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# Facile synthesis of $\text{Ru}_4(\text{CO})_{10}(\mu\text{-CO})(\mu_4\text{-Se})_2$ and its reactions with phosphine ligands

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## Abstract

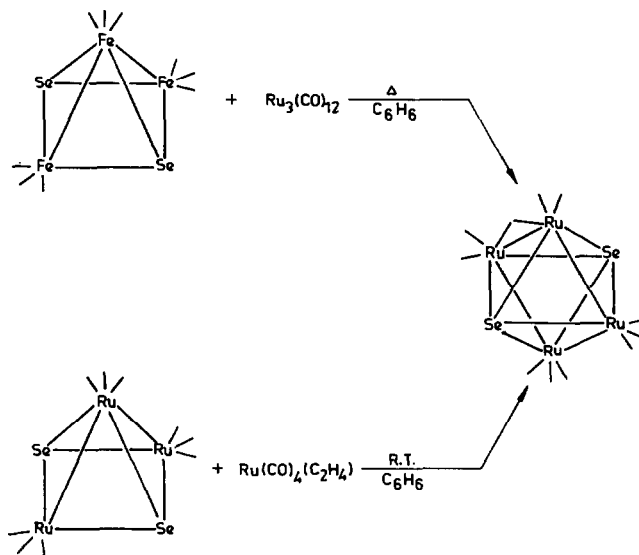
The title compound has been prepared by refluxing a benzene solution containing  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Se})_2$  and  $\text{Ru}_3(\text{CO})_{12}$  or by stirring a benzene solution containing  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-Se})_2$  and  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  at room temperature. Its reactions with triphenylphosphine, bis(diphenylphosphino)methane and bis(diphenylphosphino)ethane give tetraruthenium and triruthenium phosphine derivatives.

## 1. Introduction

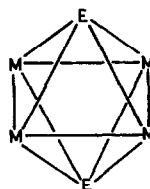
One class of clusters which has attracted much interest in recent years are the six vertex clusters (Fig. 1), where the ligand E is GeR, PR, AsR, S, Se or Te [1]. In contrast to the relatively wide use of bridging S [2] and Te [3] ligands in cluster build-up reactions, the use of Se has been limited to a few examples [4]. We have recently reported the facile synthesis of several clusters containing  $\mu_4\text{-Se}$  and  $\mu_4\text{-Te}$  in the same molecule [5]. Here we report on an extension of the same synthetic strategy to prepare  $\text{Ru}_4(\text{CO})_{10}(\mu\text{-CO})(\mu_4\text{-Se})_2$  and its reactivity towards triphenylphosphine, bis(diphenylphosphino)methane (dppm), and bis(diphenylphosphino)ethane (dppe).

## 2. Results and discussion

The tetraruthenium cluster  $\text{Ru}_4(\text{CO})_{10}(\mu\text{-CO})(\mu_4\text{-Se})_2$  was prepared by two different methods (Scheme 1). By the first method, a benzene solution containing  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Se})_2$  and  $\text{Ru}_3(\text{CO})_{12}$  was refluxed for 24 h. The second method was a room temperature reaction between  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-Se})_2$  and freshly prepared  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ . The reddish-brown  $\text{Ru}_4(\text{CO})_{10}(\mu\text{-CO})(\mu_4\text{-Se})_2$



Scheme 1.

Fig. 1. Octahedral core structure of the  $\text{M}_4\text{E}_2$  cluster.

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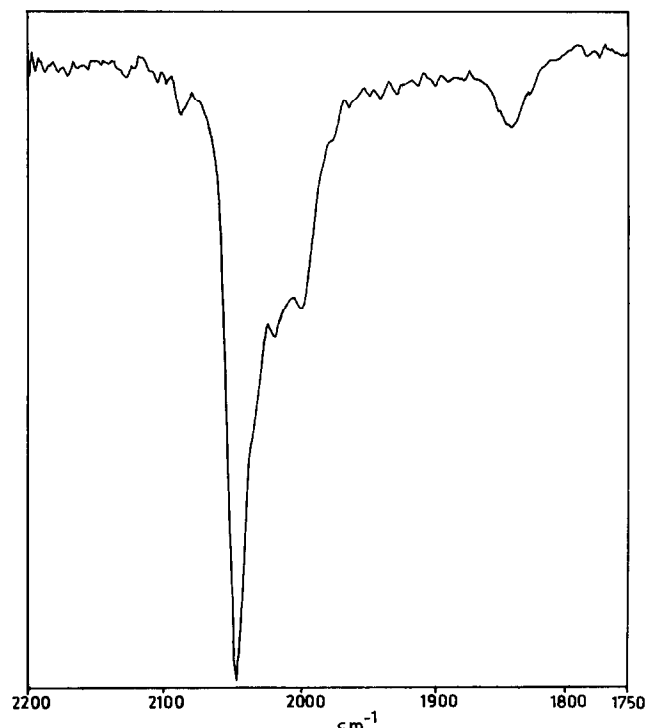


