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Syntheses and X-ray Studies of Ruthenium Clusters Obtained by Reaction of (Alkylthio)alkynes $RC\equiv CSC_2H_5$ ($R = CH_3$, C_6H_5) with $[Ru_3(CO)_{12}]$

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By reaction of $[Ru_3(CO)_{12}]$ with $RC\equiv CSC_2H_5$ ($R = CH_3$, C_6H_5), six types of compounds were obtained: (a) $[Ru_3(CO)_9(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}C\equiv CR)]$ compounds **I** ($R = CH_3$, 30% yield) and **II** ($R = C_6H_5$, 46% yield) were synthesized. Both structures are built on an open Ru_3 triangle and contain two ligands, SC_2H_5 and $C\equiv CR$, resulting from the cleavage of $RC\equiv C\text{–}SC_2H_5$. Crystals of **I** are triclinic, space group $P\bar{1}$, with $a = 9.284(3)$ Å, $b = 9.319(4)$ Å, $c = 14.036(3)$ Å, $\alpha = 83.67(3)°$, $\beta = 72.71(5)°$, $\gamma = 62.28(4)°$, and $Z = 2$. Crystals of **II** are monoclinic, space group *Cc*, with $a = 15.951(9)$ Å, $b = 12.520(4)$ Å, $c = 12.881(4)$ Å, $\beta = 113.20(2)°$, and $Z = 4$. (b) $[Ru_4(CO)_{12}(\mu_2\text{-}SC_2H_5)(\mu_4\text{-}C\equiv CR)]$ compounds **III** ($R = CH_3$) and **IV** ($R = C_6H_5$, 4% yield) were synthesized. Both structures are based on a Ru_4 square plane containing fragments of the thioalkyne. The μ_4-acetylide fragment spans one side of the square plane while the ethylthio group bridges one edge. Crystals of **III** are monoclinic, space group $P2_1/n$, with $a = 9{,}440(3)$ Å, $b = 15.822(1)$ Å, $c = 16.491(2)$ Å, $\beta = 94.24(2)°$, and $Z = 4$. Crystals of **IV** are triclinic, space group $P1$, $a = 17.282(6)$ Å, $b = 9.587(6)$ Å, $c = 9.674(4)$ Å, $\alpha = 61.38(5)°$, $\beta = 100.36(3)°$, $\gamma = 94.63(5)°$, and $Z = 2$. (c) $[Ru_5(CO)_{12}(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)(\mu_2\text{-}C\equiv CCH_3)(\mu_4\text{-}C\equiv CCH_3)]$ compound **V** (13% yield) was made. This structure is based on a Ru_4 square plane sharing an edge with a Ru_3 triangle containing fragments of two thioalkyne molecules. One ethylthio fragment bridges a Ru–Ru bond while the second bridges three ruthenium atoms. One acetylide fragment spans one side of the square plane as for **III** and **IV**, while the second is σ,π-ligated. Crystals of **V** are triclinic, space group $P\bar{1}$, with $a = 10.014(1)$ Å, $b = 10.464(2)$ Å, $c = 16.179(3)$ Å, $\alpha = 91.50(3)°$, $\beta = 101.52(2)°$, $\gamma = 111.37(1)°$, and $Z = 2$. (d) $[Ru_3(CO)_7\{\mu_3\text{-}S(C_2H_5)CC(C_6H_5)C(SC_2H_5)C(C_6H_5)CC(C_6H_5)\}(\mu_2\text{-}SC_2H_5)]$ compound **VI** (3% yield) was synthesized. The structure contains a Ru_3 chain and a pentasubstituted cyclopentadienyl μ_3-ligand which resulted from the coupling of two ligand molecules and one acetylide fragment. Crystals of **VI** are monoclinic, space group $P2_1/n$, with $a = 20.447(6)$ Å, $b = 17.924(8)$ Å, $c = 10.619(3)$ Å, $\beta = 100.86(4)°$, and $Z = 4$. (e) $[Ru_5(CO)_{13}(\mu_2\text{-}SC_2H_5)_2\{\mu_5\text{-}C(C_6H_5)CC(C_6H_5)C\}]$ compound **VII** (4.5% yield) was synthesized. The unsymmetrical structure is based on a ruthenium triangle and two $Ru(CO)_3$ groups attached with bridging fragments of two thioalkyne molecules. Each ethylthio fragment bridges two ruthenium atoms. Both acetylide fragments are coupled in a head to tail manner to yield the $\sigma,\pi\text{-}\mu_5\text{-}C(C_6H_5)CC(C_6H_5)C$ ligand. Crystals of **VII** are triclinic, space group $P\bar{1}$, with $a = 9.279(3)$ Å, $b = 12.318(8)$ Å, $c = 17.921(11)$ Å, $\alpha = 84.31(4)°$, $\beta = 83.15(4)°$, $\gamma = 69.43(4)°$, and $Z = 2$. (f) $[Ru_6(CO)_{14}(\mu_2\text{-}SC_2H_5)_2\{\mu_6\text{-}C(CH_3)CCC(CH_3)\}]$ compound **VIII** (2% yield) was synthesized. The structure is based on a rhombic six-atom-raft geometry containing fragments of two thioalkyne molecules. Each ethylthio group bridges one Ru–Ru bond. The acetylide fragments are coupled tail to tail, forming a $C(CH_3)CCC(CH_3)$ $\sigma,\pi\text{-}\mu_6$-ligand. Crystals of **VIII** are monoclinic, space group $P2_1/n$, with $a = 20.815(3)$ Å, $b = 19.254(8)$ Å, $c = 8.692(8)$ Å, $\beta = 92.49(2)°$, and $Z = 4$.

