

Selenosalicylate; a little-studied heavy-element analogue of the versatile thiosalicylate ligand

Simeon Atiga,^{1,2,*} Graham C. Saunders¹ and William Henderson¹

¹ *Chemistry, School of Science, University of Waikato, Private Bag 3105, Hamilton, New Zealand 3240*

² *Department of Chemistry, Faculty of Natural Sciences, Kogi State University, PMB 1008, Anyigba, Kogi State, Nigeria*

Electronic Supplementary Information

Contents

Crystallographic parameters and data	3
Table S1 Crystallographic data and structure refinement parameters of 4a , 4h' , 4k and 4l[†]	4
Table S2 ESI MS data of selenosalicylic acid 2 and selenosalicylate complexes 4a - 4n	5
Table S3 Selected infrared data (cm ⁻¹) of selenosalicylic acid 2 and selenosalicylate complexes.....	8
Table S4 Selected bond lengths (Å) and angles (°) of [<i>p</i> -cym)Ru(SeC ₆ H ₄ CO ₂) ₂] 4h'	8
Table S5 Selected bond lengths (Å) and angles (°) of [Cp*Rh(SeC ₆ H ₄ CO ₂) ₂] 4l	9
Table S6 Selected bond lengths (Å) and angles (°) of [Cp*Ir(SeC ₆ H ₄ CO ₂)(PPh ₃)] 4k	9
Figure S1 Positive-ion ESI mass spectrum of [Ni(SeC ₆ H ₄ CO ₂)(dppe)] 4f at a capillary exit voltage of 180 V, showing the absence of selenium loss. Insets (a) and (b) are the experimental and calculated isotope patterns of the [M + Na] ⁺ ion.....	10
Figure S2 Positive-ion ESI mass spectrum of [Cp*Rh(SeC ₆ H ₄ CO ₂)(PPh ₃)] 4j at a CEV of 60 V showing the [M + H] ⁺ and [nM + Na] ⁺ (n = 1 - 3) ions along with their fragments. Insets (a) and (b) are the experimental and calculated isotope patterns of the [2M + H] ⁺ ion, G	11
Figure S3 ¹ H NMR spectrum of selenosalicylic acid 2 in (CD ₃) ₂ SO.....	12
Figure S4 ¹³ C{ ¹ H} NMR spectrum of selenosalicylic acid 2 in (CD ₃) ₂ SO.....	12
Figure S5 ³¹ P{ ¹ H} NMR spectrum of [Ni(SeC ₆ H ₄ CO ₂)(dppe)] 4f in CDCl ₃ ; the expansion in the centre is of the doublet centred around δ 57.4.....	13
Scheme S1 Synthesis of the dinuclear complex [Pd(bipy)] ₂ (Cl)(SeC ₆ H ₄ CO ₂)Cl 4g	13
Scheme S2 Synthesis of mononuclear ruthenium, rhodium and iridium selenosalicylate complexes...14	14
Scheme S3 Reaction scheme for the synthesis of the dinuclear complex 4l	14
Scheme S4 Reaction scheme for the synthesis of the gold(III) selenosalicylate complex 4m	15

Scheme S5 Reaction scheme for the synthesis of the gold(I) selenosalicylate complex 4n , and the proposed structure of the triply-aurated complex 4n'	15
--	----

Crystallographic parameters and data

The crystallographic and refinement parameters are presented in Table S1. Molecular structure diagrams were generated using ORTEP-3ⁱ and Mercury.ⁱⁱ CCDC 2211290 – 2211293 contains the supplementary crystallographic data for these paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S1 Crystallographic data and structure refinement parameters of **4a**, **4h'**, **4k** and **4l**[†]

Complex	4a	4h'	4l	4k
Formula	C ₄₃ H ₃₄ O ₂ P ₂ PtSe	C ₃₄ H ₃₆ O ₄ Ru ₂ Se ₂	C ₃₄ H ₃₈ O ₄ Rh ₂ Se ₂	C ₇₀ H ₆₈ Ir ₂ O ₄ P ₂ Se ₂ .H ₂ O
Molecular weight	918.733	868.711	874.408	788.820
T (K)	140.00(10)	100.0(2)	140.00(10)	99.9(5)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /n	P-1
<i>a</i> , Å	11.47661(14)	9.5935(3)	11.24520(15)	8.6583(3)
<i>b</i> , Å	17.9492(2)	12.8922(3)	10.02131(11)	18.2265(6)
<i>c</i> , Å	17.0666(3)	12.4357(5)	14.11953(18)	19.3876(6)
α , °	90	90	90	86.012(3)
β , °	94.6401(10)	106.070(3)	99.2080(13)	86.316(2)
γ , °	90	90	90	82.180(3)
<i>V</i> , Å ³	3515.09(8)	1477.97(8)	1570.65(4)	3019.12(16)
<i>Z</i>	4	2	2	2
D _{calc} (g cm ⁻³)	1.737	1.952	1.849	1.755
Crystal size (mm ³)	0.183 × 0.125 × 0.102	0.123 × 0.092 × 0.07	0.144 × 0.071 × 0.023	0.26 × 0.113 × 0.027
μ (mm ⁻¹)	9.809	11.408	11.446	10.693
θ range (°)	3.57 - 73.98	4.8 to 73.97	4.68 to 74.01	3.46 to 73.98
Total reflections	20367	8600	15243	33217
Unique reflections (R _{int})	6971(0.0269)	2912 (0.0232)	3131 (0.0449)	11878 (0.0349)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	6228	2683	2842	10977
Parameters	468	193	195	774
Final indices [<i>I</i> > 2 σ (<i>I</i>)]	R ₁ = 0.0237 wR ₂ = 0.0548	R ₁ = 0.0245 wR ₂ = 0.0611	R ₁ = 0.0235 wR ₂ = 0.0510	R ₁ = 0.0323, wR ₂ = 0.0685
R indices (all data)	R ₁ = 0.0291 wR ₂ = 0.0574	R ₁ = 0.0279 wR ₂ = 0.0637	R ₁ = 0.0305 wR ₂ = 0.0532	R ₁ = 0.0369, wR ₂ = 0.0710
Weighting scheme A, B [‡]	0.025, 2.380	0.030, 3.440	0.022, 1.020	0.000, 22.900
Max., min. $\Delta\rho$ (e Å ⁻³)	1.02, -0.78	1.17, -0.91	0.71, -1.05	1.30, -1.28
T _{max, min}	1.000, 0.688	0.959, 0.790	1.000, 0.724	1.000, 0.502
Goodness of fit	1.046	1.039	1.034	1.051

