

Synthesis and Characterisation of the First Cyanodiselenoimidocarbonate $[\text{C}_2\text{N}_2\text{Se}_2]^{2-}$ Complexes

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$[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}, \text{PPh}_3$) and $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{PP})]$ ($\text{PP} = \text{dppe}, \text{dppm}, \text{dppf}$) were obtained by the reaction of the appropriate metal halide containing complex with potassium cyanodiselenoimidocarbonate. The dimeric cyanodiselenoimidocarbonate complexes $[\text{M}(\{\text{C}_2\text{N}_2\text{Se}_2(\eta^5\text{-C}_5\text{Me}_5)\}_2)]$ ($\text{M} = \text{Rh}, \text{Ir}$) were synthesised from the appropriate transition metal dimer starting material. The cy-

anodiselenoimidocarbonate ligand is *Se,Se*-bidentate in the monomeric complexes – the terminal CN group is approximately coplanar with the CSe_2 group, and the nitrogen atom is trigonal therefore reducing the planar symmetry of the ligands.

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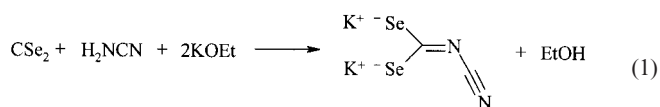
Introduction

The coordination of chalcogen donor ligands is an important area.^[1–12] Sulfur-based ligands, especially *S,S*-bidentate ligands, have a variety of industrial applications.^[9–12] Relative to the significant interest in sulfur donor ligands, the selenium analogues are a rather understudied area. Metal selenides and metal polyselenides are well known and are readily prepared by direct reaction of the elements. There has been significant interest in ZnSe and CdSe semiconductors in photovoltaic devices because of their intermediate energy bandgap.^[13] Hence organometallic compounds such as cadmium and zinc diselenocarbamate complexes^[14] and selenoimidophosphonates^[13] have been investigated as single-source precursors for deposition of these semiconductor materials. Other well-established selenium donor ligands include the selenoethers^[15–18] and the pseudohalide selenocyanate.^[19,20] However, there are very few *Se,Se*-bidentate ligands reported in the literature, which include a series of (diselenothiocarbonato)bis(phosphane)platinum compounds,^[21] two triselenocarbonate complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CSe}_3)(\text{PMe}_3)]$ ^[22] and $[\text{Ba}(\text{CSe}_3)]$,^[23] a (2,4-dioxo-3,3-pentanediselenolato)bis(phosphane)platinum complex,^[24] two diselenocarbonimidato compounds,^[25,26] $[\{\text{CH}[\text{Si}(\text{CH}_3)_3]_2\}_2\text{Sn}(\text{SeSe})\text{PC}_6\text{H}_5[\text{C}(\text{CH}_3)_3]_3]$ ^[27] and a series of $[\text{Pt}\{\text{Se}_2\text{P}(\text{Se})(\text{C}_6\text{H}_5)\}(\text{PR}_3)_2]$ complexes.^[28] As part of our program studying the properties of chalcogen donor systems we have recently reported a series of cyanodithioimidocarbonate complexes.^[29] Here we describe the synthesis of the corresponding cyanodiselenoimidocarbonate

complexes. Selected examples have been chosen for crystallographic study.

Results and Discussion

The synthesis of dipotassium cyanodiselenoimidocarbonate was reported by Jensen and Henriksen in 1970.^[30] The original synthesis involved the dropwise addition of potassium hydroxide in water to cyanamide and carbon diselenide in dioxane at 0 °C. Our synthesis is essentially the same [Equation (1)], except the reaction was carried out in ethanol and potassium ethoxide was used in place of potassium hydroxide to prevent the generation of water during the reaction.

