] Protons are numbered as in (I)–(VI). An absorption is also present at ca. 2.5–3.0 τ due to the aromatic protons. [c] The relative intensities are shown in parentheses. [d] Concentration dependent. [e] Insufficient resolution to justify analyses. [f] Obscured by aromatic protons. [g] Absorptions due to the coordinated COD are also present.

the sulphur atom has a three-coordinate pyramidal structure. The hexamers react with triphenylphosphine in boiling benzene to give complexes of formula $M(SA)_2(PPh_3)_2$ (M = Pt, Pd) in which the double bond is still uncoordinated. The reaction was carried out with a range of mole ratios of metal to ligand but no compounds containing even one coordinated double bond were isolated.

Bromination

The reaction of $Pt(OA)_2$ and $Pt(OA)_2(PPh_3)_2$ with bromine in C_6H_6 causes cleavage of the Pt–O bonds to form products which vary with the Br_2/Pt ratio.

The reaction of $Pt(SA)_2(PPh_3)_2$ with Br_2 shows that this complex behaves differently from $PtBr_2L_2$[1a] and $PtBr_2L$[14] [where L = *o*-styryl- or (*o*-allylphenyl)-dimethylarsine] which give an octahedral Pt^{IV} complex with a Pt–C σ-bond. In the case of the thio-complex the Pt atom seems to be less susceptible to attack by the polarized bromine molecule at room temperature in benzene, probably because of interaction between the *d* orbitals of sulphur and platinum, and the double bonds seem to react first. Raising the temperature can lead to splitting of the Pt–S bond by the bromine. These reactions are being investigated further.

EXPERIMENTAL

Starting materials

All solvents were dried over sodium, and tetrahydrofuran was freshly distilled from sodium/benzophenone before use. *o*-Bromostyrene was used as purchased. *o*-Allylchlorobenzene was obtained by treating the mono-Grignard of *o*-bromochlorobenzene with allyl bromide. In the preparation of the Grignard reagents, all reactions were carried under anhydrous, oxygen-free nitrogen and the apparatus dried by heating under vacuum for one hour before use. The term petrol refers to petroleum ether of b.p. 60°–80°.

Measurements

Infrared spectra were recorded with a Perkin–Elmer 225 double beam grating apparatus. Proton NMR spectra were recorded with a Perkin–Elmer R10 60 MHz or Varian HA 100-MHz instrument, deuteriochloroform solutions containing ca. 1% tetramethylsilane as internal standard being used. Melting points (uncorrected) were determined with a Gallenkamp electrically heated hot-stage apparatus. Conductance measurements were carried out on ca. 10^{-3} *M* solutions at 25° in nitromethane or nitrobenzene in a conventional cell with platinum electrodes using a Wayne–Kerr universal bridge model B221. The cell was calibrated with aqueous solutions of potassium chloride. Molecular weights were determined at 25° using a Mechrolab vapor pressure osmometer, model 301A. Microanalyses were carried out by the microanalytical laboratory of this department, and phosphorous and sulphur were determined by Alfred Bernhardt, Max Planck Institute für Kolhenforschung, Mülheim.

Preparation of compounds

o-Allylphenol. The commercial product (Ralph H. Emanuel Ltd) was repeatedly distilled under reduced pressure and stored under nitrogen at 0°. $n_D^{20} = 1.5453$, b.p. 73°/0.5 mmHg.