[†]estimated standard deviations are in parentheses. [‡]w = 1/[$\sigma^2(F_o)^2 + \{A(F_o^2 + 2F_c^2)/3\}^2 + B(F_o^2 + 2F_c^2)/3$]

Table S2 ESI MS data of selenosalicylic acid **2** and selenosalicylate complexes **4a - 4n**

Compound	Capillary Exit Voltage (CEV), V	<i>m/z</i> (%), ions
HSeC ₆ H ₄ CO ₂ H 2	90	200.95 (100) [M – H] ⁻ , 156.96 (4) [M – H – CO ₂] ⁻ , 400.87 (10) [(SeC ₆ H ₄ CO ₂ H) ₂ – H] ⁻
	120	200.95 (100) [M – H] ⁻ , 156.96 (15) [M – H – CO ₂] ⁻ , 400.87 (1) [(SeC ₆ H ₄ CO ₂ H) ₂ – H] ⁻
	150	156.96 (100) [M – H – CO ₂] ⁻ , 200.95 (96) [M – H] ⁻ , 400.87 (2) [(SeC ₆ H ₄ CO ₂ H) ₂ – H] ⁻
[Pt(SeC ₆ H ₄ CO ₂)(PPh ₃) ₂] 4a	60	919.86 (3) [M + H] ⁺ , 941.76 (100) [M + Na] ⁺ , 1860.51 (96) [2M + Na] ⁺ , 2778.24 (3) [3M + Na] ⁺ , 1598.51 (8) [2M + Na – PPh ₃] ⁺ , 2516.24 (2) [3M + Na – PPh ₃] ⁺
	240	1860.51 (100) [2M + Na] ⁺ , 1598.51 (63) [2M + Na – PPh ₃] ⁺ , 941.76 (24) [M + Na] ⁺ , 2778.24 (2) [3M + Na] ⁺ , 2516.24 (11) [3M + Na – PPh ₃] ⁺ , 1518.76 (11) [2M + Na – PPh ₃ – Se] ⁺ , 717.95 (10) [Pt(C ₆ H ₄ {PPh ₂ })(PPh ₃)] ⁺ , 679.76 (12) [M + Na – PPh ₃] ⁺ , 636.83 (12) [M + Na – PPh ₃ – CO ₂] ⁺ , 556.80 (4) ([M + Na – PPh ₃ – CO ₂ – Se] ⁺
[Pd(SeC ₆ H ₄ CO ₂)(PPh ₃) ₂] 4b	90	831.09 (38) [M + H] ⁺ , 853.07 (100) [M + Na] ⁺ , 1683.06 (10) [2M + Na] ⁺ , 2513.63 (8) [3M + Na] ⁺ , 1420.99 (36) [2M + Na – PPh ₃] ⁺ , 2250.93 (3) [3M + Na – PPh ₃] ⁺ , 1987.89 (6) [3M + Na – 2PPh ₃] ⁺ , 1136.52 (2) [2M – 2PPh ₃] ⁺
	150	831.09 (21) [M + H] ⁺ , 853.07 (76) [M + Na] ⁺ , 1683.06 (8) [2M + Na] ⁺ , 1420.99 (77) [2M + Na – PPh ₃] ⁺ , 1399.98 (2) [2M + H – PPh ₃] ⁺ , 1341.07 (4) [2M + Na – PPh ₃ – Se] ⁺ , 1319.07 (2) [2M + H – PPh ₃ – Se] ⁺ , 2250.93 (5) [3M + Na – PPh ₃] ⁺ , 1987.89 (8) [3M + Na – 2PPh ₃] ⁺ , 1725.80 (4) [3M + Na – 3PPh ₃] ⁺ , 1908.48 (3) [3M + Na – 2PPh ₃ – Se] ⁺ , 1158.89 (4) [2M + Na – 2PPh ₃] ⁺ , 568.99 (32) [M + H – PPh ₃] ⁺ , 590.97 (100) [M + Na – PPh ₃] ⁺ , 511.05 (4) [M + Na – PPh ₃ – Se] ⁺ , 546.98 (10) [M + Na – PPh ₃ – CO ₂] ⁺ , 896.82 (10) [2M + Na – 3PPh ₃] ⁺
[Pd(SeC ₆ H ₄ CO ₂)(dppe)] 4c	60	726.79 (100) [M + Na] ⁺ , 1430.60 (32) [2M + Na] ⁺ , 2134.38 (2) [3M + Na] ⁺ , 1244.71 (13) [{PdCl(SeC ₆ H ₄ CO ₂)(dppe)} ₂] ⁺

