Journal of Organometallic Chemistry, 470 (1994) 169–171

Molecular orbital calculations on $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$

Sambhu N. Datta, Rama-Krishna Kondru and Pradeep Mathur

Chemistry Department, Indian Institute of Technology, Powai, Bombay 400 076 (India)

(Received September 11, 1993)

Abstract

Molecular orbital calculations using the extended Hückel program were carried out on $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$. On the basis of a molecular orbital description, binding energy, polarity and the metal–metal bond order were found to decrease on substitution of one Fe atom of $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ by a Ru atom.

Key words: Iron; Ruthenium; Selenium; Carbonyl; Cluster; Molecular orbital calculations

1. Introduction

The Group 16 elements, S, Se and Te are useful 'clamp' ligands in numerous types of metal carbonyl cluster compounds [1]. Their versatile bonding modes have enabled several different geometries to be observed in clusters containing these ligands. The cluster compounds $M_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}E)_2$, where M = Fe, Ru and E = S, Se or Te, are an interesting group. These are formally electron deficient according to the 18 electron rule, but the octahedral geometry of the M_4E_2 core observed in these clusters conforms to the PSEP theory which predicts a 6-vertex polyhedron for the 7 SEP's present in these clusters. These types of clusters have been prepared by several different methods; UV irradiation of solutions containing $M_3(CO)_9(\mu_3\text{-}E)_2$ and $M(CO)_5$ [2], thermolysis of $Fe_3(CO)_9(\mu_3\text{-}E)_2$ and $Ru_3(CO)_{12}$ [3], room temperature addition of $Ru(CO)_4(C_2H_4)$ to $M_3(CO)_9(\mu_3\text{-}E)_2$ [4] and pyrolysis of $Ru_3(CO)_{12}$ with PhSeSePh [5]. Recently, we have reported the facile preparation of $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$, and their single crystal X-ray diffraction analysis has been carried out [6]. In order to study the effect of replacement of one Fe atom of $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ (**1**) (Fig. 1) by a Ru atom to give $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ (**2**) (Fig. 2), empirical (extended Hückel) molecular orbital calculations were performed and the results are presented.

2. Results and discussion

Molecular orbital calculations were performed using the extended Hückel program with a CDC Cyber 180/840. Eigenvectors, eigenvalues and overlap populations between atoms were computed with the mean Wolfsberg-Helmhotz formula.

Mulliken population analysis was used to determine the individual atomic overlap populations, atomic charges and the atomic orbital populations. Binding

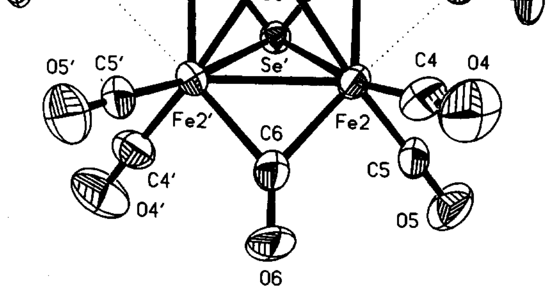

Fig. 1. Structure of $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ (**1**) with the atom numbering scheme.

Correspondence to: Dr. P. Mathur.

0022-328X/94/$7.00
SSDI 0022-328X(93)24198-E

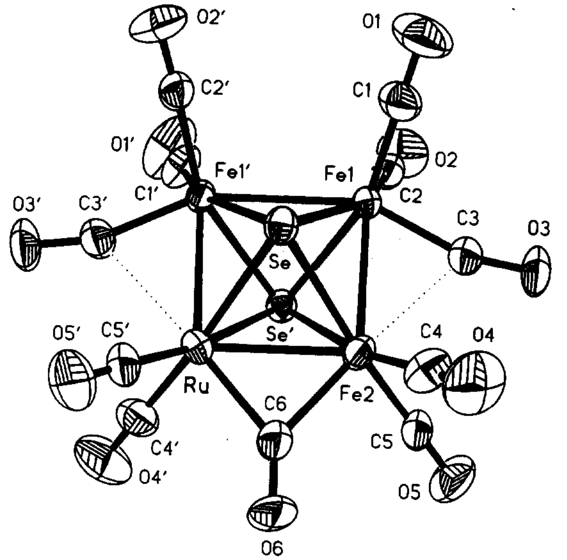

Fig. 2. Structure of $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ (2) with the atom numbering scheme.

energies were calculated by subtracting extended Hückel total energies for the constituent atoms from the extended Hückel total energy of the cluster.

