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Synthesis and characterisation of triselenocarbonate $[CSe_3]^{2-}$ complexes

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Received 25th October 2004, Accepted 17th December 2004
First published as an Advance Article on the web 18th January 2005

DOI:10.1039/b416356g

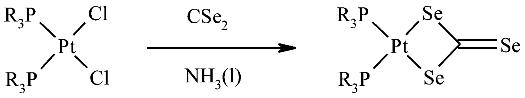
$[Pt(CSe_3)(PR_3)_2]$ ($PR_3 = PMe_3, PMe_2Ph, PPh_3, P(p\text{-tol})_3, \frac{1}{2}$ dppp, $\frac{1}{2}$ dppf) were all obtained by the reaction of the appropriate metal halide containing complex with carbon diselenide in liquid ammonia. Similar reaction with $[Pt(Cl)_2(dppe)]$ gave a mixture of triselenocarbonate and perselenocarbonate complexes. $[\{Pt(\mu\text{-}CSe_3)(PEt_3)\}_4]$ was formed when the analogous procedure was carried out using $[Pt(Cl)_2(PEt_3)_2]$. Further reaction of $[Pt(CSe_3)(PMe_2Ph)_2]$ with $[M(CO)_6]$ (M = Cr, W, Mo) yielded bimetallic species of the type $[Pt(PMe_2Ph)_2(CSe_3)M(CO)_5]$ (M = Cr, W, Mo). The dimeric triselenocarbonate complexes $[M\{(CSe_3)(\eta^5\text{-}C_5Me_5)\}_2]$ (M = Rh, Ir) and $[\{M(CSe_3)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$ (M = Ru, Os) have been synthesised from the appropriate transition metal dimer starting material. The triselenocarbonate ligand is *Se*,*Se′* bidentate in the monomeric complexes. In the tetrameric structure the exocyclic selenium atoms link the four platinum centres together.

Introduction

It is well established that reaction of carbon disulfide with alkali metal hydroxides in polar solvents leads to the trithiocarbonate dianion,[1] whereas using carbon diselenide under the same reaction conditions yields only polymeric material. The absence of a synthetic method for the generation of the triselenocarbonate dianion has meant that at present there are only three literature examples of a complex or metal salt containing this ligand. The organometallic complex $[(\eta^5\text{-}C_5H_5)Co(CSe_3)(PMe_3)]$ was formed as a reaction by-product and isolated in only 7% yield[2] and barium triselenocarbonate $Ba(CSe_3)$ was prepared by the action of carbon diselenide on BaSe in 55–60% yield.[3] Additionally, a single example of a triselenocarbonate complex in which only the selenocarbonyl (Se=C) selenium atom is bound to the metal $[(OC)_5Cr\{Se{=}C(SeEt)_2\}]$ has been reported.[4] We have previously reported the use of liquid ammonia for the synthesis of M–S–N and M–Se–N complexes as well as the preparation of bis-phosphine platinum trithiocarbonate complexes from $[PtCl_2(PR_3)_2]$ and carbon disulfide.[5] We have now found that the elusive triselenocarbonate dianion can be trapped from analogous liquid ammonia reactions giving $(CSe_3)^{2-}$ complexes in reasonable yields. Here we report examples of mononuclear, binuclear and tetranuclear complexes of this ligand including the first crystallographically characterised example of a triselenocarbonate complex.

Results and discussion

The heteroleptic complexes $[Pt(CSe_3)(PR_3)_2]$ ($PR_3 = PMe_3$, PMe_2Ph, PPh_3, $\frac{1}{2}$ dppp, $\frac{1}{2}$ dppf) were all obtained by the reaction of the appropriate $[PtCl_2(PR_3)_2]$ complex with carbon diselenide in liquid ammonia (eqn. (1)).



(1)

After ammonia was removed the products were readily extracted into dichloromethane.