Fig. 2. Infrared spectrum in the carbonyl region of  $\text{Ru}_4(\text{CO})_{10}(\mu\text{-CO})(\mu_4\text{-Se})_2$  in  $\text{CH}_2\text{Cl}_2$  solvent.

$\text{CO}(\mu_4\text{-Se})_2$  was isolated by chromatographic work-up and characterized on the basis of a comparison of its infrared spectrum in the carbonyl region with those of the previously reported clusters of the form  $\text{M}_4(\text{CO})_{11}(\mu_4\text{-E})_2$ ,  $\text{M} = \text{Fe}$ ,  $\text{E} = \text{S}$  [6];  $\text{M} = \text{Fe}$  or  $\text{Ru}$ ,  $\text{E} = \text{Te}$  [7,8] (Fig. 2) (Table 1), by mass spectrometry (FAB MS:  $M^+$   $m/z = 871$ ; there was a good match between the observed and calculated isotopic distribution pattern for the  $M^+$  ion), and by elemental analysis (Table 2). Typically, all such compounds have a trapezoidal arrangement of the metal atoms with the main group atoms occupying quadruply bridging sites on either side of the  $\text{M}_4$  plane. The presence of one bridging and two semi-bridging carbonyls is also characteristic of these compounds. Consequently, they all display an identical carbonyl stretching pattern, with the stretching frequencies dependent on the nature of the quadruply bridging atom. There is a decrease in the corresponding frequencies when the smaller bridging atom, such as S, is replaced by a larger atom, such as Te. In the mixed chalcogen series,  $\text{M}_4(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-E})(\mu\text{-E}')$ , the stretching frequencies are an almost exact mean of those observed for the analogous  $(\mu_4\text{-E})_2$  and  $(\mu_4\text{-E}')_2$  compounds [9]. The compound  $\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-Se})_2$  has recently also been prepared by vacuum pyrolysis of  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{PhSeSePh}$  and its crystal structure shows that it also has the typical

TABLE 1. Infrared spectral data in the carbonyl region (in  $\text{CH}_2\text{Cl}_2$  solution)

Compound	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )
$\text{Ru}_4\text{Se}_2(\text{CO})_{11}$	2092w, 2049vs, 2021m, sh, 2002m, sh, 1841w
$\text{Ru}_4\text{Se}_2(\text{CO})_{10}(\text{PPh}_3)$	2067m, 2029vs, 1997s, 1972w, sh, 1953w, sh, 1872w, sh, 1868w, sh, 1832m
$\text{Ru}_4\text{Se}_2(\text{CO})_9(\text{PPh}_3)_2$	2038m, 2011vs, 1992sh, 1957m, 1842m, 1805m
$\text{Ru}_3\text{Se}_2(\text{CO})_8(\text{PPh}_3)$	2078m, 2045vs, 2025m, 2006m, 1979w
$\text{Ru}_3\text{Se}_2(\text{CO})_7(\text{PPh}_3)_2$	2046s, 2013vs, 1971m, 1950w
$\text{Ru}_3\text{Se}_2(\text{CO})_6(\text{PPh}_3)_3$	2036w, 2013w, 1993vs, 1965m, 1946w, 1935w, sh
$\text{Ru}_4\text{Se}_2(\text{CO})_9(\text{dppm})$	2044m, 2012 vs, 1967m, 1807m
$\text{Ru}_3\text{Se}_2(\text{CO})_7(\text{dppm})$	2067s, 2051s, 2007 vs, 1956m, 1926w
$\text{Ru}_4\text{Se}_2(\text{CO})_9(\text{dppe})$	2044m, 2010vs, 1966m, 1941w, 1935w, 1809w, 1805w, sh
$\text{Ru}_3\text{Se}_2(\text{CO})_7(\text{dppe})$	2050vs, 2016vs, 1995w, sh, 1977m, 1966w, 1957w, sh

$\text{M}_4(\mu_4\text{-E})_2$  distorted octahedral framework with one bridging and two semibridging carbonyl groups [10].