Introduction

The reaction of phosphinoalkynes with metal carbonyls, particularly with ruthenium carbonyl, has produced a large variety of compounds.[1] This chemistry is characterized by the easy cleavage of the carbon–phosphorus bond and by the formation of polynuclear ruthenium species. Few references to ruthenium compounds with aminoalkynes have been documented in the literature. No cleavage of the carbon–nitrogen bond has been observed.[2]

It was tempting to look at the case of thioalkynes in order to investigate the possible influence of the electronegativity and/or of the size of the heteroatom on the stability of the C–heteroatom bond in reactions with metal carbonyls.

In a previous publication,[3a] we already noted the easy cleavage of the carbon–sulfur bond in reactions of a mono(ethylthio)-alkyne with iron carbonyls. The alkyne leads to an alkynyl radical and an ethylthio radical which are ligated to a polynuclear skeleton. For example, $[Fe_4(CO)_{12}(\mu_4\text{-}C\equiv CCH_3)(\mu_2\text{-}SC_2H_5)]$ was obtained by reacting $[Fe_2(CO)_9]$ with $CH_3C\equiv CSC_2H_5$ at 25 °C. On one edge of the square planar tetranuclear cluster SC_2H_5 bridges two iron atoms, behaving as a three-electron donor; the acetylide spans

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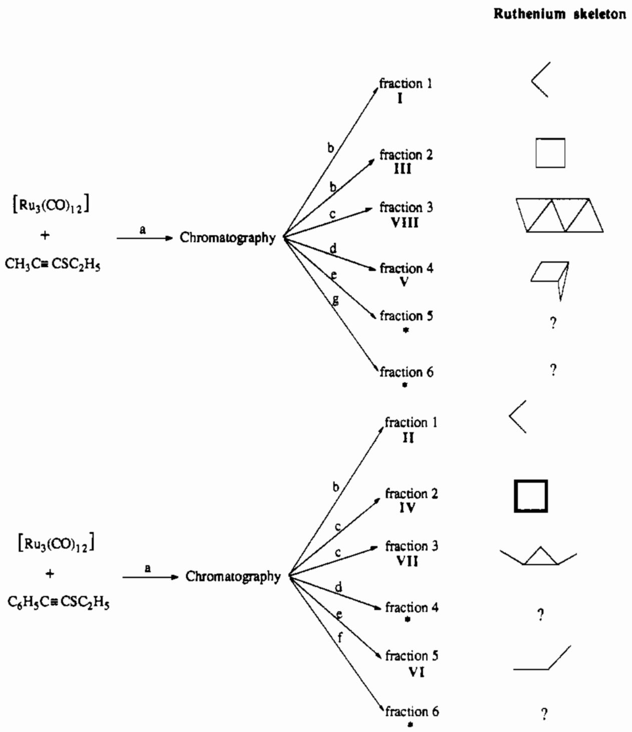
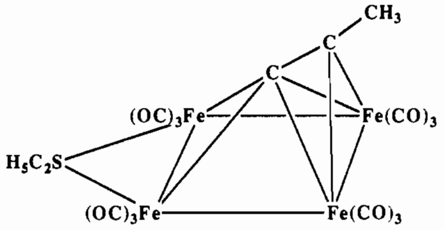
Scheme 1



a : molar ratio 1:1, refluxed hexane, 3 hours
b : eluent 95/5 C_7H_{16}/CH_2Cl_2
c : eluent 90/10 C_7H_{16}/CH_2Cl_2
d : eluent 85/15 C_7H_{16}/CH_2Cl_2
e : eluent 75/25 C_7H_{16}/CH_2Cl_2
f : eluent 60/40 C_7H_{16}/CH_2Cl_2
g : eluent 50/50 C_7H_{16}/CH_2Cl_2
• : fractions not yet fully characterized
The number of the compounds is shown for each fraction

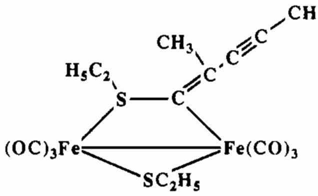
the surface of the tetrairon plane and behaves as a five electron donor (structure **1**).