o-Vinylbenzenethiol. The Grignard reagent prepared from magnesium turnings (4.8 g; 0.2 g-atom) and *o*-bromostyrene (36.6 g; 0.2 mol) in THF, was filtered under nitrogen and cooled to −15°. Sulphur (5.64 g; 0.17 mol) was then added during 1 h. The resulting yellow solution was stirred at this temperature for 1 h more, filtered while still cold into a 500 ml two-necked flask, and allowed to reach −5°. It was then hydrolyzed with 300 ml of aqueous sodium hydroxide solution (1 *N*) while the temperature rose to 0°. The solution was filtered under nitrogen to remove the insoluble magnesium compounds, and the organic layer separated and washed with a 0.1 *M* NaOH solution (3 × 20 ml). The aqueous layers were collected, washed with diethyl ether (5 × 30 ml) and concentrated to 50 ml under vacuum (0.01 mmHg) at room temperature. A portion of this solution (5 ml) was treated with HCl *N*/10 (final pH = 6.5) and the free ligand extracted with benzene. The solution was dried over sodium sulphate and filtered under nitrogen, and the solvent was evaporated under vacuum (0.01 mmHg) at room temperature to leave the *o*-vinylbenzenethiol as a pale yellowish oil. Analyses and spectra showed it to be 99% pure. [The ligand reacted with lead acetate to give a yellow precipitate in alcoholic solution which analyzed for $Pb(S{-}C_6H_4{-}CH{=}CH_2{-}o)_2$.] Attempts to distill the free thiol under reduced pressure (b.p. 57°/0.02 mmHg) and in a nitrogen atmosphere gave a considerable amount of a colourless liquid which did not react with lead(II) acetate and which did not show any bands in the infrared spectrum due to ν(S–H) or ν(C=C). It was identified as 2,3-dihydrothianaphthene. A solid residue, probably polymeric, was also formed. The sodium salt of the ligand was used in the reactions.

o-Allylbenzenethiol. The Grignard reagent from *o*-chloroallylbenzene (0.134 mol) was prepared as previously described[15]. It was filtered under nitrogen and cooled to −20° and sulphur (0.11 mol) added in small portions during 1 h. The mixture was worked up as above.

Bis(o-allylphenolato)platinum(II), $Pt(OA)_2$. Sodium tetrachloroplatinite(II) (0.670 g, 1.75 mmol) was dissolved in alcohol/water (30 ml; 1/1). To the filtered solution, saturated with nitrogen were added *o*-allylphenol (4.07 g, 30.4 mmol) and sodium hydrogen carbonate, (ca. 0.3 g). The golden yellow solution was stirred at room temperature under nitrogen for five hours, then cooled to 0° and left at this temperature overnight. The white plates which separated were collected by filtration, washed with water, cold ethanol and hexane. Recrystallization from benzene/hexane, gave the pure compound (40 %), which was soluble in chloroform, acetone, and benzene, and slightly soluble in alcohol and carbon tetrachloride.

Bis(o-allylphenolato)(pyridine)platinum(II), $Pt(OA)_2Py$. A solution of $Pt(OA)_2$ (0.15 g; 0.325 mmol) in dry toluene (3 ml) was treated with pyridine (0.17 mmol) in toluene (1 ml), and the solution was stirred at 10° for 3 h. Petrol was added and the solution cooled to $-10°$. The solid was filtered off, washed with cold petrol, and crystallized from hexane to give the monopyridine derivative. This compound slowly loses pyridine at room temperature in the solid state.

Bis(o-allylphenolato)bis(pyridine)platinum(II), $Pt(OA)_2Py_2$. A solution of $Pt(OA)_2$ (0.15 g; 0.325 mmol) in dry benzene (5 ml) was treated with an excess of pyridine (0.9 mmol) under reflux for 10 min and then allowed to cool to room temperature. The solvent was partly evaporated at room temperature under vacuum, and addition of petrol followed by cooling gave the bis-pyridine derivative. This was filtered off, washed with cold pentane, and dried at low temperature. The complex loses pyridine at room temperature.

Bis(o-allylphenolato)bis(triphenylpyosphine)platinum(II), $Pt(OA)_2(PPh_3)_2$. A solution of $Pt(OA)_2$(0.25 g, 0.54 mmol) in 10 ml dry benzene was treated with triphenylphosphine (0.290 g, 1.11 mmol). The pale yellow solution was heated under reflux for 30 min, then cooled and filtered, and the solvent was evaporated off under vacuum to ca. 3 ml. Slow addition of hexane precipitated a white microcrystalline compound, which was recrystallized from petrol/chloroform (90% yield).