	180	726.79 (100) [M + Na] ⁺ , 1430.60 (44) [2M + Na] ⁺ , 2134.38 (2) [3M + Na] ⁺ , 682.81 (60) [M + Na – CO ₂] ⁺ , 1244.71 (9) [{Pd(dppe)} ₂ (Cl)(SeC ₆ H ₄ CO ₂)] ⁺
[Pd(SeC ₆ H ₄ CO ₂)(phen)] 4d	90	508.62 (51) [M + Na] ⁺ , 994.34 (86) [2M + Na] ⁺ , 1480.08 (100) [3M + Na] ⁺ , 1966.78 (11) [4M + Na] ⁺ , 2451.55 (2) [5M + Na] ⁺ , 1401.19 (13) [3M + Na – Se] ⁺ , 914.46 (10) [2M + Na – Se] ⁺ , 814.34 (10) [2M + Na – phen] ⁺
	210	814.34 (100) [2M + Na – phen] ⁺ , 508.62 (32) [M + Na] ⁺ , 994.34 (40) [2M + Na] ⁺ , 1480.08 (21) [3M + Na] ⁺ , 1966.78 (3) [4M + Na] ⁺ , 464.64 (23) [M + Na – CO ₂] ⁺ , 428.73 (27) [M + Na – Se] ⁺ , 1401.19 (2) [3M + Na – Se] ⁺ , 914.46 (8) [2M + Na – Se] ⁺ , 770.37 (26) [2M + Na – phen – CO ₂] ⁺
[Pd(SeC ₆ H ₄ CO ₂)(dppf)] 4e	60	860.56 (9) [M + H] ⁺ , 882.53 (100) [M + Na] ⁺ , 1742.18 (52) [2M + Na] ⁺ , 2602.88 (2) [3M + Na] ⁺
	210	860.56 (4) [M + H] ⁺ , 882.53 (100) [M + Na] ⁺ , 1742.18 (44) [2M + Na] ⁺ , 838.53 (28) [M + Na – CO ₂] ⁺
[Ni(SeC ₆ H ₄ CO ₂)(dppe)] 4f	90	656.86 (8) [M + H] ⁺ , 678.90 (100) [M + Na] ⁺ , 1334.68 (45) [2M + Na] ⁺ , 1990.51 (3) [3M + Na] ⁺
	180	656.86 (13) [M + H] ⁺ , 678.90 (100) [M + Na] ⁺ , 1334.68 (60) [2M + Na] ⁺ , 1990.51 (2) [3M + Na] ⁺ , 634.85 (39) [M + Na – CO ₂] ⁺
[{Pd(bipy)} ₂ (Cl)(SeC ₆ H ₄ CO ₂)]Cl	90	760.68 (100) [M] ⁺
4g	150	760.68 (100) [M] ⁺ , 716.70 (12) [M – CO ₂] ⁺
[(<i>p</i> -cym)Ru(SeC ₆ H ₄ CO ₂)(PPh ₃)]	90	720.66 (100) [M + Na] ⁺ , 1416.43 (40) [2M + Na] ⁺ , 2114.19 (2) [3M + Na] ⁺ , 1587.22 (12) [3M + Na – 2PPh ₃] ⁺ , 1154.42 (4) [2M + Na – PPh ₃] ⁺ , 892.45 (6) [2M + Na – 2PPh ₃] ⁺ , 458.67 (14) [M + Na – PPh ₃] ⁺
4h	120	720.66 (100) [M + Na] ⁺ , 1416.43 (54) [2M + Na] ⁺ , 2114.19 (4) [3M + Na] ⁺ , 1587.22 (19) [3M + Na – 2PPh ₃] ⁺ , 1154.42 (17) [2M + Na – PPh ₃] ⁺ , 892.45 (23) [2M + Na – 2PPh ₃] ⁺ , 458.67 (82) [M + Na – PPh ₃] ⁺
[(C ₆ Me ₆)Ru(SeC ₆ H ₄ CO ₂)(PPh ₃)]	60	748.90 (11) [M + Na] ⁺ , 486.85 (6) [M + Na – PPh ₃] ⁺ , 948.74 (100) [2M + Na – 2PPh ₃] ⁺ , 1410.60 (3) [3M + Na – 3PPh ₃] ⁺ , 1872.46 (31) [4M + Na – 4PPh ₃] ⁺
4i		486.85 (66) [M + Na – PPh ₃] ⁺ , 948.74 (100) [2M + Na – 2PPh ₃] ⁺ , 1410.60 (3) [3M + Na – 3PPh ₃] ⁺ , 1872.46 (24)