For all the complexes **1**–**6** the microanalyses were within the specified limits and the anticipated M^+ were observed in their mass spectra (Table 1) and the appropriate isotope distribution patterns were observed. The ν(C=Se) vibrations are observed at *ca.* 900 cm^{-1} and the ν(Pt–Se) bands are noted in the region 242–285 cm^{-1} (Table 2). The $^{31}P\{^1H\}$ NMR spectra of the platinum(bisphosphino) triselenocarbonates **1**–**6** (Table 2) have similar δ values to the analogous trithiocarbonate complexes.[5i] The $^1J(^{195}Pt\text{–}^{31}P)$ coupling constants lie in the range 2871–3218 Hz and are of approximately the same magnitude as the corresponding trithiocarbonate species.[5i] The $^{31}P\{^1H\}$ NMR spectra of **1**–**6** consist of singlets with ^{77}Se satellites. The most comparable compound is $[Pt(Se_2CH_2)(PPh_3)_2]$.[6] The spectra of $[Pt(Se_2CH_2)(PPh_3)_2]$ was analysed in detail as an AA′X system and **1**–**6** have the same spin system. The spectra reported here do not contain sufficient detail to determine all of the *J* values in **1**–**6**, however if we assume a $^3J(^{31}P\text{–}^{31}P)$ of *ca.* 20 Hz (*cf.* 21.8 Hz in $[Pt(Se_2CH_2)(PPh_3)_2]$[6]) then the *trans* and *cis* $^2J(^{77}Se\text{–}^{31}P)$ we determine from simulations are approximately 35 and 8 Hz respectively (*cf.* 31 and 11 Hz in $[Pt(Se_2CH_2)(PPh_3)_2]$[6]). **2** is the first crystallographically characterised example of this class of compound. The X-ray analysis of **2** (Fig. 1, Table 3) shows that the platinum core lies at the centre of a distorted square planar coordination sphere consisting of two phosphorus and two selenium atoms. The P(1)–Pt(1)–P(2) angle is 95.49(11)° showing deviation from idealized 90° square planar geometry and is directly comparable to the platinum (bis-phosphino) trithiocarbonate complexes which fall in the range 93.2(1)–98.99(6)°.[5i] The corresponding Se(1)–Pt(1)–Se(2) angle is 76.23(4)° which

Table 1 Microanalytical data (calculated values in parentheses) and mass spectral data for complexes **1**–**6**, **8**–**15**

Complex	C	H	*m*/*z*
1 $[Pt(CSe_3)(PMe_3)_2]$	14.14 (14.10)	3.08 (3.04)	599[a]
2 $[Pt(CSe_3)(PMe_2Ph)_2]$	27.96 (28.35)	2.87 (3.08)	720[a]
3 $[Pt(CSe_3)(PPh_3)_2]$	45.56 (45.88)	2.65 (3.12)	970[a]
4 $[Pt(CSe_3)(P(p\text{-tol})_3)_2]$	48.71 (49.06)	3.89 (4.02)	1052[a]
5 $[Pt(CSe_3)(dppp)]$	39.44 (39.27)	2.74 (3.06)	856[a]
6 $[Pt(CSe_3)(dppf)]$	42.35 (42.11)	2.63 (2.83)	998[a]
8 $[\{Pt(\mu\text{-}CSe_3)(PEt_3)\}_4]$	15.39 (14.96)	2.52 (2.69)	—
9 $[Pt(PMe_2Ph)_2(CSe_3)Cr(CO)_5]$	28.77 (28.96)	2.23 (2.43)	912[b]
10 $[Pt(PMe_2Ph)_2(CSe_3)Mo(CO)_5]$	27.84 (27.63)	2.01 (2.32)	956[b]
11 $[Pt(PMe_2Ph)_2(CSe_3)W(CO)_5]$	24.98 (25.31)	2.12 (1.78)	1044[b]
12 $[\{Rh(CSe_3)(\eta^5\text{-}C_5Me_5)\}_2$	26.68 (27.13)	2.84 (3.10)	979[a]
13 $[\{Ir(CSe_3)(\eta^5\text{-}C_5Me_5)\}_2]$	23.14 (22.92)	2.17 (2.62)	1154[b]
14 $[\{Ru(CSe_3)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$	27.59 (27.29)	3.07 (2.91)	969[a]
15 $[\{Os(CSe_3)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$	23.46 (23.04)	2.44 (2.46)	1148[a]

[a] Measured by electrospray. [b] Measured by fast atom bombardment. *m*/*z* values reported are for , the spectra contained parent ions with the appropriate isotopomer distributions.

Table 2 $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 109.4 MHz) and selected IR data for complexes **1–6**, **9–11**

Complex	δ(P)/ppm	$^1J(^{195}Pt–^{31}P)$/Hz	ν(C=O)/cm^{-1}	ν(C=Se)/cm^{-1}	ν(Pt–Se)/cm^{-1}
1 $[Pt(CSe_3)(PMe_3)_2]$	−29.2	2970	—	907	285, 255
2 $[Pt(CSe_3)(PMe_2Ph)_2]$	−18.6	3017	—	902	282, 242
3 $[Pt(CSe_3)(PPh_3)_2]$	19.1	3146	—	908	280
4 $[Pt(CSe_3)(P(p\text{-tol})_3)_2]$	17.1	3162	—	923	256, 242
5 $[Pt(CSe_3)(dppp)]$	−2.7	2871	—	900	282, 247
6 $[Pt(CSe_3)(dppf)]$	17.5	3218	—	915	283, 250
9 $[Pt(PMe_2Ph)_2(CSe_3)Cr(CO)_5]$	−19.3	3038	1972, 1925, 1905	891	282, 247
10 $[Pt(PMe_2Ph)_2(CSe_3)Mo(CO)_5]$	−18.5	3041	1984, 1931, 1885	909	279, 244
11 $[Pt(PMe_2Ph)_2(CSe_3)W(CO)_5]$	−18.3	3045	1975, 1919, 1889	909	281, 244