Bis(o-allylphenolato)(triphenylphosphine)palladium(II), $Pd(OA)_2PPh_3$. *o*-Allylphenol (0.402 g, 3 mmol) in anhydrous benzene (5 ml) was treated with sodium (2 mmol) under nitrogen and the solution stirred until the reaction was complete. Dichlorobis(triphenylphosphine)palladium(II) (0.702 g, 1 mmol) was slowly added (30 min), and the resulting red solution was stirred at room temperature for 6 h. Oxygen-free distilled water (10 ml) was added to dissolve the sodium chloride, and the organic layer was separated, dried over $MgSO_4$, filtered and concentrated under vacuum (0.1 mmHg) to 5 ml. Addition of pentane (20 ml) gave an orange precipitate, which was crystallized twice from benzene/pentane to give 0.8 g of the pure complex as micro-crystals. It was stable in the air in the solid state, but the solution darkened slowly as decomposition occurred. In chloroform, decomposition gives a green solution, from which a greenish chlorine-containing product was isolated.

μ,μ-Bis(o-allylphenolato)bis(1,5-cyclooctadiene)dirhodium(I), $[Rh(OA)COD]_2$. *o*-Allylphenol (0.89 mmol) was treated with sodium (3.84 mmol) in anhydrous THF (25 ml) under nitrogen and the solution was added dropwise to a solution of [1,5-(COD)RhCl]$_2$ (1.92 mmol) in THF (30 ml). The solution was stirred under nitrogen until the colour was pale yellow (4 h), and the solvent evaporated off under vacuum (0.1 mmHg) to ca. 2 ml. Petrol (20 ml) was then added, and the solution was cooled to $-20°$ for 1 h and then filtered. The solid was washed thoroughly with water, dried *in vacuo*, and recrystallized from benzene/pentane to give pale yellow needles of the pure product. It was very soluble in organic solvents at room temperature.

Bis(o-vinylbenzenethiolato)platinum(II), $[Pt(SV)_2]_n$. A filtered solution of potassium tetrachloroplatinite(II) (0.450 g, 1.08 mmol) in 20 ml ethanol/water (1/1) was slowly added under nitrogen with stirring to a solution of sodium vinylbenzenethiolate (2.5 mmol) in 10 ml water. The solution was stirred for 4 h at room temperature and the yellow precipitate which formed was washed with water, cold ethanol, hexane and dried *in vacuo* (15 mmHg) at room temperature. It was insoluble in water, and very slightly soluble in organic solvents, but could be crystallized from large volumes of chloroform or acetone to give a pale yellow solid (73 % yield base on Pt).

The palladium analogue was prepared analogously from potassium chloropalladite(II). This complex had properties similar to those of the platinum compound.

Bis(o-allylbenzenethiolato)platinum(II), $[Pt(SA)_2]_6$. The analogous procedure, using sodium *o*-allylbenzenethiolate complex gave the product as a yellow microcrystalline solid, soluble in chloroform, benzene, and acetone, but not water. It was crystallized from chloroform/light petroleum (70 % yield). The palladium complex was prepared analogously; like the platinum complex it was soluble in organic solvents and could be recrystallized from benzene/hexane.

Bis(o-vinylbenzenethiolato)bis(triphenylphosphine)platinum(II), $Pt(SV)_2(PPh_3)_2$. A solution of triphenylphosphine (0.530 g, 2.02 mmol) was slowly added (20 min) to a well-stirred suspension of bis(*o*-vinylbenzenethiolato)platinum(II) (0.465 g, 1 mmol) in refluxing benzene (10 ml). The solution was refluxed until no solid could be seen (ca. 2 h), and then cooled and filtered. The solvent was evaporated to 3 ml, and pentane added to precipitate a yellow crystalline product, which was filtered, washed with pentane, and dried *in vacuo*. The analogous palladium(II) complexes were obtained similarly as orange crystals. The bis(*o*-allylbenzenethiolato)bis(triphenylphosphine)-complexes of Pt^{II} and Pd^{II} were obtained as yellow and orange crystals, respectively, and were recrystallized from diethyl ether/pentane.

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