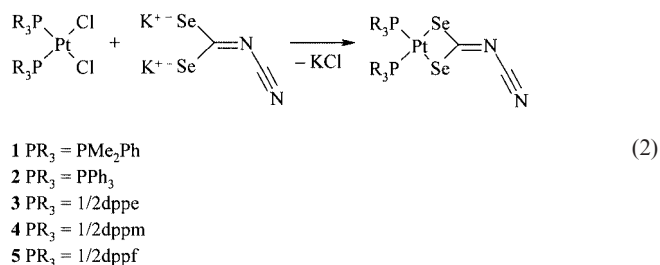


After suction filtration under nitrogen, the product was obtained as an impure off-yellow solid. In the IR spectrum, a strong $\nu(\text{C}\equiv\text{N})$ band at 2127 cm^{-1} and a strong band at 1347 cm^{-1} assigned as $\nu(\text{C}=\text{N})$ are observed. Purification proved unsuccessful, hence the dipotassium cyanodiselenoimidocarbonate was used as obtained for subsequent reaction.

The bis(phosphane)platinum complexes $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}, \text{PPh}_3$) and $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{PP})]$ ($\text{PP} = \text{dppe}, \text{dppm}, \text{dppf}$) were obtained by reaction of the appropriate $[\text{PtCl}_2(\text{PR}_3)_2]$ or $[\text{PtCl}_2(\text{PP})]$ complex with excess potassium cyanodiselenoimidocarbonate in tetrahydrofuran. A large excess of the dipotassium salt was used as

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this gave a cleaner reaction. The solvent was evaporated under reduced pressure, and dichloromethane was added. The mixture was filtered through a Celite pad to remove precipitated KCl and any residual dipotassium cyanodiselenoimidocarbonate, and the filtrate was then concentrated to dryness to give the product [Equation (2)].



The microanalyses of all compounds were satisfactory, and all compounds showed the anticipated $[\text{M}^+]$ peak in their mass spectra (Table 1). The $\nu(\text{C}\equiv\text{N})$ vibrations are observed in the range $2174\text{--}2179\text{ cm}^{-1}$, and the $\nu(\text{C}=\text{N})$ vibrations can be seen in the region of $1492\text{--}1495\text{ cm}^{-1}$ (Table 2); these values are comparable with the corresponding (cyanodithioimidocarbonate)bis(phosphane)platinum complexes.^[29] The $\nu(\text{Pt}–\text{Se})$ bands all lie within the range $246\text{--}294\text{ cm}^{-1}$ (Table 2). The (cyanodiselenoimidocarbonate)bis(phosphane)platinum complexes **1–5** (Table 2) all show sharp singlets with platinum and selenium satellites in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, and have similar δ values to the sulfur analogues.^[29] The $^1J(^{195}\text{Pt}–^{31}\text{P})$ coupling constants lie in the range $2620\text{--}3263\text{ Hz}$, and the variations reflect the nature of the phosphane group. In all the complexes, *cis* and *trans* $^2J(^{31}\text{P}–^{77}\text{Se})$ couplings can be observed (Table 2). The values noted are of similar magnitude to those found in the literature for bis(phosphane)platinum complexes containing selenium donor ligands. Some com-

parable examples are $[\text{PtSe}_2\text{C}_2(\text{CO}_2\text{CH}_3)_2(\text{PPh}_3)_2]$ ^[31] [$^2J(^{31}\text{P}–^{77}\text{Se})$ 52 Hz], $[\text{Pt}\{\text{C}_6\text{H}_2(\text{CF}_3)_3\}\text{Se}_2(\text{PPh}_3)_2]$ ^[32] [$^2J(^{31}\text{P}–^{77}\text{Se})$ 47 Hz] and $[(\text{CO})_6\text{Fe}_2(\mu_3\text{Se})_2\text{Pt}(\text{PPh}_3)_2]$ ^[33] [$^2J(^{31}\text{P}–^{77}\text{Se})$ 24 Hz]. The X-ray crystal structures of both **1** (Table 3, Figure 1) and **3** (Table , Figure 2) were obtained. In both examples, the X-ray analysis shows that the platinum core lies at the centre of a distorted square-planar coordination sphere. The distortion from idealised square-planar geometry (90°) can be illustrated by the $\text{P}(1)–\text{Pt}(1)–\text{P}(2)$ bond angle of $94.46(9)^\circ$ in **1** and $86.64(8)^\circ$ in **3**. The corresponding $\text{Se}(1)–\text{Pt}(1)–\text{Se}(2)$ bite angles in **1** and **3** are $77.37(4)^\circ$ and $77.81(3)^\circ$, respectively. In the PtSe_2C ring for **1**, the $\text{Pt}–\text{Se}–\text{C}$ angles are $86.1(3)^\circ$ and $86.9(3)^\circ$. The $\text{Se}(1)–\text{C}(1)–\text{Se}(2)$ angle is $109.5(5)^\circ$. In compound **3**, the $\text{Pt}–\text{Se}–\text{C}$ angles are $86.1(2)^\circ$ and $85.9(2)^\circ$. The $\text{Se}(1)–\text{C}(1)–\text{Se}(2)$ angle is $110.2(4)^\circ$. The nonbonded selenium distance is $3.08\text{ \AA}$ and $3.09\text{ \AA}$ for **1** and **3**, respectively, and both these values correspond to about 81% of the van der Waals radii of selenium, which implies that there is a significant interaction between the two selenium atoms. As observed in the sulfur analogues, $\text{N}(1)$ is trigonal therefore reducing the planar symmetry of the ligand in both **1** and **3**. In **1**, the cyanodiselenoimidocarbonate ligand lies within the coordination plane with the exception of $\text{C}(1)–\text{N}(1)–\text{C}(2)–\text{N}(2)$, which is hinged at an angle of 9° to the plane. In **3**, the whole complex is almost planar, however, there is a small hinge angle of 2° with respect to the coordination plane.

