Synthesis and Characterization of Bis-triphenylphosphine Selenide complexes $[RhL(SePh_3)_2]ClO_4$ (L = COD, COT, NBD)

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The cationic rhodium(1) complexes with diolefin and phosphine and arsine oxides as ligands, have been prepared and characterized recently [1, 2]. So far as we are aware, the literature contains no reports of organometallic rhodium(1) complexes with phosphine selenides. We now report the first synthesis of such complexes.

Experimental

All operations were performed in air. The starting complexes $[RhClL]_2$ (L = COD, COT, NBD) were prepared as reported elsewhere [3, 4]. Triphenylphosphine selenide was used as obtained from Ega-Chemie Chemical Co.

The ^{31}P NMR spectrum was run in 20% CD_2Cl_2 in CH_2Cl_2 on a Jeol FX-90QFT spectrometer. The mass spectrum was obtained on a RMU-GL Hitachi–Perkin-Elmer mass spectrometer. IR spectra were recorded with a Perkin-Elmer 1430 ration recording spectrophotometer. The conductance measurements were run on a WTW LF530 conductivity bridge.

Preparation of the Complexes

All complexes were prepared according to the following procedure employed for the preparation of **I**.

A solution of $[Rh(COD)Cl]_2$ (0.099 g, 0.2 mmol) in acetone (40 ml) was treated with $AgClO_4$ (0.083 g, 0.4 mmol). After the removal of the AgCl, $SePPh_3$ (0.273 g, 0.8 mmol) was added and the colour of the solution became brown. It was then stirred for 15 min, concentrated to a small volume (3 ml) and diethylether added (10 ml), giving an amorphous residue. Evaporation to dryness followed by successive recrystallizations from CH_2Cl_2/Et_2O and Me_2CO/Et_2O afforded microcrystals (0.3 g) of **I**, which were washed with ether (3 X 3 ml) and dried in air.

Results and Discussion

The title compounds have been prepared by addition of selenide to an acetonic solution of $[RhL(Me_2CO)_x]ClO_4$ (L = COD, COT, NBD) in a 2:1 molar ratio. The solutions of $[RhL(Me_2CO)_x]ClO_4$ were obtained by treating $[RhClL]_2$ with $AgClO_4$, the formed AgCl being removed by filtration. The sequence of the reactions is as follows:

$$\frac{1}{2}\,[RhClL]_2 \xrightarrow[Me_2CO]{AgClO_4} [RhL(Me_2CO)_x]ClO_4 \xrightarrow{2SePPh_3} [RhL(SePPh_3)_2]ClO_4 + xMe_2CO$$

L = COD, COT and NBD

Complexes **I**, **II**, **III** are formed in good yields and they are air-stable.

The ^{31}P NMR spectrum of **III** shows a sharp peak at 31 ppm and small ^{77}Se satellites for which $J(P-Se)$ is 640 Hz, the free ligand ($SePPh_3$) values being 37 ppm and 740 Hz, respectively [5].

As it can be seen from the aforementioned NMR data the $J(P-Se)$ decreases upon coordination indicating weakening of the P–Se bond, and this is in accord with previous observations [6].

The IR spectra of all complexes contain one $\nu(Se=P)$ band at *ca.* 545 cm^{-1} shifted to lower wavenumbers in comparison to that of the free selenide (Table 1). The conductance data in acetone solutions indicate that the complexes are essentially 1:1 electrolytes.

The mass spectrum of **I** is not very informative, however, peaks at *m/e* 342 and 262 were detected

TABLE I. Analytical Results, Molar Conductivities, Yields, Colours and IR Data for $[RhL(SePPh_3)_2]ClO_4$ Complexes (L = COD, COT, NBD)

Complex	Found (calc.) (%)		Λ_M (ohm^{-1} cm^2 mol^{-1})	Colour	Yield (%)	IR bands $\nu(Se=P)$ (cm^{-1})
	C	H				
I $[Rh(COD)(SePPh_3)_2]ClO_4$	54.07 (53.43)	4.16 (4.28)	125	dark-khaki	76	542
II $[Rh(COT)(SePPh_3)_2]ClO_4$	53.10 (53.65)	3.74 (3.89)	116	mustard	79	548
III $[Rh(NBD)(SePPh_3)_2]ClO_4$	53.08 (53.08)	3.92 (3.94)	142	dark-khaki	66	544

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which can be assigned to ($SePPh_3^+$) and (PPh_3^+), respectively.

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