We have previously reported that the cluster  $\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-Te})_2$  reacts with  $\text{PPh}_3$  to give  $\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)(\mu_4\text{-Te})_2$  and  $\text{Ru}_3(\text{CO})_6(\text{PPh}_3)_3(\mu_3\text{-Te})_2$  under mild conditions [8]. We observe that when  $\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-Se})_2$  and  $\text{PPh}_3$  are stirred in benzene solvent, tetraruthenium and triruthenium phosphine derivatives are formed. The tetraruthenium derivatives are  $\text{Ru}_4\text{Se}_2(\text{CO})_{11-x}(\text{PPh}_3)_x$ ,  $x = 1$  and 2, and the triruthenium derivatives formed are  $\text{Ru}_3\text{Se}_2(\text{CO})_{9-x}$ ,  $x = 1, 2$  and 3. Like the parent cluster, the phosphine derivatives also display characteristic infrared spectra in the carbonyl region. Thus, the infrared spectrum of  $\text{Ru}_4\text{Se}_2(\text{CO})_{10}(\text{PPh}_3)$  was found to be similar to that of

TABLE 2. Elemental analyses

Compound	C (%) (found (calc.))	H (%) (found (calc.))
$\text{Ru}_4\text{Se}_2(\text{CO})_{11}$	15.7 (15.2)	
$\text{Ru}_4\text{Se}_2(\text{CO})_{10}(\text{PPh}_3)$	30.8 (30.4)	1.45 (1.35)
$\text{Ru}_4\text{Se}_2(\text{CO})_9(\text{PPh}_3)_2$	40.9 (40.4)	2.88 (2.24)
$\text{Ru}_3\text{Se}_2(\text{CO})_8(\text{PPh}_3)$	32.7 (32.9)	1.92 (1.58)
$\text{Ru}_3\text{Se}_2(\text{CO})_7(\text{PPh}_3)_2$	43.9 (43.7)	2.91 (2.54)
$\text{Ru}_3\text{Se}_2(\text{CO})_6(\text{PPh}_3)_3$	51.4 (50.9)	3.84 (3.18)
$\text{Ru}_4\text{Se}_2(\text{CO})_9(\text{dppm})$	33.7 (34.1)	2.17 (1.83)
$\text{Ru}_3\text{Se}_2(\text{CO})_7(\text{dppm})$	36.6 (36.8)	2.51 (2.11)
$\text{Ru}_4\text{Se}_2(\text{CO})_9(\text{dppe})$	34.1 (34.6)	2.13 (1.98)
$\text{Ru}_3\text{Se}_2(\text{CO})_7(\text{dppe})$	37.0 (37.5)	2.56 (2.27)

$Ru_4Te_2(CO)_{10}(PPh_3)_2$ , which has been structurally characterized [8]. Similarly, the identity of  $Ru_4Se_2(CO)_9(PPh_3)_2$ ,  $Ru_3Se_2(CO)_{9-x}(PPh_3)_x$ ,  $x = 1, 2$  and  $3$ , is based on the comparison of their infrared spectra with those of the structurally characterized  $Ru_4S_2(CO)_9(PMe_2Ph)_2$  [11],  $Fe_3Te_2(CO)_8(PPh_3)_3$ ,  $Fe_3Te_2(CO)_7(PPh_3)_2$  [12] and  $Ru_3Te_2(CO)_6(PPh_3)_3$  [8], respectively. All the compounds gave satisfactory elemental analyses (Table 2). The  $Ru_3Se_2(CO)_7(PPh_3)_2$  and  $Ru_3Se_2(CO)_6(PPh_3)_3$  were also obtained from the room temperature reaction of  $Ru_3Se_2(CO)_9$  and  $PPh_3$ .

The room temperature reaction of  $Ru_4Se_2(CO)_{11}$  with the bidentate phosphines, dppm and dppe, also gave both tetranuclear derivatives,  $Ru_4Se_2(CO)_9(P^2P)$  and the triruthenium derivatives,  $Ru_3Se_2(CO)_7(P^2P)$ . All four compounds were identified by comparison of their carbonyl stretching pattern with those reported for the related Te analogues [8] and elemental analysis. The triruthenium derivatives were also obtained directly from the room temperature reactions of  $Ru_3Se_2(CO)_9$  and dppm or dppe.

We are presently investigating the designed synthesis of other selenium-bridged clusters and their reactivity towards organic species.