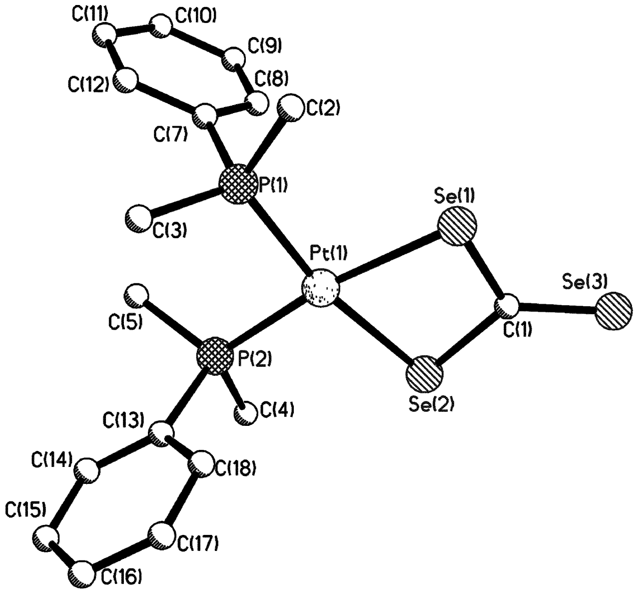


Fig. 1 Crystal structure of **2**.

Table 3 Selected bond lengths and angles for compounds **2** and **8**

Compound	**2**	**8**
Pt(1)–P(1)	2.264(3)	2.254(2)
Pt(1)–P(2)	2.274(3)	—
Pt(1)–Se(1)	2.4561(12)	2.4325(9)
Pt(1)–Se(2)	2.4630(13)	2.4961(9)
Pt(1)–Se(3A)	—	2.4242(9)
Se(1)–C(1)	1.860(13)	1.879(8)
Se(2)–C(1)	1.884(13)	1.839(9)
C(1)–Se(3)	1.794(13)	1.823(8)
Se(1)–Pt(1)–Se(2)	76.23(4)	76.29(3)
P(1)–Pt(1)–P(2)	95.49(11)	—
P(1)–Pt(1)–Se(3A)	—	92.01(6)
Se(1)–C(1)–Se(3)	126.5(7)	120.7(5)
Se(2)–C(1)–Se(3)	125.0(7)	129.4(5)
Pt(1)–Se(1)–C(1)	87.9(4)	87.4(3)
Pt(1)–Se(2)–C(1)	87.2(4)	86.3(2)
P(2)–Pt(1)–Se(1)	170.15(9)	—
P(1)–Pt(1)–Se(2)	169.39(8)	169.54(6)
Se(1)–Pt(1)–Se(3A)	—	167.71(4)

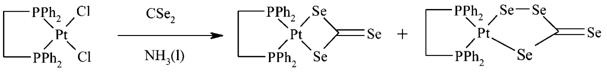
Table 4 Details of the X-ray data collections and refinements for compounds **2** and **8**[a]

Compound	**2**	**8**
Empirical formula	$C_{17}H_{22}P_2PtSe_3$	$C_{28}H_{60}P_4Pt_4Se_{12}$
Crystal system	Triclinic	Tetragonal
Space group	$P\bar{1}$	$P\bar{4}2(1)c$
a/Å	8.9878(14)	12.5946(11)
b/Å	11.0937(18)	12.5946(11)
c/Å	11.6242(19)	16.047(2)
α/°	86.035(3)	90
β/°	76.775(3)	90
γ/°	69.554(3)	90
U/Å^3	1057.1(3)	2545.5(4)
Z	2	2
M	720.26	2248.52
μ/mm^{-1}	11.949	19.683
Measured reflections	6302	14330
Independent reflections (R_{int})	3753(0.0543)	2283(0.0914)
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0517, 0.1090	0.0277, 0.0610

[a] **7** was not of sufficient quality for a full refinement. Monoclinic, $P2(1)/c$, $a = 14.965(3)$, $b = 20.192(3)$, $c = 18.125(3)$ Å, $\beta = 97.420(4)$, $U = 5431.0(16)$ Å^3, 100 K, Rigaku Mercury, 6639 unique observed data gave $R = 18.86\%$.