	210	$[4M + Na - 4PPh_3]^+$, 442.87 (19) $[M + Na - PPh_3 - CO_2]^+$
$[Cp^*Rh(SeC_6H_4CO_2)(PPh_3)]$ 4j	60	700.91 (24) $[M + H]^+$, 722.90 (81) $[M + Na]^+$, 1400.82 (13) $[2M + H]^+$, 1422.81 (100) $[2M + Na]^+$, 2120.70 (18) $[3M + Na]^+$, 1858.66 (4) $[3M + Na - PPh_3]^+$, 1596.63 (15) $[3M + Na - 2PPh_3]^+$, 1081.24 (13) $[2M + Na - PPh_3 - Se]^+$, 1000.92 (9) $[2M + Na - PPh_3 - 2Se]^+$, 898.73 (8) $[2M + Na - 2PPh_3]^+$
	150	1400.82 (2) $[2M + H]^+$, 1422.81 (48) $[M + Na]^+$, 2120.70 (6) $[3M + Na]^+$, 1858.66 (2) $[3M + Na - PPh_3]^+$, 1596.63 (6) $[3M + Na - 2PPh_3]^+$, 1081.24 (1) $[2M + Na - PPh_3 - Se]^+$, 1000.92 (3) $[2M + Na - PPh_3 - 2Se]^+$, 898.73 (51) $[2M + Na - 2PPh_3]^+$, 460.86 (100) $[M + Na - PPh_3]^+$, 416.89 (16) $[M + Na - PPh_3 - CO_2]^+$, 1160.78 (33) $[2M + Na - PPh_3]^+$
$[Cp^*Ir(SeC_6H_4CO_2)(PPh_3)]$ 4k	60	791.19 (5) $[M + H]^+$, 813 (92) $[M + Na]^+$; 1601.27 (100) $[2M + Na]^+$, 2389.32 (11) $[3M + Na]^+$
	210	813 (26) $[M + Na]^+$; 1601.27 (78) $[M + Na]^+$, 1339.18 (87) $[2M + Na - PPh_3]^+$, 1077.10 (100) $[2M + Na - 2PPh_3]^+$, 551.07 (86) $[M + Na - PPh_3]^+$, 529.09 (16) $[M + H - PPh_3]^+$, 507.08 (42) $[M + Na - PPh_3 - CO_2]^+$
$[\{ Cp^*Rh(SeC_6H_4CO_2) \}_2]$ 4l	60	876.56 (6) $[M + H]^+$, 898.70 (100) $[M + Na]^+$, 1772.40 (51) $[2M + Na]^+$, 1334.55 (4) $[2M + Na - Cp^*RhSeC_6H_4CO_2]^+$, 460.36 (5) $[M + Na - Cp^*RhSeC_6H_4CO_2]^+$
	210	876.72 (2) $[M + H]^+$, 854.72 (1) $[M + Na - CO_2]^+$, 898.70 (100) $[M + Na]^+$, 1772.40 (26) $[2M + Na]^+$, 1334.55 (2) $[2M + Na - Cp^*RhSeC_6H_4CO_2]^+$, 460.36 (61) $[M + Na - Cp^*RhSeC_6H_4CO_2]^+$, 438.86 (7) $[M + H - Cp^*RhSeC_6H_4CO_2]^+$, 416.85 (15) $[M + H - Cp^*RhSeC_6H_4CO_2 - CO_2]^+$
$[(bp)Au(SeC_6H_4CO_2)]$ 4m	90	587.86 (100) $[M + Na]^+$, 1152.72 (49) $[2M + Na]^+$, 1715.56 (34) $[3M + Na]^+$, 2280.37 (3) $[4M + Na]^+$
	210	543.88 (12) $[M + Na - CO_2]^+$, 587.86 (100) $[M + Na]^+$, 1152.72 (36) $[2M + Na]^+$, 1715.56 (2) $[3M + Na]^+$
$[(PPh_3Au)_2(SeC_6H_4CO_2)]$ 4n	90	1118.62 (100) $[M + H]^+$, 1140.59 (30) $[M + Na]^+$, 1577.85 (8) $[M + Au(PPh_3)]^+$

Table S3 Selected infrared data (cm⁻¹) of selenosalicylic acid **2** and selenosalicylate complexes

Compound	2	4a	4b	4c	4d	4e	4f	4g
C=O	1672	1621 1583	1614 1594	1592 1582	1629 1582	1613 1592	1598 1582	1599 1573
C–O	1264	1320	1330	1342	1383	1347	1335	1360
C–Se	738	743	742	745	752	744	744	765
Compound	4h	4i	4j	4k	4l	4m	4n	
C=O	1591	1614 1602	1583 1566	1612 1592	1634 1588	1595 1579	1636 1583	
C–O	1345	1336	1358	1336	1353	1349	1383	
C–Se	745	750	744	744	765	754	744	

Table S4 Selected bond lengths (Å) and angles (°) of [*(p-cym)Ru(SeC₆H₄CO₂)*]₂ **4h'**

Ru1 - O1	2.099(2)	Ru1 - Se1	2.5139(4)
Ru1 - Se1'	2.4862(4)	Se1 - C1	1.926
O1 - C7	1.286(4)	C7 - O2	1.226(4)
C1 - C2	1.392(5)	C2 - C3	1.397(5)
C3 - C4	1.389(5)	C4 - C5	1.382(6)
C5 - C6	1.376(5)	C6 - C1	1.400(4)
Ru1 - C8	2.222(3)	Ru1 - C9	2.201(3)
Ru1 - C10	2.222(3)	Ru1 - C11	2.152(3)
Ru1 - C12	2.161(3)	Ru1 - C13	2.252(3)
Se1' - Ru1 - Se1	81.77(10)	O1 - Ru1 - Se1'	76.48(6)
O1 - Ru1 - Se1	87.79(6)	Ru1' - Se1 - Ru1	98.23(10)
Ru1 - Se1 - C1	111.08(9)	Ru1 - O1 - C7	135.7(2)
Se1 - Ru1' - Se1'	81.77(10)	Ru1 - Se1' - Ru1'	98.23(10)
Se1 - Ru1' - O1'	76.48(6)	Se1' - Ru1' - O1'	87.78(6)
Ru1' - Se1 - C1	101.28(9)	Se1 - C1 - C2	123.4(2)
O1 - C7 - O2	122.4(3)	O1 - C7 - C2	119.4(3)
C1 - C2 - C7	124.5(3)	O2 - C7 - C2	118.0(3)
C2 - C3 - C4	121.2(3)	C1 - C2 - C3	118.4(3)
C4 - C5 - C6	120.4(3)	C3 - C4 - C5	119.4(3)
C6 - C1 - C2	120.3(3)	C5 - C6 - C1	120.2(3)

Table S5 Selected bond lengths (Å) and angles (°) of [$\{\text{Cp}^*\text{Rh}(\text{SeC}_6\text{H}_4\text{CO}_2)\}_2$] **4l**