$[Fe_4(CO)_{12}(\mu\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CCH_3)]^{3a}$

1

The complex $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)\{\mu\text{-}S(C_2H_5)C[{=}C(CH_3)\text{-}C{\equiv}CCH_3]\}]$ illustrates another type of reaction. This complex contains one ethylthio bridge while the acetylide fragment combined with another thioalkyne molecule to yield the bridging ligand $S(C_2H_5)C[{=}C(CH_3)C{\equiv}CCH_3]$ (structure **2**).



$[Fe_2(CO)_6(\mu\text{-}SC_2H_5)\{\mu\text{-}S(C_2H_5)C[{=}C(CH_3)(C{\equiv}CCH_3)]\}]^{3a}$

2

In the case of iron carbonyls, coupling of two thioalkyne molecules as well as C–S bond cleavage were observed. The combination of these two features led us to increase in a controlled manner the nuclearity from two to five iron atoms.[3b]

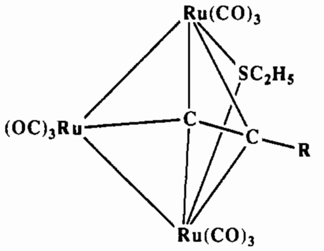
This paper reports the synthesis and the characterization of eight clearly identified compounds (six different structures) obtained from the reaction of two thioalkynes with $[Ru_3(CO)_{12}]$. Two compounds are triangular with an open edge, and two others are tetranuclear based on a square plane. Another open triangular compound presents an unusual structure; this synthesis involved three thioalkyne molecules. Two other products are pentanuclear with two different geometries; one is a triangular prism with one sulfur atom in the frame, and the other is a Ru_3 triangle with two $Ru(CO)_3$ moieties attached via bridging groups. The eighth product is a hexanuclear raft-rhombic compound.

Results and Discussion

The reaction of $[Ru_3(CO)_{12}]$ with thioalkynes $RC{\equiv}CSC_2H_5$ ($R = CH_3$, C_6H_5) leads to six products for each thioalkyne (Scheme 1), eight of which have been characterized. The same features observed with iron carbonyls, i.e. C–C coupling and C–S cleavage, were found in the complexes described hereunder, $[Ru_3(CO)_9(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}C{\equiv}CR)]$ compounds **I** ($R = CH_3$) and **II** ($R = C_6H_5$), $[Ru_4(CO)_{12}(\mu_2\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CR)]$ compounds **III** ($R = CH_3$) and **IV** ($R = C_6H_5$), $[Ru_5(CO)_{12}(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)(\mu_2\text{-}C{\equiv}CCH_3)(\mu_4\text{-}C{\equiv}CCH_3)]$ compound **V**, $[Ru_3(CO)_7\text{-}\{\mu_3\text{-}S(C_2H_5)CC(C_6H_5)C(SC_2H_5)C(C_6H_5)CC(C_6H_5)\}(\mu_2\text{-}S\text{-}C_2H_5)]$ compound **VI**, $[Ru_5(CO)_{13}(\mu_2\text{-}SC_2H_5)_2\{\mu_5\text{-}C(C_6H_5)CC\text{-}(C_6H_5)C\}]$ compound **VII**, and $[Ru_6(CO)_{14}(\mu_2\text{-}SC_2H_5)_2\{\mu_6\text{-}C(CH_3)CCC(CH_3)\}]$ compound **VIII**.

Compound I, $[Ru_3(CO)_9(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}C{\equiv}CCH_3)]$, and Compound II, $[Ru_3(CO)_9(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}C{\equiv}CC_6H_5)]$. The trinuclear complexes **I** and **II**, $[Ru_3(CO)_9(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}C{\equiv}CR)]$ ($R = CH_3$, C_6H_5) are based on a Ru_3 triangle with an open edge (Figure 1). There are only two Ru–Ru bonds, equal to 2.843(1) and 2.847(1) Å for $R = CH_3$ and to 2.8391(8) and 2.8524(8) Å for $R = C_6H_5$. Each ruthenium atom is ligated to three carbonyl groups. The two ruthenium atoms of the open edge are separated by 3.337 Å for $R = CH_3$ and 3.357 Å for $R = C_6H_5$ and connected by two bridging groups, C_2H_5S and $RC{\equiv}C$. The carbon–sulfur bond linking the ethylthio and the acetylide groups of the reactant $RC{\equiv}CSC_2H_5$ was broken. The propynyl or phenylethynyl group is actually ligated to the three ruthenium atoms. It is bonded to Ru(1) and Ru(2) by the four π electrons and to Ru(3) by a σ bond involving the acetylide C(1) atom previously bound to sulfur. The $C(1){\equiv}C(2)$ bond now is equal to 1.29(1) Å for $R = CH_3$ and to 1.28(1) Å for $R = C_6H_5$.