Calculations were performed on crystal structures of $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ and the substituted compound $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$. The atomic coordinates were generated from the X-ray crystallographic data [7] by the MAT-LAB program. Molecule 1 contains a C2 rotation axis that is crystallographically imposed. The bridging carbonyl C(6)–O(6) lies on the z axis that passes tangentially to the plane defined by the four metal atoms. The y axis and the perpendicular to the plane defined by the metal atoms are inclined to each other at angles of 88.36(1)° and 87.06(1)° for compounds 1 and 2 respectively. Deviation from planarity of the four metal atoms is 0.43(2)° and 0.57(2)° for compounds 1 and 2 respectively. In compound 2, the Ru atom can be at either end of the bridging carbonyl C(6)–O(6) because of C2 symmetry. For computational purposes the position of Ru has been taken as the site occupied by Fe′(2) in compound 1. All results have been computed accordingly.

Compound 1 consists of a trapezoidal arrangement of four metal atoms which are bridged on each side by a quadruply bridged Se ligands. The shortest metal–metal bond, Fe(2)–Fe′(2), in 1 contains a bridging carbonyl group and has a length of 2.535(2) Å. The corresponding bond in 2 is the Ru–Fe bond (2.721(2) Å) and this is also the longest metal–metal bond in cluster 2. The sides of the trapezoid in 1 which contains semibridging carbonyl ligands are Fe′(1)–Fe′(2) (2.593(2) Å) and Fe(1)–Fe(2) (2.595(2) Å). These are shorter by 0.081–0.085 Å than the corresponding bonds in cluster 2 (Table 1). The semibridging effect is significantly stronger in 2 [Fe(1)–C(3)–O(3) = 158.0(5)°] than in 1 [Fe(1)–C(3)–O(3) = 161.6(5)°]. Metal–seleniuum bond lengths show a slight increase in compound 2 from that in compound 1.

TABLE 1. Intramolecular distances for $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$

$Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$		$Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$	
Fe(1)–Fe(2)	2.595(2)	Fe(1)–Fe(2)	2.676(2)
Fe(2)–Fe′(2)	2.535(2)	Fe(2)–Ru	2.721(2)
Fe′(1)–Fe′(2)	2.593(2)	Fe′(1)–Ru	2.678(2)
Fe(1)–Fe′(1)	2.694(2)	Fe(1)–Fe′(1)	2.718(2)
Se–Fe(1)	2.405(2)	Se–Fe(1)	2.443(2)
Se–Fe′(1)	2.397(2)	Se–Fe′(1)	2.433(2)
Se–Fe(2)	2.449(2)	Se–Fe(2)	2.546(2)
Se–Fe′(2)	2.458(2)	Se–Fe′(2)	2.562(2)
Se′–Fe(1)	2.397(2)	Se′–Fe(1)	2.432(2)
Fe′–Fe′(1)	2.407(2)	Se′–Fe′(1)	2.433(2)
Se′–Fe(2)	2.458(2)	Se′–Fe(2)	2.562(2)
Se′–Fe′(2)	2.448(2)	Se′–Fe′(2)	2.548(2)

Both compounds 1 and 2 have 154 valence electrons, hence the 77th molecular orbital is the HOMO and the 78th orbital is the LUMO. The difference in energy between the HOMO and LUMO in compound 1 is 0.173 eV whereas in compound 2 the corresponding difference is 0.582 eV.

Orbital energies for 1 and 2 are listed in Table 2. The HOMO of 1 includes little contribution from the orbitals of the four Fe atoms and the two Se atoms; the main contribution comes from the orbitals of carbon atoms of the carbonyl group ligands. The LUMO of 1

TABLE 2. Extended Hückel molecular orbital energies in eV

Molecular orbital	Occupancy	$Fe_4(CO)_{11}(\mu_4\text{-}Se)_2$	$Fe_3Ru(CO)_{11}(\mu_4\text{-}Se)_2$
82	0	−8.746	−8.651
81	0	−9.354	−8.884
80	0	−10.282	−9.607
79	0	−10.472	−10.320
78 (LUMO)	0	−11.083	−10.359
77 (HOMO)	2	−11.256	−10.941
76	2	−11.390	−11.407
75	2	−12.118	−11.461
74	2	−12.208	−11.478
73	2	−12.568	−11.581

TABLE 3. Computed, total and binding energies of $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ in atomic units

	$Fe_4(CO)_{10}(\mu\text{-}CO)$ $(\mu_4\text{-}Se)_2$	$Fe_3Ru(CO)_{10}(\mu\text{-}CO)$ $(\mu_4\text{-}Se)_2$
Total energy	−112.272	−110.547
Binding energy	−7.072	−6.999

TABLE 4. Net charges on the heavier atoms in $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$ and $Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$

$Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$		$Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$	
	Net charge		Net charge
Se	+1.991	Se	+1.468
Se′	+1.810	Se′	+1.548
Fe(1)	−1.739	Fe(1)	−1.811
Fe′(1)	−1.821	Fe′(1)	−1.951
Fe(2)	−1.737	Fe(2)	−2.015
Fe′(2)	−1.596	Ru	+2.199

is built from the 4p orbitals of selenium and the orbitals of carbon atoms. Once a hetero metal atom is introduced as in **2**, both the real and imaginary parts of the HOMO are influenced by the $4d_{xz}$ and $4d_{yz}$ orbitals of the hetero atom. The LUMO of **2** contains, as before, the p orbitals of selenium and carbon atoms mixed in it, but an additional contribution is given by $4d_{m=+2}$ and $4d_{m=-1}$ orbitals of Ru. In summary, the substitution of Ru for Fe causes the HOMO and LUMO to be mixed with the hetero metal atom orbitals.

Binding energies of the two clusters are shown in Table 3. It is clear that compound **2** is less stable by about 2 eV. Net atomic charges in the two compounds are given in Table 4. Compound **1** is clearly more polar, with Fe atoms being rich in electrons. However, in compound **2**, the Ru atom has a charge of approximately +2 whereas the three Fe atoms remain rich in electrons as before, and therefore, the net positive charge on Se atom is less in compound **2** than in compound **1**. The net effect is that there is less charge distributed among the carbonyl groups in the Ru substituted compound **2**.

Comparing the overlap populations between the metal atoms for the three types of metal–metal bonds in both compounds **1** and **2** (Table 5), one can observe the effect of substitution of Fe by Ru. When the hetero metal atom, Ru, is introduced, all the metal-metal overlap populations decrease in value. The largest decrease in atomic overlap population occurs for the bridged Ru–Fe bond, which is shown in Table 6. However, the metal atom could be restricted by the bridging carbonyl ligand from moving further apart. The semi-bridging Fe′(1)–Fe′(2)/Ru and Fe(1)–Fe(2) show a decrease in overlap of 0.047 and 0.017 respectively. Since the semi-bridging ligands are presumably not as supportive as the fully bridging ligands, the Fe(1)–Fe(2) and Fe′(1)–Fe′(2)/Ru bonds might be lengthened when the hetero metal atom is introduced. The unbridged Fe–Fe bond shows the smallest decrease in overlap population (0.009) and therefore, the bond length effect might remain small on the Fe–Fe bond. In short, all the metal–metal bonds expand upon substitution, and this expansion is confirmed by the change in atomic overlap populations which are proportional to bond orders.

TABLE 5. Comparision of the net overlap populations

$Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$		$Fe_3Ru(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Se)_2$	
	Net overlap population		Net overlap population
Fe(1)–Fe′(1)	−0.155	Fe(1)–Fe′(1)	−0.146
Fe′(1)–Fe′(2)	−0.151	Fe′(1)–Ru	−0.104
Fe′(2)–Fe(2)	−0.145	Ru–Fe(2)	−0.080
Fe(2)–Fe(1)	−0.147	Fe(2)–Fe(1)	−0.130

TABLE 6. Changes in bond length and in net overlap populations when Fe′(2) is replaced by Ru

	Bond length change	Decrease in magnitude of overlap population
Fe(1)–Fe′(1)	0.024	0.009
Fe′(1)–Fe′(2)/Ru	0.085	0.047
Fe′(2)/Ru–Fe(2)	0.186	0.065
Fe(1)–Fe(2)	0.081	0.017

References

1 L.C. Roof and J.W. Kolis, *Chem. Rev.*, *93* (1993) 1037; N.A. Compton, R.J. Erington and N.C. Norman, *Adv. Organomet. Chem.*, *31* (1990) 91; K. Whitmire, *J. Coord. Chem.*, *17* (1988) 95.

2 R.D. Adams, J.E. Babin, J. Estrada, J-G. Wang, M.B. Hall and A.A. Low, *Polyhedron*, *8* (1989) 1885.

3 P. Mathur, B.H.S. Thimmappa and A.L. Rheingold, *Inorg. Chem.*, *29* (1990) 4658; P. Mathur, Md. M. Hossain and R.S. Rashid, *J. Organomet. Chem.*, *448* (1993) 211.

4 P. Mathur, Md. M. Hossain and R.S. Rashid, *J. Organomet. Chem.*, *460* (1993) 83.

5 B.F.G. Johnson, J.M. Layer, J. Lewis, A. Martin and P.R. Raithby, *J. Organomet. Chem.*, *429* (1992) C41.

6 P. Mathur, Md. M. Hossain and R.S. Rashid, *J. Organomet. Chem.*, in press.

7 *International Tables for X-ray Crystallography, Vol. IV*, Kynoch Press, Birmingham, UK, 1975.