Rh1 - O1	2.1000(18)	Rh1 - Se1'	2.4617(3)
Rh1 - Se1	2.5060(3)	Se1 - C1	1.923(3)
O1 - C7	1.283(3)	C7 - O2	1.231(3)
C1 - C2	1.406(4)	C2 - C3	1.395(4)
C3 - C4	1.385(5)	C4 - C5	1.388(5)
C5 - C6	1.383(4)	C6 - C1	1.393(4)
Rh1 - C8	2.183(2)	Rh1 - C9	2.157(3)
Rh1 - C10	2.151(3)	Rh1 - C11	2.164(3)
Rh1 - C12	2.176(3)	O1 - Rh1 - Se1'	75.76(5)
Se1' - Rh1 - Se1	84.88(10)	Rh1' - Se1 - Rh1	95.56(10)
O1 - Rh1 - Se1	88.71(5)	Rh1 - O1 - C7	134.89(18)
Rh1 - Se1 - C1	99.32(8)	Rh1 - Se1' - Rh1'	95.56(10)
Se1 - Rh1' - Se1'	84.88(10)	Rh1' - Se1 - C1	115.43(8)
Se1 - Rh1' - O1'	75.76(5)	Se1' - Rh1' - O1'	88.71(5)
O1 - C7 - C2	120.7(2)	Se1 - C1 - C2	125.4(2)
O1 - C7 - O2	122.0(3)	O2 - C7 - C2	117.3(2)
C1 - C2 - C7	125.2(2)	C1 - C2 - C3	117.9(3)
C2 - C3 - C4	121.8(3)	C3 - C4 - C5	120.0(3)
C4 - C5 - C6	119.0(3)	C5 - C6 - C1	121.5(3)
C6 - C1 - C2	119.8(3)		

Table S6 Selected bond lengths (Å) and angles (°) of [$\text{Cp}^*\text{Ir}(\text{SeC}_6\text{H}_4\text{CO}_2)(\text{PPh}_3)$] **4k**

Ir1 - O1	2.110(3)	Ir1 - Se1	2.4733(5)
Ir1 - P1	2.3058(11)	Se1 - C1	1.909(5)
O1 - C7	1.280(6)	C7 - O2	1.241(6)
C1 - C2	1.406(7)	C2 - C3	1.402(7)
C3 - C4	1.384(8)	C4 - C5	1.375(8)
C5 - C6	1.389(7)	C6 - C1	1.401(7)
Ir1 - C8	2.244(5)	Ir1 - C9	2.169(5)
Ir1 - C10	2.223(4)	Ir1 - C11	2.220(4)
Ir1 - C12	2.230(4)	O1 - Ir1 - P1	90.34(9)
P1 - Ir1 - Se1	87.32(3)	O1 - Ir1 - Se1	86.05(9)
Ir1 - Se1 - C1	98.12(14)	Ir1 - O1 - C7	131.3(3)
Se1 - C1 - C2	124.8(4)	O1 - C7 - C2	123.4(4)
O2 - C7 - C2	116.9(5)	O1 - C7 - O2	119.7(5)
C1 - C2 - C7	125.3(4)	C1 - C2 - C3	118.0(5)
C2 - C3 - C4	121.6(5)	C3 - C4 - C5	120.3(5)
C4 - C5 - C6	119.3(5)	C5 - C6 - C1	121.3(5)
C6 - C1 - C2	119.4(5)		

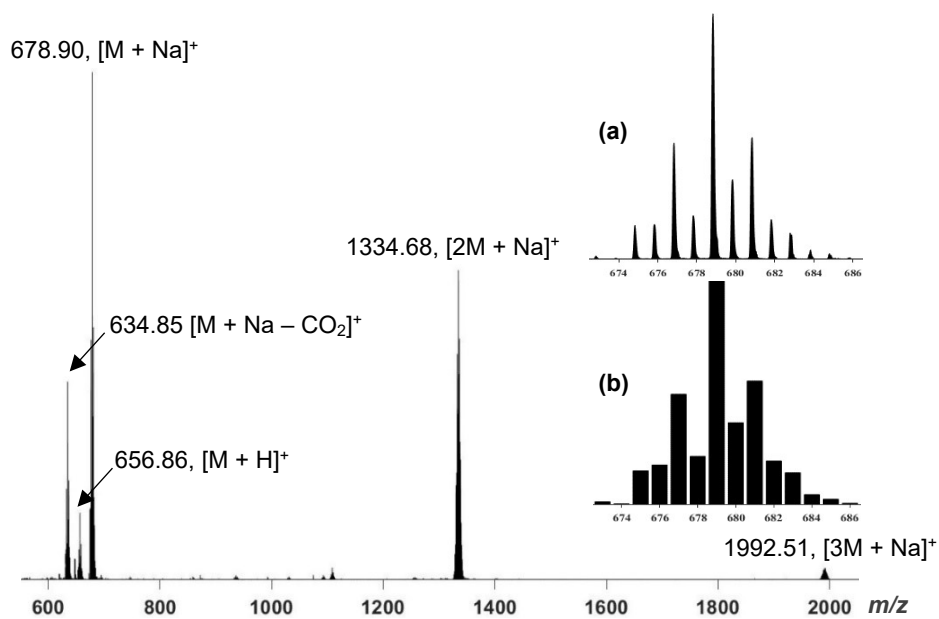


Figure S1 Positive-ion ESI mass spectrum of $[Ni(SeC_6H_4CO_2)(dppe)]$ **4f** at a capillary exit voltage of 180 V, showing the absence of selenium loss. Insets (a) and (b) are the experimental and calculated isotope patterns of the $[M + Na]^+$ ion.