### 3. Experimental details

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All solvents were dried and distilled before use. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer. Elemental analysis was carried out on a Carlo Erba automatic analyser. The compound  $Fe_3(CO)_9(\mu_3-Se)_2$  was prepared by photolysis of a hexane solution containing  $Fe_2(CO)_6(\mu-Se)_2$  [13] and  $Fe(CO)_5$ .  $Ru_3(CO)_9(\mu_3-Se)_2$  was prepared using a method similar to that used for the preparation of  $Ru_3(CO)_9(\mu_3-Te)_2$  from the thermolysis of  $Fe_2Ru_3(CO)_{17}(\mu_3-Te)(\mu_4-Te)$  [3].

#### 3.1. Preparation of $Ru_4(CO)_{11}(\mu_4-Se)_2$

Method (a): A mixture of  $Fe_3(CO)_9(\mu_3-Se)_2$  (0.043 g, 0.075 mmol) and  $Ru_3(CO)_{12}$  (0.048 g, 0.075 mmol) in benzene (100 ml) was refluxed for 24 h. After allowing the solution to cool to room temperature, it was filtered through a Celite pad and the solvent was removed *in vacuo*. The residue was chromatographed on a silica column. Using neat hexane, the following compounds eluted in trace amounts: the unreacted  $Fe_3(CO)_9(\mu_3-Se)_2$  and  $Ru_3(CO)_{12}$ , brown  $H_2Ru_4(CO)_{13}$  [14] and red  $FeRu_2(CO)_{12}$  [15]. Further elution with a hexane/dichloromethane mixture (70:30) afforded the reddish-brown band of  $Ru_4Se_2(CO)_{11}$  (0.044 g, 66%).

Method (b): A solution of  $Ru_3(CO)_{12}$  (0.011 g, 0.024 mmol) in hexane (120 ml) was irradiated with UV light for 10 min under a constant purge of ethylene gas. The colourless solution containing  $Ru(CO)_4(C_2H_4)$  was added to a benzene/hexane mixture (50:50) (100 ml) containing  $Ru_3Se_2(CO)_9$  (0.012 g, 0.016 mmol). The mixture was stirred at room temperature for 3 h. The solvent was removed *in vacuo*. Chromatographic work-up on a silica column using hexane/dichloromethane (70:30) gave  $Ru_4Se_2(CO)_{11}$  (0.21 g, 28%).

#### 3.2. Reaction of $Ru_4(CO)_{11}(\mu_4-Se)_2$ with $PPh_3$

To a solution of  $Ru_4(CO)_{11}(\mu_4-Se)_2$  (0.1 g, 0.11 mmol) in dichloromethane (50 ml) was added solid  $PPh_3$  (0.058 g, 0.22 mmol) and the mixture was stirred at room temperature for 0.5 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica TLC plates. Using a hexane/dichloromethane mixture (50:50) as eluant, the following bands were separated, in order of elution: orange  $Ru_3Se_2(CO)_8(PPh_3)$  (0.03 g, 22%), reddish-brown  $Ru_4Se_2(CO)_{10}(PPh_3)$  (0.021 g, 18%), orange  $Ru_3Se_2(CO)_7(PPh_3)_2$  (0.035 g, 20%), orange  $Ru_4Se_2(CO)_9(PPh_3)_2$  (0.013 g, 8%) and red  $Ru_3Se_2(CO)_6(PPh_3)_3$  (0.025 g, 12%).

#### 3.3. Reaction of $Ru_3(CO)_9(\mu_3-Se)_2$ with $PPh_3$

A mixture of  $Ru_3(CO)_9(\mu_3-Se)_2$  (0.05 g, 0.07 mmol) and  $PPh_3$  (0.037 g, 0.14 mmol) in dichloromethane solvent (50 ml) was stirred at room temperature for 10 min. The solvent was removed *in vacuo* and the residue was chromatographed on silica TLC plates. A hexane/dichloromethane mixture (50:50) as eluant separated the following bands, in order of elution: orange  $Ru_3Se_2(CO)_7(PPh_3)_2$  (0.027 g, 33%), red  $Ru_3Se_2(CO)_6(PPh_3)_3$  (0.055 g, 55%) and trace amounts of  $Ru_3(CO)_{12}$ .