is slightly enlarged compared to the S(1)–Pt–S(2) angle in $[Pt(CS_3)(PR_3)_2]$ complexes which are typically 73–74°. The Pt–P distances are comparable to those in $[Pt(CS_3)(PMe_2Ph)_2]$ and as expected the Pt–Se distances are longer than the corresponding Pt–S distances. The C–Se bond lengths in the $[CSe_3]^{2-}$ ligand are longer for the coordinated selenium atoms compared to the exocyclic selenium atom. Within the $PtSe_2C$ ring the Pt–Se–C angles are 87.2(4)–87.9(4)°. The bond lengths and angles in **2** are comparable to those for $[Pt(Se_2CH_2)(PPh_3)_2]$[6] however the Se(1)–C(1)–Se(2) angle is much larger in **2** (108.4(6)° compared to 101.1(3)° in $[Pt(Se_2CH_2)(PPh_3)_2]$). The difference in Se(1)–C(1)–Se(2) angle is due to sp^2 nature of **2** compared to the sp^3 nature of $[Pt(Se_2CH_2)(PPh_3)_2]$. The Se(1)–Se(2) non bonded distance is 3.04 Å, which is 80% of sum of the van der Waals radii of selenium and implies that there is a significant interaction between the two selenium atoms. In the P(1)–P(2)–Pt(1)–Se(1)–Se(2) mean plane the maximum deviation from planarity is for Se(2) which lies 0.05 Å above the coordination plane. C(1) and Se(3) lie 0.13 Å and 0.4 Å above the plane respectively. The hinge angle between the P(1), P(2), Pt(1), Se(1), Se(2) mean plane and the Se(1), Se(2), C(1), Se(3) mean plane is 7.9°.

In contrast to the other phosphines the reaction of $[PtCl_2(dppe)]$ with carbon diselenide in liquid ammonia results in the formation of a mixture of the expected triselenocarbonate product $[Pt(CSe_3)(dppe)]$ and the perselenocarbonate complex $[Pt(CSe_4)(dppe)]$ (eqn. (2)). Attempts to separate these two species have proven unsuccessful, however the presence of both species is clearly evident in the $^{31}P\{^1H\}$ NMR spectrum.



(2)

A single sharp resonance corresponding to the triselenocarbonate complex is observed at 45.2 ppm with the expected platinum satellites [$^1J(^{195}Pt–^{31}P)$ 3005 Hz]. Selenium satellites are also noted but we do not have sufficient detail to determine the $^2J(^{77}Se–^{31}P)$ values. The perselenocarbonate complex exhibits an AX type system $\delta(P_A)$ 44.4(d), $^1J(^{195}Pt–^{31}P)$ 2927 Hz and $\delta(P_X)$ 45.5(d), $^1J(^{195}Pt–^{31}P)$ 2595 Hz with a $^2J(^{31}P_A–^{31}P_X)$ of 9 Hz. In the IR spectrum two different ν(C=Se) vibrations are observed at 898 and 907 cm^{-1} corresponding to the two different species. The ν(Pt–Se) bands are noted in the region 250 to 290 cm^{-1}. A crystallographic study confirmed the existence of both species

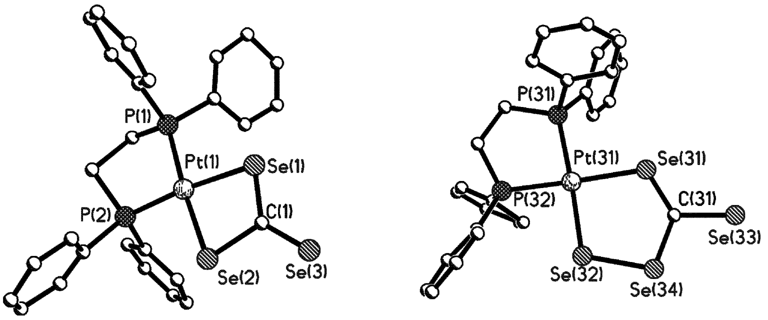
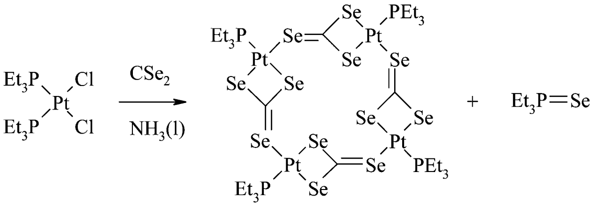


Fig. 2 Crystal structure of **7**. Although the data is adequate for confirmation of connectivity it is not of sufficient quality to allow discussion of any metrical parameters.

(Fig. 2) and established atom connectivity however, despite repeated attempts at crystallization/measurement, the data is of too poor quality to allow discussion of bond lengths or angles. There are currently only two examples of perselenocarbonate complexes in the literature. A zinc salt $[PPh_4]_2[Zn(CSe_4)_2]$[7] isolated from a solution of carbon diselenide with sodium metal in the presence of zinc(II) chloride and $[PPh_4]Br$ and a manganese carbonylate species $[(PPh_3)_2N]_2[\{Mn(CSe_4)(CO)_3\}_2]$[8] prepared by the reaction of elemental selenium with $[Mn_2(CO)_{10}]$ and KOH. We are currently investigating methods for the rational synthesis of a series of perselenocarbonate complexes.

We have found that reaction of $[PtCl_2(PEt_3)_2]$ with carbon diselenide in liquid ammonia generates the novel tetramer $[Pt(CSe_3)(PEt_3)]_4$ (eqn. (3)).