Compounds I and II



$[Ru_3(CO)_9(\mu\text{-}SC_2H_5)(\mu_3\text{-}C{\equiv}CR)]$

Similar structures were observed by Carty et al.[1d] and by Aime et al.[4] In the first, the isoelectronic $P(C_6H_5)_2$ group replaces the SC_2H_5 group and the acetylide fragment $C{\equiv}CC(CH_3)_3$ contains a bulky *tert*-butyl group. In the second, the open edge of the triangle is bridged by a chloride atom and the acetylide $C{\equiv}CC_6H_5$ is the same as in compound **II**. A comparison of the distances in the four open triangles, taking into account experimental errors,

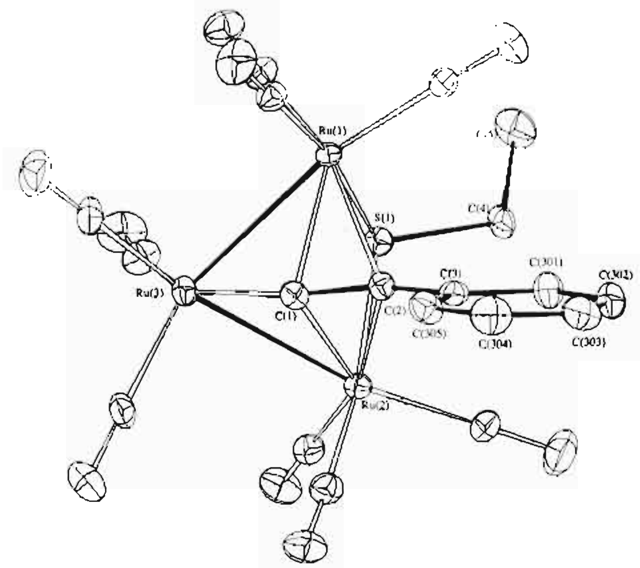


Figure 1. Molecular structure of compound **II**, $[Ru_3(CO)_9(\mu\text{-}SC_2H_5)(\mu_3\text{-}C{\equiv}CC_6H_5)]$.

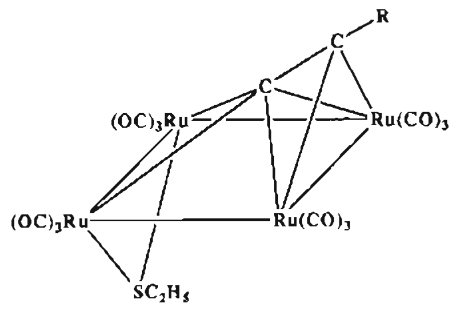
shows a slight deviation from a perfectly symmetrical isosceles triangle with increasing bulk of radicals.

The SC_2H_5 group is a 3-electron donor and the C≡CR group is a 5-electron donor. Thus, compounds **I** and **II** are characterized by the 50 valence electrons expected for a cluster based on an open triangle, i.e. 48 + 2, as for compounds described by Carty[1d] and by Aime.[4]

Compound III, $[Ru_4(CO)_{12}(\mu_2\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CCH_3)]$, and Compound IV, $[Ru_4(CO)_{12}(\mu_2\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CC_6H_5)]$. A similar compound has been previously observed with $CH_3C{\equiv}CSC_2H_5$ and iron carbonyl,[3a] i.e. $[Fe_4(CO)_{12}(\mu_2\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CCH_3)]$ (structure 1).

Structures of compounds **III** and **IV** have been determined by X-ray methods. These tetranuclear compounds are based on a square of Ru–Ru bonds, and each ruthenium is ligated to three terminal carbonyl groups (Figure 2). The square is planar within experimental error with a deviation from planarity of ±0.01 Å for the four atoms in both cases, R = CH_3 or C_6H_5. The ethylthio group bridges Ru(1) and Ru(2). The acetylide $C{\equiv}CCH_3$ or $C{\equiv}CC_6H_5$ spans the surface of the square. The two π electron pairs of the C≡C group are donated to Ru(3) and Ru(4), respectively. The terminal carbon C(1) is bonded to Ru(1) and Ru(2). If C–S cleavage of the thioalkyne $RC{\equiv}C\text{-}SC_2H_5$ leaves one electron on each of the C and S atoms, then the two Ru(1)–C(1) and Ru(2)–C(1) bonds may be described, in a simplified approach, as a three center two electron bond. To support this view, let us compare structures of compounds **II** and **IV**. They each contain an acetylide, but the terminal carbon is σ-bonded to one ruthenium in **II** and to two rutheniums in **IV**. The two distances Ru(1)–C(1) = 2.14(1) Å and Ru(2)–C(1) = 2.12(1) Å of compound **IV** are significantly longer than the Ru(3)–C(1) distance of compound **II**, which is equal to 1.927(3) Å. The ligation of the acetylide ligand in compounds $[Ru_3(CO)_9\{\mu_2\text{-}P(C_6H_5)_2\}\{\mu_3\text{-}C{\equiv}CC(CH_3)_3\}]$[1d] and $[Ru_5(CO)_{13}\{\mu_2\text{-}P(C_6H_5)_2\}(\mu_4\text{-}C{\equiv}CC_6H_5)]$,[1e,5] described by Carty et al., presents the same characteristics, since distances between the terminal acetylide carbon atom with ruthenium atoms equivalent to those of **IV** are 1.960 Å for the Ru_3 compound and 2.114 and 2.095 Å for the Ru_5 compound. Of course, this view is a very simplified approach since the bonding scheme of the cluster is not treated as a whole, as has been carried out by Saillard et al.;[6] i.e. as a face-capped cluster incorporating the C≡CR fragment into the skeleton. Bonds are viewed through a "localized" description, taking the C≡CR group as donating its two π electron pairs to two ruthenium atoms and using the remaining electron of the terminal carbon atom for other Ru–C bonds.