The dimeric cyanodiselenoimidocarbonate complexes $[\text{M}\{(\text{C}_2\text{N}_2\text{Se}_2)(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ [$\text{M} = \text{Rh}$ (**6**), Ir (**7**)] were synthesised and isolated in a similar manner to the (cyanodiselenoimidocarbonate)bis(phosphane)platinum complexes **1–5** by reaction of excess dipotassium salt with the appropriate transition metal dimer starting material [Equation (3)]. Compounds **6** and **7** both gave satisfactory microanalyses and show the anticipated $[\text{M}^+]$ peak in their mass spectra (Table 1). The $\nu(\text{C}\equiv\text{N})$ vibrations are observed at

Table 1. Microanalytical (calculated values in parentheses) and mass spectrometric data for complexes **1–7**

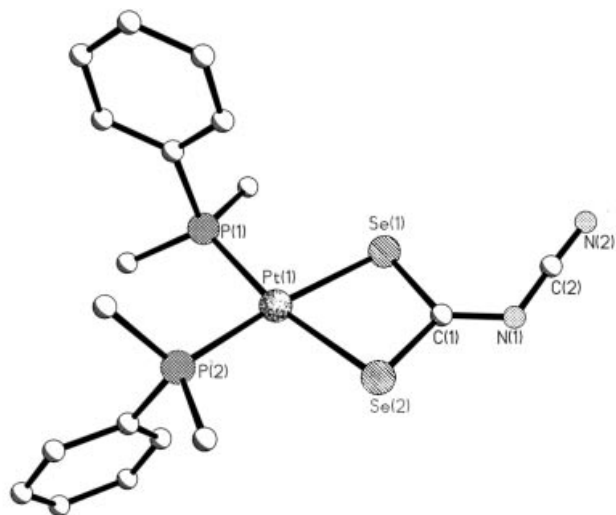
Complex	C	H	N	<i>m/z</i>
1 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{PMe}_2\text{Ph})_2]$	31.60 (31.73)	3.01 (3.25)	3.83 (4.11)	682
2 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{PPh}_3)_2]$	49.41 (49.10)	2.85 (3.25)	2.76 (3.01)	931
3 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{dppe})]$	41.88 (41.86)	2.79 (3.01)	3.29 (3.49)	804
4 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{dppm})]\cdot\text{CH}_2\text{Cl}_2$	38.89 (38.46)	2.68 (2.77)	3.13 (3.20)	791
5 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{dppf})]\cdot\text{CH}_2\text{Cl}_2$	42.83 (42.55)	2.64 (2.69)	2.37(2.68)	960
6 $[\{\text{Rh}(\text{C}_2\text{N}_2\text{Se}_2)(\eta^5\text{-C}_5\text{Me}_5)\}_2]$	32.44 (32.17)	3.77 (3.37)	5.76 (6.25)	898
7 $[\{\text{Ir}(\text{C}_2\text{N}_2\text{Se}_2)(\eta^5\text{-C}_5\text{Me}_5)\}_2]$	27.21 (26.82)	2.39 (2.81)	5.65 (5.21)	1077