(3)

In the $^{31}P-\{^1H\}$ NMR (CD_2Cl_2) of the crude reaction mixture four different phosphorous containing species are observed. These include triethylphosphine selenide (δ(P) 45.2, $^1J(^{77}Se-^{31}P)$ 690 Hz), possibly $[Pt(CSe_3)(PEt_3)_2]$ (δ(P) 4.7, $^1J(^{195}Pt-^{31}P)$ 3017 Hz) assigned based on comparison with the trithiocarbonate analogue[5i] and two unknown platinum species δ(P) 14.2, $^1J(^{195}Pt-^{31}P)$ 2160 Hz and δ(P) 5.3, $^1J(^{195}Pt-^{31}P)$ 3249 Hz. From this crude reaction mixture **8** was obtained in a 15% yield as insoluble dark red crystals by crystallization. In the IR spectrum of **8** the $\nu(C{=}Se)$ stretch can be seen at 875 cm^{-1} and $\nu(Pt-Se)$ bands are found at 283 and 257 cm^{-1}. The microanalysis gave satisfactory results. A single crystal X-ray diffraction study clearly shows the tetrameric structure of **8** (Fig. 3, Table 3). The platinum atom lies at the centre of a distorted square planar coordination sphere. The P(1)–Pt(1)–Se(3A) angle is 92.01(6)° showing considerable deviation from idealized 90° square planar geometry. The Se(1)–Pt(1)–Se(2) angle is 76.29(3)°, which is comparable to compound **2**. The Pt–P distance is 2.254(2) Å which is slightly shorter than in **2**. The Se(1)–C(1) and Se(2)–C(1) (1.879(8) and 1.839(9) Å respectively) in the $[CSe_3]^{2-}$ ligand are approximately the same length as is complex **2**. The selenocarbonyl Se=C bond Se(3)–C(1) in **8** is 1.823(8) Å compared to 1.794(13) Å in **2**. The longer Se(3)–C(1) bond in **8** is due to Se(3) being three coordinate. The 16-membered macrocycle is disposed about a crystallographic −4 point in the centre of the molecule. The four platinum atoms adopt a distorted square planar (or flattened tetrahedral) geometry [Pt(1)–centre–Pt(1C) 154°, Pt(1)–centre–Pt(1B) 93°] resulting in a puckered geometry with the Se(2) atoms alternately up/down around the ring.

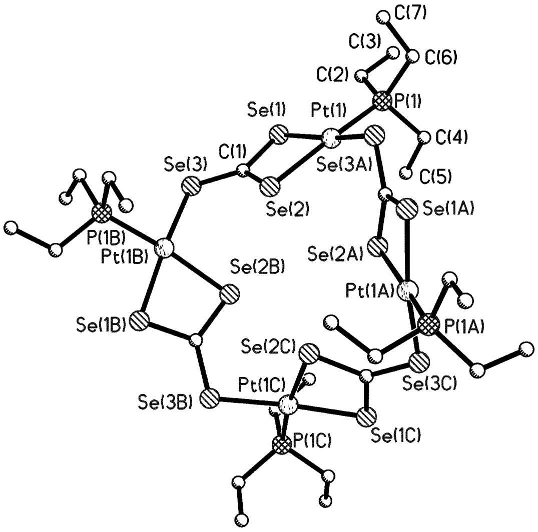
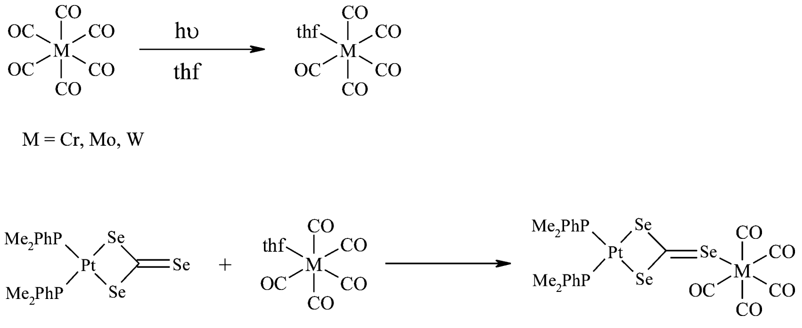


Fig. 3 Crystal structure of **8**.

