

### Synthesis and Characterization of Bis-triphenylphosphine Selenide complexes $[\text{RhL}(\text{SePPh}_3)_2]\text{ClO}_4$ (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  $[\text{RhCIL}]_2$  (L = COD, COT, NBD) were prepared as reported elsewhere [3, 4]. Triphenylphosphine selenide was used as obtained from Ega-Chemie Chemical Co.

The  $^{31}\text{P}$  NMR spectrum was run in 20%  $\text{CD}_2\text{Cl}_2$  in  $\text{CH}_2\text{Cl}_2$  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

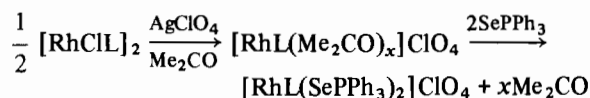
All complexes were prepared according to the following procedure employed for the preparation of **I**.

A solution of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  (0.099 g, 0.2 mmol) in acetone (40 ml) was treated with  $\text{AgClO}_4$  (0.083 g, 0.4 mmol). After the removal of the  $\text{AgCl}$ ,  $\text{SePPh}_3$

(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  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  and  $\text{Me}_2\text{CO}/\text{Et}_2\text{O}$  afforded microcrystals (0.3 g) of **I**, which were washed with ether (3 × 3 ml) and dried in air.

#### Results and Discussion

The title compounds have been prepared by addition of selenide to an acetonic solution of  $[\text{RhL}(\text{Me}_2\text{CO})_x]\text{ClO}_4$  (L = COD, COT, NBD) in a 2:1 molar ratio. The solutions of  $[\text{RhL}(\text{Me}_2\text{CO})_x]\text{ClO}_4$  were obtained by treating  $[\text{RhCIL}]_2$  with  $\text{AgClO}_4$ , the formed  $\text{AgCl}$  being removed by filtration. The sequence of the reactions is as follows:



L = COD, COT and NBD

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

The  $^{31}\text{P}$  NMR spectrum of **III** shows a sharp peak at 31 ppm and small  $^{77}\text{Se}$  satellites for which  $J(\text{P}-\text{Se})$  is 640 Hz, the free ligand ( $\text{SePPh}_3$ ) values being 37 ppm and 740 Hz, respectively [5].

As it can be seen from the aforementioned NMR data the  $J(\text{P}-\text{Se})$  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  $\nu(\text{Se}=\text{P})$  band at ca.  $545\text{ cm}^{-1}$  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  $[\text{RhL}(\text{SePPh}_3)_2]\text{ClO}_4$  Complexes (L = COD, COT, NBD)

Complex	Found (calc.) (%)		$\Lambda_M$ ( $\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ )	Colour	Yield (%)	IR bands $\nu(\text{Se}=\text{P})$ ( $\text{cm}^{-1}$ )
	C	H				
<b>I</b> $[\text{Rh}(\text{COD})(\text{SePPh}_3)_2]\text{ClO}_4$	54.07 (53.43)	4.16 (4.28)	125	dark-khaki	76	542
<b>II</b> $[\text{Rh}(\text{COT})(\text{SePPh}_3)_2]\text{ClO}_4$	53.10 (53.65)	3.74 (3.89)	116	mustard	79	548
<b>III</b> $[\text{Rh}(\text{NBD})(\text{SePPh}_3)_2]\text{ClO}_4$	53.08 (53.08)	3.92 (3.94)	142	dark-khaki	66	544

which can be assigned to  $(\text{SePPh}_3^+)$  and  $(\text{PPh}_3^+)$ , respectively.

#### References

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