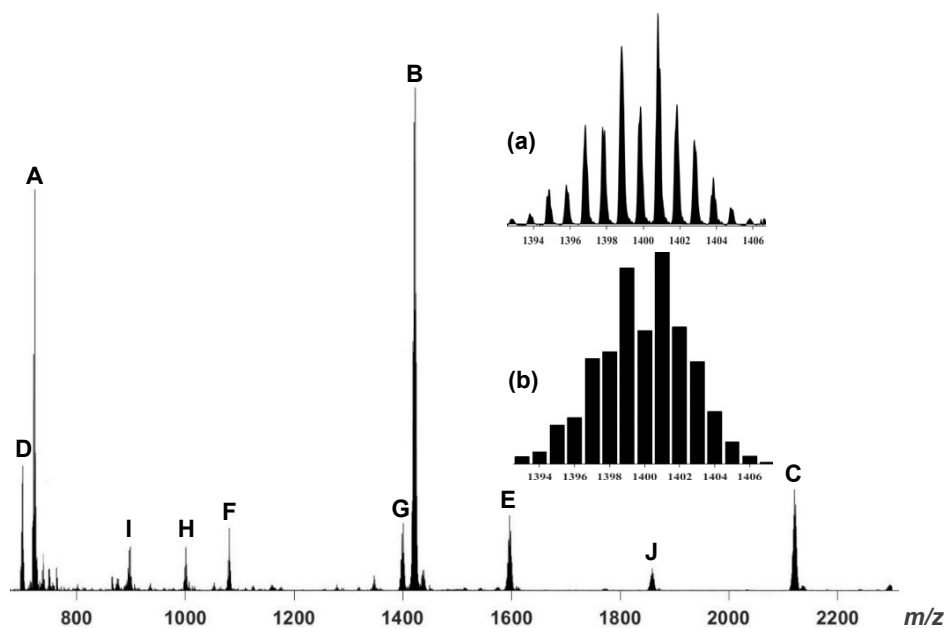


Figure S2 Positive-ion ESI mass spectrum of $[\text{Cp}^*\text{Rh}(\text{SeC}_6\text{H}_4\text{CO}_2)(\text{PPh}_3)]$ **4j** at a CEV of 60 V showing the $[\text{M} + \text{H}]^+$ and $[\text{nM} + \text{Na}]^+$ ($\text{n} = 1 - 3$) ions along with their fragments. Insets **(a)** and **(b)** are the experimental and calculated isotope patterns of the $[2\text{M} + \text{H}]^+$ ion, **G**.

Legend: **A** = $[\text{M} + \text{Na}]^+$ ($m/z = 722.90$); **B** = $[2\text{M} + \text{Na}]^+$ ($m/z = 1422.81$); **C** = $[3\text{M} + \text{Na}]^+$ ($m/z = 2120.70$); **D** = $[\text{M} + \text{H}]^+$ ($m/z = 700.91$); **E** = $[3\text{M} + \text{Na} - 2\text{PPh}_3]^+$ ($m/z = 1596.63$); **F** = $[2\text{M} + \text{Na} - \text{PPh}_3 - \text{Se}]^+$ ($m/z = 1081.24$); **G** = $[2\text{M} + \text{H}]^+$ ($m/z = 1400.82$); **H** = $[2\text{M} + \text{Na} - \text{PPh}_3 - 2\text{Se}]^+$ ($m/z = 1000.92$), **I** = $[2\text{M} + \text{Na} - 2\text{PPh}_3]^+$ ($m/z = 898.73$), **J** = $[3\text{M} + \text{Na} - \text{PPh}_3]^+$ ($m/z = 1858.66$).

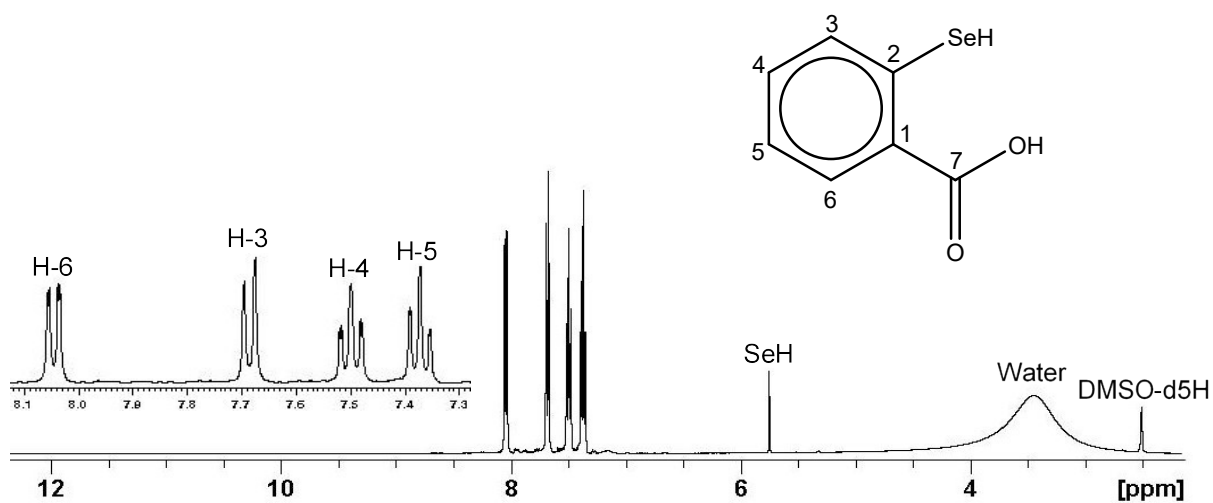


Figure S3 ^1H NMR spectrum of selenosalicylic acid **2** in $(\text{CD}_3)_2\text{SO}$.