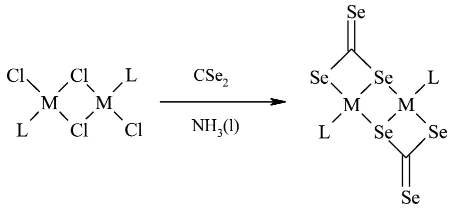
Further reaction of $[Pt(CSe_3)(PMe_2Ph)_2]$, **2**, with $[M(CO)_5(thf)]$ (M = Cr, W, Mo) (Scheme 1) yielded bimetallic species of the type $[Pt(PMe_2Ph)_2(CSe_3)M(CO)_5]$ (M = Cr, W, Mo, **9**–**11**). For **9**–**11** the microanalyses results were within acceptable limits and all showed the anticipated in their mass spectra



Scheme 1

(Table 1). The observation of three carbonyl stretching bands in the infrared spectrum of **9**–**11** in the region 1885 to 1984 cm^{-1} further confirmed that the desired products had been formed. Only very subtle shifts in the frequency of ν(C=Se) and ν(Pt–Se) bands were observed (Table 2). In the $^{31}P\{^1H\}$ NMR spectrum as expected only a very slight change in chemical shift is noted and the $^1J(^{195}Pt–^{31}P)$ coupling constant increases from 3017 Hz in **2** to *ca.* 3040 Hz in **9**–**11** (Table 2).

The dimeric triselenocarbonate complexes $[\{M\{(CSe_3)(\eta^5\text{-}C_5Me_5)\}_2]$ (M = Rh, **12**, Ir, **13**)and $[\{M(CSe_3)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$ (M = Ru, **14**, Os, **15**) have been synthesised and isolated in a similar fashion to the platinum(bis-phosphine) triselenocarbonate complexes **1**–**6** by reacting carbon diselenide in liquid ammonia with the appropriate transition metal dimer starting material (eqn. (4)).**12**–**14** all gave satisfactory microanalysis results and displayed the expected in their mass spectra (Table 1). The ν(C=Se) vibrations and the bands for ν(M–Se) were all observed in the anticipated regions (Table 2). Proton NMR clearly identified the respective alkyl groups present. Unfortunately no crystallographic data was obtained for **12**–**14**; a feasible structure noted before in *E*,*E* bidentate ligands[8,9] is proposed above (eqn. (4)).



M = Rh **12**, Ir **13**, Ru **14**, Os **15**
L = η^5-C_5Me_5 **12** and **13**, η^6-*p*-$MeC_6H_4{}^iPr$ **14** and **15** (4)

Experimental

General

All operations were carried out under an oxygen-free nitrogen atmosphere and using standard Schlenk techniques. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. Diethyl ether was purified by reflux over sodium benzophenone and distillation under nitrogen. Carbon diselenide was prepared as a dichloromethane solution by passing dichloromethane over elemental selenium at 600 °C.[10] Ammonia (BOC) was used as received. CD_2Cl_2 (99.6+ atom D) was used as received. The metal complexes $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$,[11] $[\{IrCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$,[11] $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$[12] and $[\{OsCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$,[12] were prepared according to literature procedures. The complexes $[PtCl_2(PMe_3)_2]$, $[PtCl_2(PMe_2Ph)_2]$, $[PtCl_2(PEt_3)_2]$, $[PtCl_2(PPh_3)_2]$, $[PtCl_2(P(p\text{-}tol)_3)_2]$, [Pt($[PtCl_2$(dppe)] (dppe = bis(diphenylphosphino)ethane), $[PtCl_2$(dppp)] (dppp = bis(diphenylphosphino)propane)and $[PtCl_2$(dppf)] (dppf = bis(diphenylphosphino)ferrocene) were prepared by the addition of stoichiometric quantities of the appropriate free phosphine or diphosphine to a dichloromethane solution of $[PtCl_2$(cod)] (cod = cycloocta-1,5-diene). $[Cr(CO)_6]$, $[Mo(CO)_6]$ and $[W(CO)_6]$ (all Aldrich) were used as received.

Infrared spectra were recorded (IR spectra as KBr discs unless otherwise stated) on a Perkin-Elmer System 2000 FT/IR/Raman spectrometer. ^{31}P and ^1H NMR spectra were recorded using a JEOL DELTA GSX 270 FT NMR spectrometer. Microanalysis was performed by the University of St. Andrews service. Fast atom bombardment (FAB) and electrospray (ES) mass spectra were performed by the EPSRC National Mass Spectrometer Service and the University of St. Andrews Mass Spectrometer Service.

$[Pt(CSe_3)(PMe_3)_2]$ (1). Liquid ammonia (approximately 20 cm^3) was distilled into a Schlenk tube that had previously been cooled to −78 °C. $[PtCl_2(PMe_3)_2]$ (0.100 g, 0.239 mmol) was added as a solid in one portion followed by carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol). The resulting mixture was stirred for 2 h at −78 °C and then slowly warmed to room temperature with continual stirring until the excess ammonia had evaporated. The remaining solvent was removed under reduced pressure and the red residue was extracted three times with dichloromethane (3 × 20 cm^3). The mixture was filtered through a celite pad and the resulting red solution was reduced in volume to approximately 10 cm^3, and diethyl ether (50 cm^3) was added slowly to precipitate the product as a bright red crystalline solid. Yield: 0.044 g, 31%. ^1H NMR (CD_2Cl_2): δ 1.61 (d, 18H, PMe_3, $^3J(^{195}Pt–^1H)$ 35 Hz, $^2J(^{31}P–^1H)$ 10 Hz).