#### 3.4. Reaction of $Ru_4(CO)_{11}(\mu_4-Se)_2$ with dppm and dppe

A mixture of  $Ru_4(CO)_{11}(\mu_4-Se)_2$  (0.1 g, 0.11 mmol) and dppm (0.085 g, 0.22 mmol) in dichloromethane solvent (50 ml) was stirred at room temperature for 3 h. The solvent was removed *in vacuo* and chromatographic work-up on silica TLC plates using a mixture of hexane/dichloromethane (50:50) gave the following two compounds, in order of elution: brick-red  $Ru_3Se_2(CO)_7(dppm)$  (0.083 g, 54%) and orange  $Ru_4Se_2(CO)_9(dppm)$  (0.031 g, 23%). Using the identical reaction conditions and work-up procedures, the reaction of  $Ru_4(CO)_{11}(\mu_4-Se)_2$  with dppe yielded brick-red  $Ru_3Se_2(CO)_7(dppe)$  (53%) and  $Ru_4Se_2(CO)_9(dppe)$  (16%).

#### 3.5. Reaction of $Ru_3(CO)_9(\mu_3-Se)_2$ with dppm and dppe

Solid dppm (0.054 g, 0.14 mmol) was added to a dichloromethane (50 ml) solution of  $Ru_3(CO)_9(\mu_3-Se)_2$

(0.05 g, 0.07 mmol) and the mixture was stirred at room temperature for 10 min. After evaporation of the solvent, chromatography of the residue on silica TLC plates, using a hexane/dichloromethane mixture (50:50) as eluant gave the following bands, in order of elution:  $Ru_3Se_2(CO)_7(dppe)$  (0.034 g, 48%) and trace amounts of  $Ru_3(CO)_{12}$ . Using the same conditions as for the reaction of  $Ru_3(CO)_9(\mu_3-Se)_2$  and  $dppe$ ,  $Ru_3Se_2(CO)_7(dppe)$  (56%) was obtained.

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### References

- 1 K. Whitmire, *J. Coord. Chem.*, **17** (1988) 95; N. A. Compton, R. J. Errington and N. C. Norman, *Adv. Organomet. Chem.*, **31** (1990) 91; J-F. Halet, R. Hoffmann and J-Y. Saillard, *Inorg. Chem.*, **24** (1985) 1695.
- 2 R. D. Adams, *Polyhedron*, **4** (1985) 2003; R. D. Adams, J. E. Babin and J.-G. Wang, *Polyhedron*, **8** (1989) 2351.
- 3 P. Mathur, I. J. Mavunkal and A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, (1989) 382; P. Mathur, I. J. Mavunkal and V. Rugmini, *Inorg. Chem.*, **28** (1989) 3616; L. E. Bogan, T. B. Rauchfuss and A. L. Rheingold, *J. Am. Chem. Soc.*, **107** (1985) 3843.
- 4 R. D. Adams and I. T. Horvath, *Inorg. Chem.*, **23** (1984) 4718.
- 5 P. Mathur, D. Chakrabarty and Md. M. Hossain, *J. Organomet. Chem.*, **401** (1991) 167.
- 6 R. D. Adams, J. E. Babin, J. Estrada, J.-G. Wang, M. B. Hall and A. A. Low, *Polyhedron*, **8** (1989) 1885.
- 7 P. Mathur, I. J. Mavunkal, V. Rugmini and M. F. Mahon, *Inorg. Chem.*, **29** (1991) 4838.
- 8 P. Mathur, B. H. S. Thimmappa and A. L. Rheingold, *Inorg. Chem.*, **29** (1990) 4658.
- 9 P. Mathur, D. Chakrabarty and Md. M. Hossain, *J. Organomet. Chem.*, **416** (1991) 415; P. Mathur, D. Chakrabarty, Md. M. Hossain and R. S. Rashid, *J. Organomet. Chem.*, **420** (1991) 79.
- 10 B. F. G. Johnson, T. M. Layer, J. Lewis, A. Martin and P. R. Raithby, *J. Organomet. Chem.*, **429** (1992) C41.
- 11 R. D. Adams, J. E. Babin and M. Tasi, *Inorg. Chem.*, **25** (1986) 4514.
- 12 I. J. Mavunkal, *PhD thesis*, Indian Institute of Technology, Bombay, 1989.
- 13 P. Mathur, D. Chakrabarty, Md. M. Hossain, R. S. Rashid, V. Rugmini and A. L. Rheingold, *Inorg. Chem.*, **31** (1992) 1106.
- 14 B. F. G. Johnson, J. Lewis and I. G. Williams, *J. Chem. Soc. A*, (1970) 901.
- 15 D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc. A*, (1969) 502.