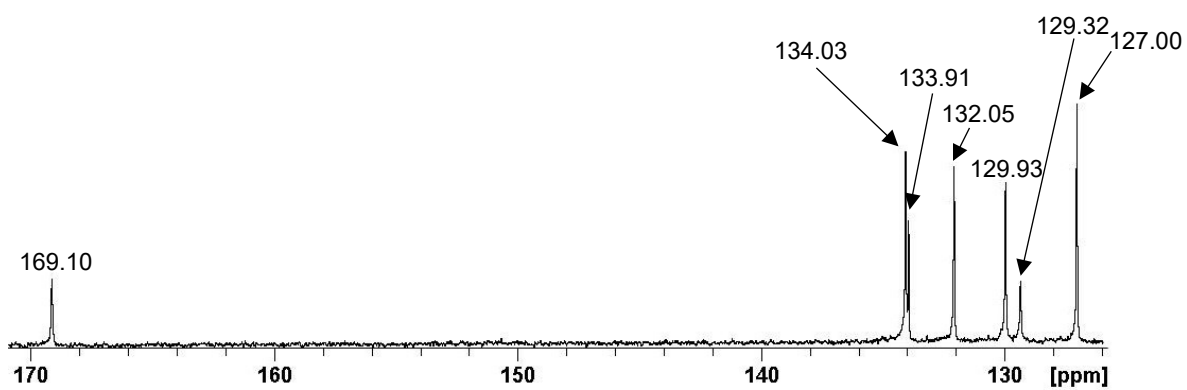


Figure S4 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of selenosalicylic acid **2** in $(\text{CD}_3)_2\text{SO}$.

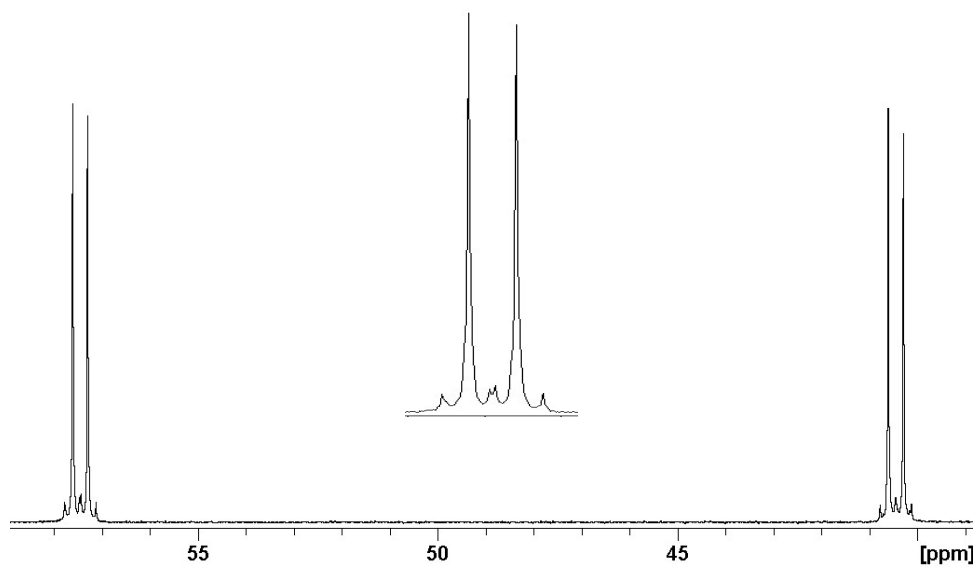
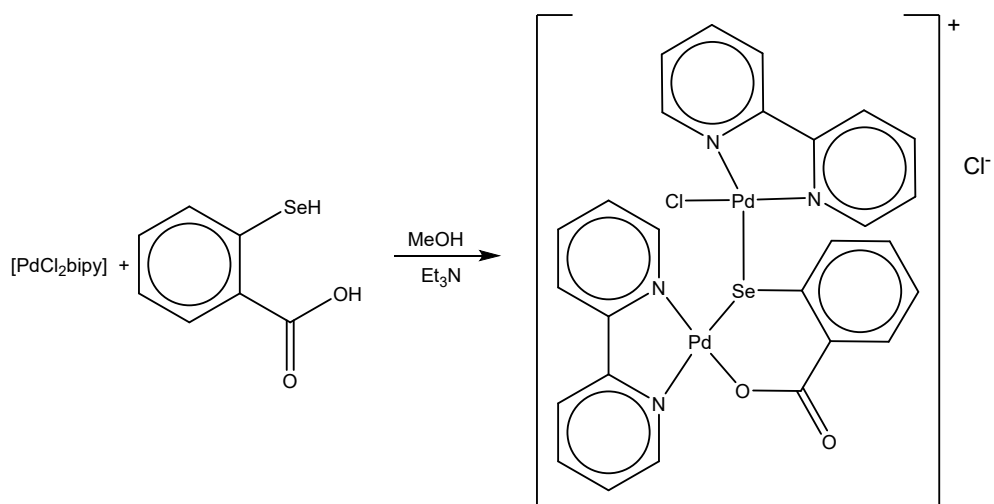
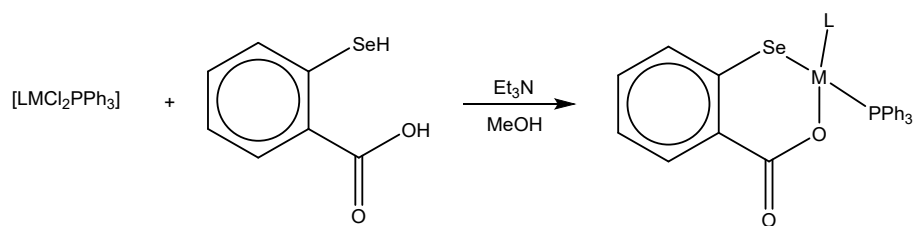


Figure S5 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ni}(\text{SeC}_6\text{H}_4\text{CO}_2)(\text{dppe})]$ **4f** in CDCl_3 ; the expansion in the centre is of the doublet centred around δ 57.4.