Compounds III and IV



$[Ru_4(CO)_{12}(\mu\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CR)]$

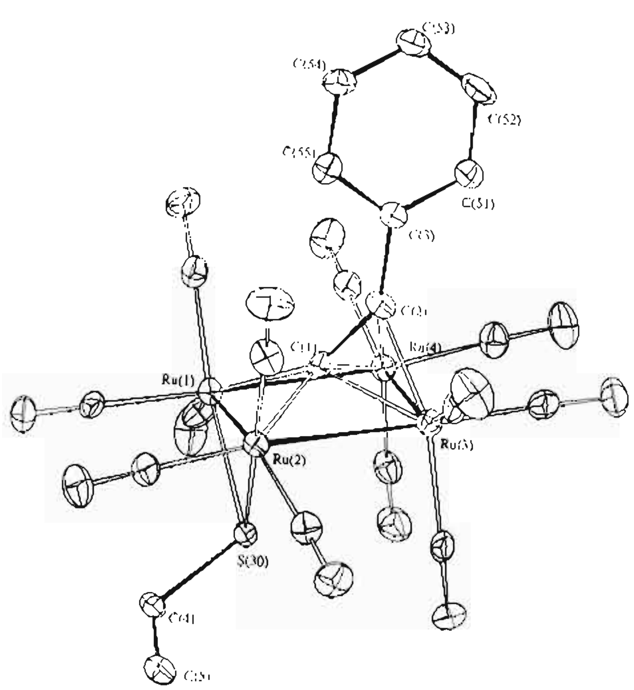


Figure 2. Molecular structure of compound **IV**, $[Ru_4(CO)_{12}(\mu\text{-}SC_2H_5)\text{-}(\mu_4\text{-}C{\equiv}CC_6H_5)]$. The asymmetrical unit contains two independent molecules.

Square planar tetranuclear clusters are well-known.[7,8] Whether the skeleton is homo- or heterometallic, the cluster is usually capped by two ligands, e.g., $[Fe_4(CO)_{11}\{P(C_6H_4CH_3)\}_2]$,[8a,b] $[Ru_4(CO)_{11}\{P(C_6H_5)\}_2]$,[8c] $[Ag_2Au_2(C{\equiv}CC_6H_5)_4\{P(C_6H_5)_3\}_2]$,[8d] $[Os_4S(CO)_{12}(C{=}CHC_6H_5)]$,[8e] $[Co_2Fe_2(CO)_{11}\{(PC_6H_5)\}_2]$,[8a] and $[Fe_4(CO)_{11}\{P(OCH_3)_3\}(PC_6H_4CH_3)_2]$.[8f,g] Compounds **III** and **IV** and the similar iron compound have an uncommon feature, since only one of the square faces is capped by an acetylide ligand.

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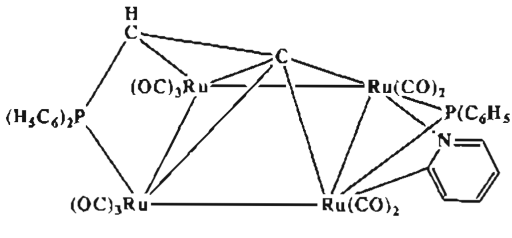
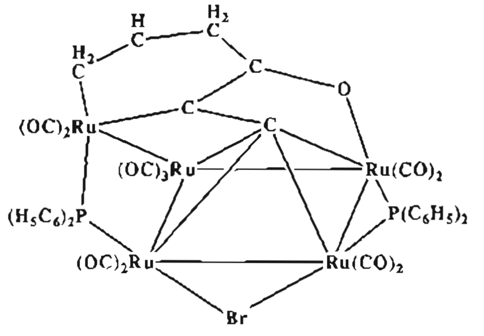
This feature was observed by Bruce et al.[1g,9] for the compound $[Ru_4\{\mu_4\text{-}CCHP(C_6H_5)_2)\}\{\mu_2\text{-}P(C_6H_5)_2\}(\mu_2\text{-}NC_5H_4)(CO)_{10}]$, although the Ru_4 core is a rhombus bent about a diagonal, and for a more complicated pentanuclear complex $[Ru_5\{\mu_5\text{-}CCC(O)(CH_2\text{-}CH{=}CH_2\}\{\mu_2\text{-}P(C_6H_5)_2\}_2(\mu_2\text{-}Br)(CO)_{11}]$ (structures **3a,b**).