$[Pt(CSe_3)(PMe_2Ph)_2]$ (2). This was prepared in the same fashion as platinum complex **1** using $[PtCl_2(PMe_2Ph)_2]$ (0.150g, 0.225 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a brick red powder. Yield: 0.092 g, 48%. ^1H NMR (CD_2Cl_2): δ 7.50–7.30 (m, 10 H, aromatic) and 1.57 (d, 12 H, $^3J(^{195}Pt–^1H)$ 35 Hz, $^2J(^{31}P–^1H)$ 10 Hz, PMe).

$[Pt(CSe_3)(PPh_3)_2]$ (3). This was prepared in the same fashion as platinum complex **1** using $[PtCl_2(PPh_3)_2]$ (0.100g, 0.126 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a brick red powder. Yield: 0.038 g, 31%. ^1H NMR (CD_2Cl_2): δ 7.78–7.14 (m, 30 H, PPh_3).

$[Pt(CSe_3)(P(p\text{-}tol)_3)_2]$ (4). This was prepared in the same fashion as platinum complex **1** using $[PtCl_2(P(p\text{-}tol)_3)_2]$ (0.110 g, 0.126 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a brown powder. Yield: 0.037 g, 28%. ^1H NMR (CD_2Cl_2): δ 7.59–7.01 (m, 24 H, aromatic) and 2.38 (s, 18 H, CH_3).

$[Pt(CSe_3)$(dppp)] (5). This was prepared in the same fashion as platinum complex **1** using $[PtCl_2$(dppp)] (0.100 g, 0.179 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a dark orange powder. Yield: 0.046 g, 35%. ^1H NMR (CD_2Cl_2): δ 7.61–7.35 (m, 20 H, aromatic) and 2.81-2.54 (m, 6 H, CH_2).

$[Pt(CSe_3)$(dppf)] (6). This was prepared in the same fashion as platinum complex **1** using $[PtCl_2$(dppf)] (0.100 g, 0.122 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the product as a light brown powder. Yield: 0.083 g, 68%. ^1H NMR (CD_2Cl_2): δ 7.74–7.39 (m, 20 H, aromatic) 4.42 (br, m, 4H, α-CH (C_5H_4)), 4.37 (br, m, 4H, β-CH (C_5H_4)).

$[Pt(CSe_3)$(dppe)]/$[Pt(CSe_4)$(dppe)] (7). This was prepared in the same fashion as platinum complex **1** using $[PtCl_2$(dppe)] (0.300 g, 0.451 mmol) and carbon diselenide (6 cm^3 10% solution in dichloromethane, 0.265 mmol) to give the mixture as a brick red powder. Yield: 0.252 g, 66%. ^{31}P-$\{^1H\}$ NMR (CD_2Cl_2): δ(P) 45.2 (s). $^1J(^{195}Pt–^{31}P)$ 3005 Hz. $\delta(P_A)$ 44.4(d), $^1J(^{195}Pt–^{31}P)$ 2927 Hz and $\delta(P_X)$ 45.5(d), $^1J(^{195}Pt–^{31}P)$ 2595 Hz $^2J(^{31}P_A–^{31}P_X)$ 9 Hz. ^1H NMR (CD_2Cl_2): δ 7.81–7.32 (m, 20 H, aromatic) and 2.59-2.41(m, 4 H, PCH_2CH_2P).

$[\{Pt(\mu\text{-}CSe_3)(PEt_3)\}_4]$ (8). This was prepared in the same fashion as platinum complex **1** using $[PtCl_2(PEt_3)_2]$ (0.100 g, 0.199 mmol) and carbon diselenide (2 cm^3 10% solution in dichloromethane, 0.265 mmol). The remaining solvent was removed under reduced pressure and the red residue was extracted three times with dichloromethane (3 × 20 cm^3) and the mixture was filtered through a celite pad. The product was obtained as a dark red crystalline solid by crystallization from the resulting dichloromethane solution. Yield: 0.018 g, 15%.

$[Pt(PMe_2Ph)_2(CSe_3)Cr(CO)_5]$ (9). $[Cr(CO)_6]$ (0.021 g, 0.0971 mmol) was dissolved in tetrahydrofuran (30 cm^3) and the solution was irradiated with a 125 W UV lamp for 20 min. Complex **2** (0.070 g, 0.0971 mmol) was added as a solid in one portion. The resulting mixture was stirred for 24 h followed by evaporation of the solvent under reduced pressure. The dark red residue was dissolved in the minimum volume of dichloromethane (3 cm^3) and diethyl ether (50 cm^3) was added slowly to precipitate the product as a brick red powder. Yield: 0.068 g, 76%. ^1H NMR (CD_2Cl_2): δ 7.48–7.36 (m, 10 H, aromatic) and 1.59 (d, 12 H, $^3J(^{195}Pt–^1H)$ 36 Hz, $^2J(^{31}P–^1H)$ 12 Hz, PMe).