Table 2. $^{31}\text{P}\{^1\text{H}\}$ NMR (109.4 MHz) and selected IR data for complexes **1–5**

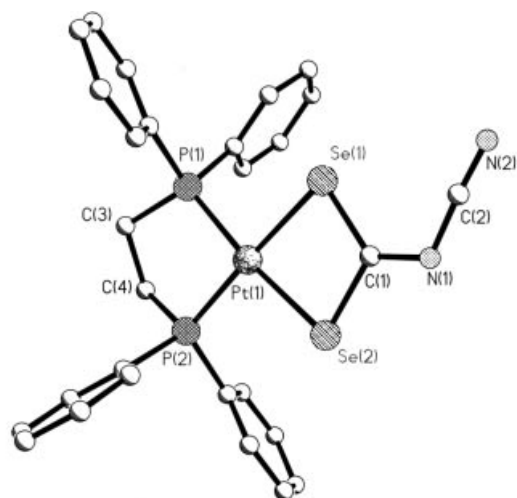
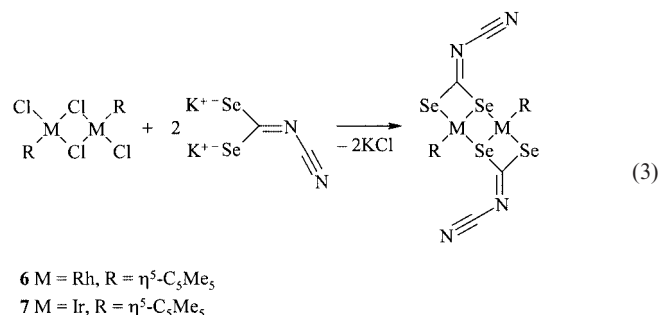
Complex	$\delta(\text{P})$ [ppm]	$^1J(^{195}\text{Pt}–^{31}\text{P})$ [Hz]	$^2J(^{77}\text{Se}–^{31}\text{P})$ [Hz]	$\nu(\text{C}\equiv\text{N})$ [cm^{-1}]	$\nu(\text{C}=\text{N})$ [cm^{-1}]	$\nu(\text{Pt}–\text{Se})$ [cm^{-1}]
1 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{PMe}_2\text{Ph})_2]$	−19.6	3063	42, 23	2179	1494	294, 254
2 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{PPh}_3)_2]$	17.3	3190	68, 42	2177	1497	282, 246
3 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{dppe})]$	44.8	3049	73, 49	2178	1492	280, 246
4 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{dppm})]$	−54.2	2620	40, 19	2175	1492	282, 258
5 $[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{dppf})]$	16.4	3263	47, 28	2174	1495	279, 252

Table 3. Selected bond lengths [Å] and angles [°] for compounds **1** and **3**

Compound	1	3
Pt(1)–P(1)	2.271(2)	2.245(2)
Pt(1)–P(2)	2.266(3)	2.236(2)
Pt(1)–Se(1)	2.4570(12)	2.4577(9)
Pt(1)–Se(2)	2.4725(11)	2.4617(9)
Se(1)–C(1)	1.916(9)	1.880(8)
Se(2)–C(1)	1.856(10)	1.886(7)
C(1)–N(1)	1.305(13)	1.333(9)
N(1)–C(2)	1.329(13)	1.350(10)
C(2)–N(2)	1.184(12)	1.167(10)
Se(1)–Pt(1)–Se(2)	77.37(4)	77.81(3)
P(1)–Pt(1)–P(2)	94.46(9)	86.64(8)
Se(1)–C(1)–N(1)	126.6(7)	127.9(6)
Se(2)–C(1)–N(1)	123.9(7)	121.8(6)
Pt(1)–Se(1)–C(1)	86.1(3)	86.1(2)
Pt(1)–Se(2)–C(1)	86.9(3)	85.9(2)
P(1)–Pt(1)–Se(1)	92.96(7)	95.71(6)
P(2)–Pt(1)–Se(2)	95.11(7)	99.83(6)
C(1)–N(1)–C(2)	119.1(8)	115.0(6)
N(1)–C(2)–N(2)	175.9(12)	175.8(9)

Figure 1. Crystal structure of **1**

approximately 2180 cm^{-1} , and the $\nu(\text{C}=\text{N})$ vibrations can be seen in the region of $1459\text{--}1492\text{ cm}^{-1}$. The bands for $\nu(\text{M}=\text{Se})$ are all observed in the range $240\text{--}282\text{ cm}^{-1}$.