$[Ru_4(CO)_{10}\{\mu_4\text{-}CCHP(C_6H_5)_2\}\{\mu\text{-}P(C_6H_5)_2\}(\mu\text{-}NC_5H_4)]$ [1g,9]

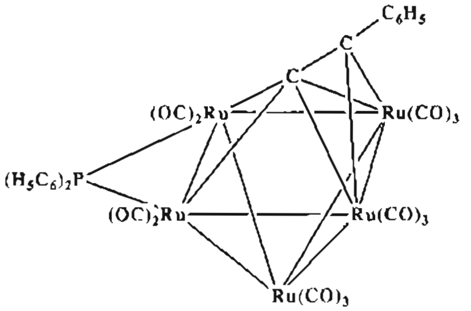
3a



$[Ru_5(CO)_{11}\{\mu_5\text{-}CCC(O)CH_2CH{=}CH_2\}\{\mu\text{-}P(C_6H_5)_2\}(\mu\text{-}Br)]$ [1g,9]

3b

It is worthwhile to compare carefully the structures of **III** and **IV** with $[Ru_5(CO)_{13}\{\mu_2\text{-}P(C_6H_5)_2\}(\mu_4\text{-}C{\equiv}CC_6H_5)]$ (structure **4**)



$[Ru_5(CO)_{13}\{\mu\text{-}P(C_6H_5)_2\}(\mu_4\text{-}C{\equiv}CC_6H_5)]$ [1c,5]

4

prepared by Carty et al.[1c,5] This pentanuclear compound contains a μ_2-PR_2 bridge instead of the isoelectronic μ_2-SR bridge; also, a fifth ruthenium atom belonging to a $Ru(CO)_3$ group caps the Ru_4 square plane, building a Ru_5 square pyramid. The acetylide spans its base. There is a difference in the position of the bridging heteroatom with respect to the Ru_4 plane. In compounds **III** and **IV**, the dihedral angle between plane Ru(1)–S–Ru(2) and the Ru_4 mean square plane is 94.7° in the case of R = CH_3 and 93.7° in the case of R = C_6H_5. The same dihedral angle for the Ru_5 pentanuclear compound is 170.7°. The phosphorus position is clearly related to the presence of the $Ru(CO)_3$ group capping the Ru_4 square plane. The sulfur atom might have occupied the phosphorus position, but it seems to prefer a position under the square plane.

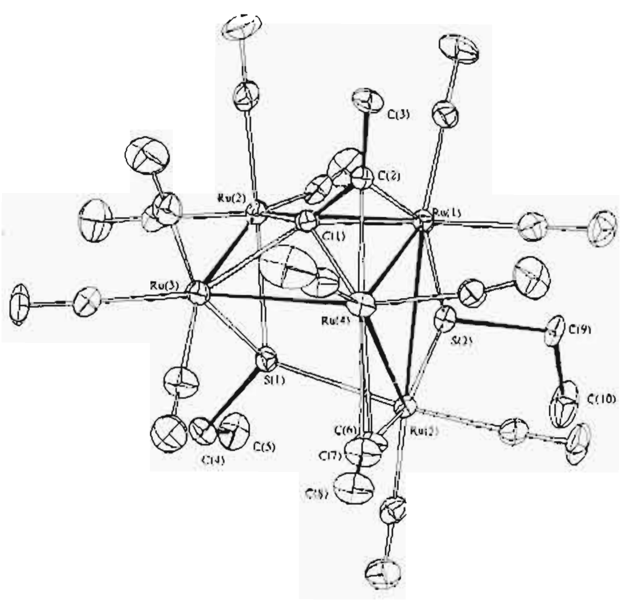
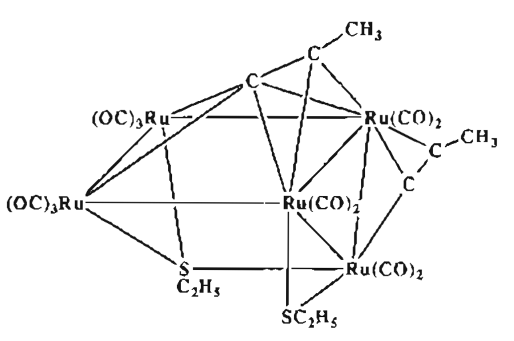


Figure 3. Molecular structure of compound V, $[Ru_5(CO)_{12}(\mu\text{-}C{\equiv}CCH_3)(\mu\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CCH_3)]$.