[Pt(PMe_2Ph)$_2$(CSe_3)Mo(CO)$_5$] (10). This was prepared in the same fashion as platinum complex **9** using [Mo(CO)$_6$] (0.022 g, 0.0833 mmol) and **2** (0.060 g, 0.0833 mmol) to give the product as a brown powder. Yield: 0.020 g, 25%. ^1H NMR (CD_2Cl_2): δ 7.47–7.36 (m, 10 H, aromatic) and 1.58 (d, 12 H, $^3J(^{195}Pt–^1H)$ 36 Hz, $^2J(^{31}P–^1H)$ 11 Hz, PMe).

[Pt(PMe_2Ph)$_2$(CSe_3)W(CO)$_5$] (11). This was prepared in the same fashion as platinum complex **9** using [W(CO)$_6$] (0.034 g, 0.0972 mmol) and **2** (0.070 g, 0.0972 mmol) to give the product as a brown powder. Yield: 0.043 g, 42%. ^1H NMR (CD_2Cl_2): δ 7.54–7.30 (m, 10 H, aromatic) and 1.57 (d, 12 H, $^3J(^{195}Pt–^1H)$ 36 Hz, $^2J(^{31}P–^1H)$ 12 Hz, PMe).

[{Rh(CSe_3)(η^5-C_5Me_5)}$_2$] (12). This was prepared in the same fashion as platinum complex **1** using [{RhCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (0.080g, 0.129 mmol) and carbon diselenide (4 cm^3 10% solution in dichloromethane, 0.530 mmol) to give the product as a brick red powder. Yield: 0.106 g, 84%. ^1H NMR (CD_2Cl_2): δ 1.85–1.73 (m, 30 H, η^5-C_5Me_5). Selected IR data (KBr, cm^{-1}): 851 *ν*(C=Se), 281w *ν*(Rh–Se).

[{Ir(CSe_3)(η^5-C_5Me_5)}$_2$] (13). This was prepared in the same fashion as platinum complex **1** using [{IrCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (0.080g, 0.104 mmol) and carbon diselenide (4 cm^3 10% solution in dichloromethane, 0.530 mmol) to give the product as a brown powder. Yield: 0.065 g, 54%. ^1H NMR (CD_2Cl_2): δ 1.94–1.64 (m, 30 H, η^5-C_5Me_5). Selected IR data (KBr, cm^{-1}): 857s *ν*(C=Se), 279w, 246w *ν*(Ir–Se).

[{Ru(CSe_3)(η^6-*p*-$MeC_6H_4{}^iPr$)}$_2$] (14). This was prepared in the same fashion as platinum complex **1** using [{RuCl(μ-Cl)(η^6-*p*-$MeC_6H_4{}^iPr$)}$_2$] (0.140g, 0.229 mmol) and carbon diselenide (6 cm^3 10% solution in dichloromethane, 0.795 mmol) to give the product as a brown powder. Yield: 0.096 g, 43%. ^1H NMR (CD_2Cl_2): δ 5.61 and 5.47 (AB system, $^3J(^1H–^1H)$ 6 Hz, 4 H, aromatic) 2.84 (sept, 1 H, $CHMe_2$) 2.28 (s, 3 H, CH_3) and 1.19 (d, $(CH_3)_2CH$, 6 H). Selected IR data (KBr, cm^{-1}): 849s *ν*(C=Se), 274w, 247w *ν*(Ru–Se).

[{Os(CSe_3)(η^6-*p*-$MeC_6H_4{}^iPr$)}$_2$] (15). This was prepared in the same fashion as platinum complex **1** using [{OsCl(μ-Cl)(η^6-*p*-$MeC_6H_4{}^iPr$)}$_2$] (0.080 g, 0.101 mmol) and carbon diselenide (4 cm^3 10% solution in dichloromethane, 0.530 mmol) to give the product as a dark brown powder. Yield: 0.034 g, 29%. ^1H NMR (CD_2Cl_2): δ 6.01 and 5.86 (AB system, $^3J(^1H–^1H)$ 6 Hz, 4 H, aromatic) 2.83 (sept, 1 H, $CHMe_2$) 2.40 (s, 3 H, CH_3) and 1.30 (d, $(CH_3)_2CH$, 6 H). Selected IR data (KBr, cm^{-1}): 851s *ν*(C=Se), 277w, 245w *ν*(Os–Se).

X-Ray crystallography

Table 4 lists details of data collections and refinements for **2** and **8**. Data were collected at 125 K using a Bruker SMART diffractometer with graphite monochromated Mo radiation. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[13]

CCDC reference numbers 220004, 224471 and 253757.

See http://www.rsc.org/suppdata/dt/b4/b416356g/ for crystallographic data in CIFor other electronic format.

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