Figure 2. Crystal structure of **3**

Experimental Section

General: Unless otherwise stated, operations were carried out under oxygen-free nitrogen by using standard Schlenk techniques. All solvents and reagents were purchased from Aldrich, Alfa Aesar, BDH, Fisons and Strem and used as received. We are grateful to Johnson Matthey PLC for the loan of the precious metal salts. Diethyl ether and tetrahydrofuran were purified by reflux in the presence of sodium/benzophenone and by distillation under nitrogen. Hexane was purified by reflux in the presence of sodium and by distillation under nitrogen. Dichloromethane was heated to reflux in the presence of powdered calcium hydride and distilled under nitrogen. CD_2Cl_2 (99.6+ atom D) was used as received. Carbon diselenide was prepared as a dichloromethane solution by passing dichloromethane over elemental selenium at $600\text{ }^\circ\text{C}$.^[34,35] The metal complexes $[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]^{[36]}$ and $[\{\text{IrCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]^{[36]}$ were prepared according to literature procedures. The complexes $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$, $[\text{PtCl}_2(\text{PPh}_3)_2]$, $[\text{PtCl}_2(\text{dppe})]$ [dppe = bis(diphenylphosphanyl)ethane], $[\text{PtCl}_2(\text{dppm})]$ and $[\text{PtCl}_2(\text{dppf})]$ [dppf = bis(diphenylphosphanyl)ferrocene] were prepared by the addition of stoichiometric quantities of the appropriate free phosphane or diphosphane to a dichloromethane solution of $[\text{PtCl}_2(\text{cod})]$ (cod = cycloocta-1,5-diene). Infrared spectra were recorded (IR spectra as KBr discs, unless otherwise stated) with a Perkin–Elmer System 2000 FT/IR/Raman spectrometer. ^{31}P , ^{13}C and ^1H NMR spectra were recorded with a JEOL DELTA GSX 270 FT NMR spectrometer. Microanalysis was performed by the University of St. Andrews service. Fast atom bombardment (FAB) and electron ionisation (EI) mass spectra were performed by the EPSRC National Mass Spectrometer service.

$[\text{Pt}(\text{C}_2\text{N}_2\text{Se}_2)(\text{PMe}_2\text{Ph})_2]$ (1**):** $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$ (0.050 g, 0.0769 mmol) was dissolved in THF (20 mL), and potassium cyanodiselenoimidocarbonate (0.167 g, 0.580 mmol) was added as a solid in one portion. The resulting orange solution was stirred in the absence of light for 48 h. The solvent was evaporated in vacuo, and the remaining solid was extracted with dichloromethane (20 mL). The mixture was filtered through a Celite pad to remove precipitated KCl and washed with additional dichloromethane (30 mL). The filtrate was concentrated to dryness in vacuo to give a pale orange powder. The following compounds **2–7** were prepared and worked up in the same manner as platinum complex **1**. The product was recrystallised by vapour diffusion from chloroform/hexane to give X-ray quality crystals. Yield 0.027 g (52%). ^1H NMR

Table 4. Details of the X-ray data collections and refinements for compounds **1** and **3**

Compound	1	3
Empirical formula	C ₁₈ H ₂₂ N ₂ P ₂ PtSe ₂	C ₂₈ H ₂₄ N ₂ P ₂ PtSe ₂
Crystal dimensions [mm]	0.1 × 0.03 × 0.03	0.13 × 0.05 × 0.05
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /n
<i>a</i> [Å]	33.596(8)	12.1941(18)
<i>b</i> [Å]	11.542(3)	18.081(3)
<i>c</i> [Å]	10.974(3)	12.6978(19)
β [°]	91.536(5)	105.898(3)
<i>V</i> [Å ³]	4253.5(19)	2692.6(7)
<i>Z</i>	8	4
<i>M</i>	681.33	803.44
<i>D_c</i> [g·cm ⁻³]	2.128	1.982
μ [mm ⁻¹]	10.175	8.054
Measured reflections	13027	11392
Independent reflections (<i>R</i> _{int})	3804 (0.0937)	3816 (0.0613)
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0426, 0.0687	0.0314, 0.0533

(CD₂Cl₂): δ = 1.63 [d, ³*J*(¹⁹⁵Pt–¹H) = 36 Hz, ²*J*(³¹P–¹H) = 10 Hz, 12 H, PMe], 7.48–7.69 (m, 10 H, aromatic H) ppm.