$[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)\{\mu_2\text{-}P(C_6H_5)_2\}]$[1c,5] has 74 electrons in agreement with the EAN rule for a Ru_5 square pyramid. The formal transformation of closo Ru_5C into nido Ru_4C should imply withdrawal of $Ru(CO)_2$, which does not change the number of skeletal electron pairs. Actually, the two-electron donor μ_4-$Ru(CO)_3$ of $[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)\{\mu_2\text{-}P(C_6H_5)_2\}]$[1c,5] is replaced by two CO, since the formulas of **III** and **IV** are $[Ru_4(CO)_{12}(\mu_4\text{-}C{\equiv}CR)(\mu_2\text{-}SC_2H_5)]$. This increases the number of skeletal electron pairs by 1, leading to 8 pairs. The PSEP rule is not applicable, but the inert-gas rule for compounds **III** and **IV** is fulfilled since they have 64 valence electrons. They are described as formally deriving from butterfly geometry by breaking the metal–metal hinge.[7] There are other examples of compounds of that type such as $[Ag_2Au_2(C{\equiv}CC_6H_5)_4\{P(C_6H_5)_3\}_2]$,[7,8d] $[Os_4S(CO)_{12}(C{=}CHC_6H_5)]$,[7,8e] $[Co_2Fe_2(CO)_{11}\{(PC_6H_5)\}_2]$,[7,8a] and $[Fe_4(CO)_{11}\{P(OCH_3)_3\}(PC_6H_4CH_3)_2]$.[7,8f,g] None of them may be described by the PSEP rule, but they all have 64 valence electrons following the EAN rule for a M_4 square plane.

Compound V, $[Ru_5(CO)_{12}(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)(\mu_2\text{-}C{\equiv}CCH_3)(\mu_4\text{-}C{\equiv}CCH_3)]$. The metallic framework of this pentanuclear compound (Figure 3) is made of a square plane and of a triangle sharing an edge, with a dihedral angle of 87°. The square planar moiety bears a μ_4-$CCCH_3$ ligand, and the μ_3-SC_2H_5 ligand bridges

Compound V



$[Ru_5(CO)_{12}(\mu\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)(\mu\text{-}C{\equiv}CCH_3)(\mu_4\text{-}C{\equiv}CCH_3)]$

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(9) (a) Adams, C. J.; Bruce, M. I.; Liddell, M. J.; Nicholson, B. K. *J. Organomet. Chem.* **1991**, *420*, 105. (b) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *445*, 211.

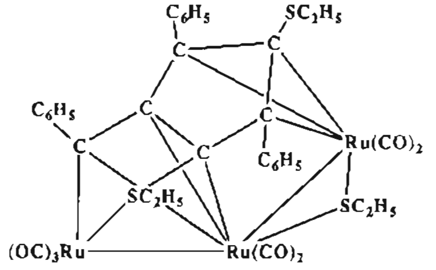
the edge opposed to the shared edge. The square plane is identical to that in compound III except that the shared edge is elongated, i.e. 2.972(1) Å for compound V instead of 2.796(2) Å for compound III. The two other sides of the Ru_3 triangle are even longer: Ru(1)–Ru(5) = 2.983(1) Å and Ru(4)–Ru(5) = 3.051(1) Å. They are bridged respectively by a second SC_2H_5 ligand and a second acetylide which is σ bonded to Ru(5) and π bonded to Ru(4). In addition, Ru(5) receives a lone pair from S(1), so that this sulfur is tetrahedrally surrounded, with three Ru–S(1) distances equal to 2.384(3), 2.442(3), and 2.401(3) Å. Hence compound V may be also described as a triangular prismatic Ru_5S cluster. Indeed, the dihedral angle between the two bases of the prism, i.e. the Ru(1)–Ru(4)–Ru(5) plane and the Ru(2)–Ru(3)–S(1) plane, is equal to 15.3°.

The formula $[Ru_5(CO)_{12}(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)(\mu_2\text{-}C{\equiv}CCH_3)(\mu_4\text{-}C{\equiv}CCH_3)]$ corresponds to 80 electrons. Only one of the two sulfur atoms has a free lone pair. The μ_4-acetylide is a 5-electron donor and the μ_2-acetylide is a 3-electron donor. If the compound Ru_5C were considered as derived from a Ru_6 triangular prism where a metal carbonyl fragment has been replaced by a nonmetallic isolobal fragment, one should get 90 − 10 = 80 electrons.[7] This is consistent with the number of electrons found. It has been mentioned above that this compound may also be viewed as a cluster with a square plane (64 electrons) and a triangle (48 electrons) which share one edge. The electron count would then be 64 + 48 − 34 = 78.[7] As a consequence, compound V is better described as a Ru_5S cluster for which the inert gas rule is followed.