Scheme S1 Synthesis of the dinuclear complex $[\{\text{Pd}(\text{bipy})\}_2(\text{Cl})(\text{SeC}_6\text{H}_4\text{CO}_2)]\text{Cl}$ **4g**.



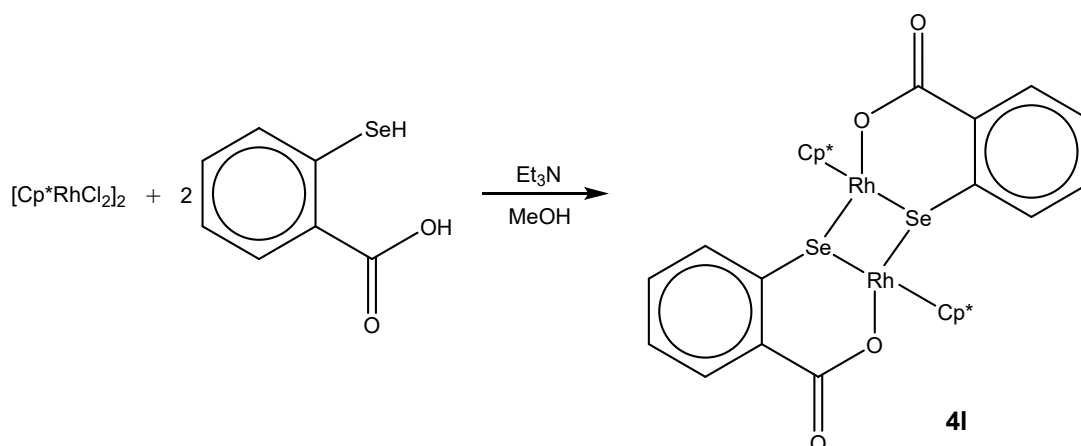
4h: $M = Ru$; $L = \eta^6\text{-}p\text{-cymene}$

4i: $M = Ru$; $L = \eta^6\text{-}C_6Me_6$

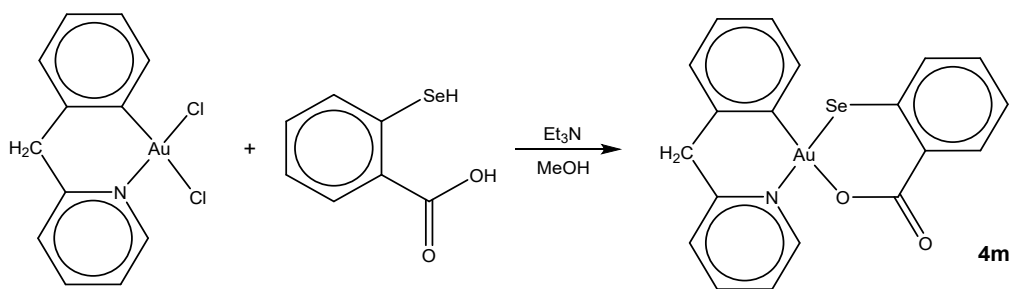
4j: $M = Rh$; $L = \eta^5\text{-}C_5Me_5$ (Cp^*)

4k: $M = Ir$; $L = Cp^*$

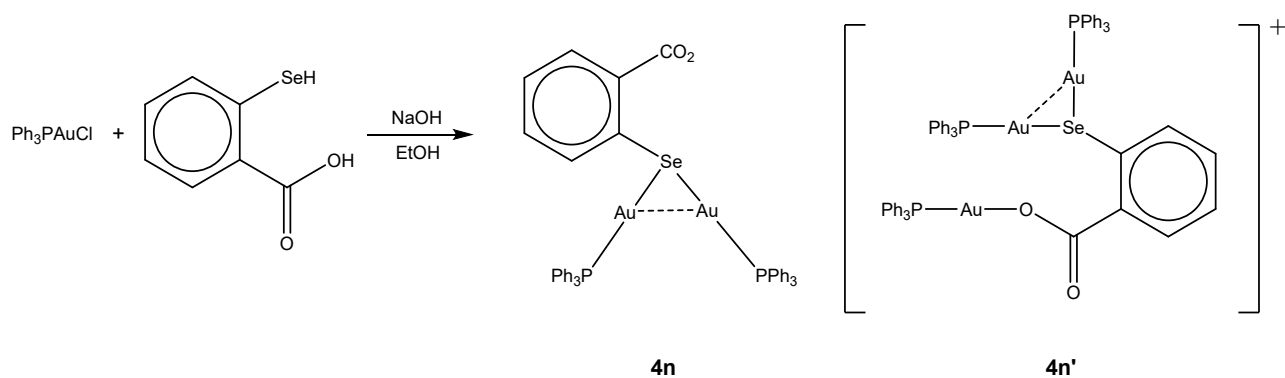
Scheme S2 Synthesis of mononuclear ruthenium, rhodium and iridium selenosalicylate complexes.



Scheme S3 Reaction scheme for the synthesis of the dinuclear complex **4l**.



Scheme S4 Reaction scheme for the synthesis of the gold(III) selenosalicylate complex **4m**.



Scheme S5 Reaction scheme for the synthesis of the gold(I) selenosalicylate complex **4n**, and the proposed structure of the triply-aurated complex **4n'**.

i L.J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849-854.

ii C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler and J. Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.