[Pt(C₂N₂Se₂)(PPh₃)₂] (**2**): [PtCl₂(PPh₃)₂] (0.050 g, 0.0632 mmol) and potassium cyanodiselenoimidocarbonate (0.208 g, 0.722 mmol) gave the product as a beige powder. Yield 0.029 g (49%). ¹H NMR (CD₂Cl₂): δ = 7.24–7.52 (m, 30 H, aromatic H).

[Pt(C₂N₂Se₂)(dppe)] (**3**): [PtCl₂(dppe)] (0.060 g, 0.0903 mmol) and potassium cyanodiselenoimidocarbonate (0.227 g, 0.788 mmol) gave the product as an orange powder. The product was recrystallised by vapour diffusion from chloroform/hexane to give X-ray quality crystals. Yield 0.049 g (67%). ¹H NMR (CD₂Cl₂): δ = 2.40–2.59 (m, 4 H, PCH₂CH₂P), 7.48–7.69 (m, 20 H, aromatic H) ppm.

[Pt(C₂N₂Se₂)(dppm)] (**4**): [PtCl₂(dppm)] (0.060 g, 0.0923 mmol) and potassium cyanodiselenoimidocarbonate (0.211 g, 0.732 mmol) gave the product as a yellow powder. Yield 0.022 g (30%). ¹H NMR (CD₂Cl₂): δ = 3.89–4.18 (m, 2 H, PCH₂P), 7.25–7.71 (m, 20 H, aromatic H) ppm.

[Pt(C₂N₂Se₂)(dppf)] (**5**): [PtCl₂(dppf)] (0.080 g, 0.0975 mmol) and potassium cyanodiselenoimidocarbonate (0.085 g, 0.295 mmol) gave the product as a yellow powder. Yield 0.044 g (45%). ¹H NMR (CD₂Cl₂): δ = 4.36 [br. m, 4 H, β-CH (C₅H₄)], 4.44 [br. m, 4 H, α-CH (C₅H₄)], 7.36–7.88 (m, 20 H, aromatic) ppm.

[{Rh(C₂N₂Se₂)(η⁵-C₅Me₅)₂}] (**6**): [{RhCl(μ-Cl)(η⁵-C₅Me₅)₂}] (0.060 g, 0.0971 mmol) and potassium cyanodiselenoimidocarbonate (0.359 g, 1.246 mmol) gave a very dark red powder. Yield 0.037 g (42%). ¹H NMR (CD₂Cl₂): δ = 1.54–1.89 (m, 30 H, η⁵-C₅Me₅) ppm. Selected IR data (KBr): $\tilde{\nu}$ = 2162 [s, ν(C≡N)], 1492 [br., s, ν(C=N)], 279 (w), 259 [w, ν(Rh–S)] cm⁻¹.

[{Ir(C₂N₂Se₂)(η⁵-C₅Me₅)₂}] (**7**): [{IrCl(μ-Cl)(η⁵-C₅Me₅)₂}] (0.040 g, 0.0502 mmol) and potassium cyanodiselenoimidocarbonate (0.268 g, 0.9308 mmol) gave an orange powder. Yield 0.021 g (39%). ¹H NMR (CD₂Cl₂): δ = 1.57–1.86 (m, 30 H, η⁵-C₅Me₅) ppm. Selected IR data (KBr): $\tilde{\nu}$ = 2192 [s, ν(C≡N)], 1459 [br., s, ν(C=N)], 282 (w), 240 [w, ν(Ir–S)] cm⁻¹.

X-ray Crystallography: Tables 3 and 4 list details of data collections and refinements. For **1** and **3**, data were collected at 125 K with a Bruker SMART system. 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.^[37] CCDC-233740 and -233741 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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