It should be noted that compound V was also obtained by reacting $[Ru_3(CO)_{12}]$ with compound IV in refluxing hexane for 24 h. The purpose of this reaction was to prepare the pentanuclear Ru_5C octahedral compound structurally identical to $[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)\{\mu_2\text{-}P(C_6H_5)_2\}]$ prepared by Carty et al.[1c,5] It seems that the octahedral geometry is not possible in our case, perhaps due to the existence of the lone pair of the sulfur atom which easily ligates one ruthenium atom.

Compound VI, $[Ru_3(CO)_7\{\mu_3\text{-}S(C_2H_5)CC(C_6H_5)C(SC_2H_5)C(C_6H_5)CC(C_6H_5)\}(\mu_2\text{-}SC_2H_5)]$. The crystal used for X-ray analysis did not provide data good enough to give accurate interatomic distances. Structure VI (Figure 4) is based on an open edge triangular Ru_3 cluster with an angle Ru(3)–Ru(2)–Ru(1) equal to 131.3(2)°, much larger than in compounds I and II, 71.81(3) and 72.30(2)°. The Ru(2)–Ru(3) bond is bridged by an ethylthio group. The organic ligand bound to the three ruthenium atoms results from the coupling of two $C_6H_5C{\equiv}CSC_2H_5$ molecules and of $C_6H_5C{\equiv}C$ acetylide. This ligand may be viewed as a cyclopentadienyl C(3)–C(7)–C(8)–C(11)–C(12) radical pentasubstituted by two phenyl groups linked to C(8) and C(12), by two ethylthio groups linked to C(7) and C(11), and by a benzylidyne CC_6H_5 fragment linked to C(3). Thus the two alkyne molecules coupled in a head to tail manner. The C(4) carbon of the benzylidyne fragment bridges the Ru(1)–Ru(2) bond. Ru(1) is also bonded to S(2) linked to the C_5 ring. The C(4)–C(3)–C(7) fragment is π bonded to Ru(2). Although standard deviations of the C(4)–C(3) = 1.47(6) and C(3)–C(7) = 1.54(5) Å distances are large, these bonds are characteristic of an allylic group, in accord with the three corresponding Ru(2)–C distances, i.e. 2.26(4), 2.29(4), and 2.12(4) Å for C(4), C(3), and C(7), respectively. Ru(3) is bonded to C(8), C(11), and C(12). Similarly the observed C–C and Ru(3)–C distances, taking into account standard deviations, would suggest that C(8)–C(11)–C(12) also behaves as an allylic fragment. Thus the ligand could be described as a $\kappa^2{:}\kappa^3{:}\kappa^3$.

Compound VI



$[Ru_3(CO)_7\{\mu_3\text{-}S(C_2H_5)CC(C_6H_5)C(SC_2H_5)C(C_6H_5)CC(C_6H_5)\}(\mu\text{-}SC_2H_5)]$

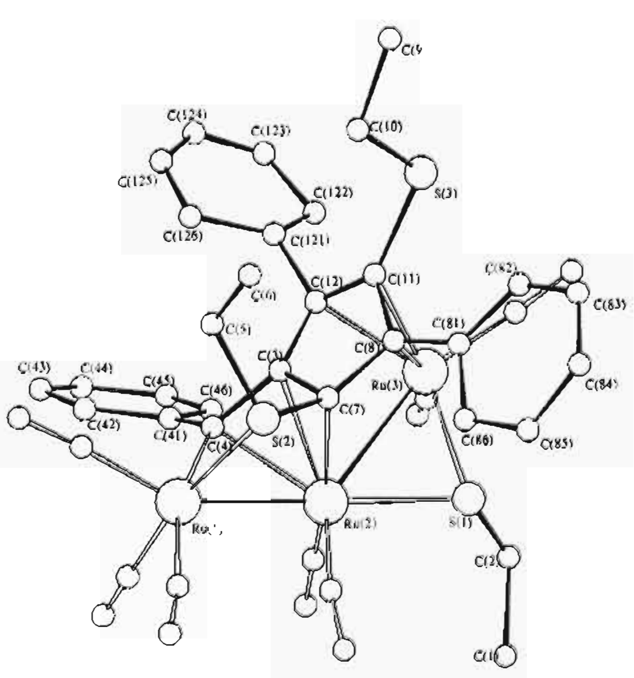


Figure 4. Molecular structure of compound VI, $[Ru_3(CO)_7(\mu\text{-}SC_2H_5)\{\mu_3\text{-}S(C_2H_5)CC(C_6H_5)C(SC_2H_5)C(C_6H_5)CC(C_6H_5)\}]$.

Each ruthenium atom has 18 electrons and the total electron count is 50 electrons, as expected for a chain of three metal atoms, i.e. an open triangle, and as is also found for compounds I and II.

Compound VII, $[Ru_5(CO)_{13}(\mu_2\text{-}SC_2H_5)_2\{\mu_5\text{-}C(C_6H_5)CC(C_6H_5)C\}]$. This compound was obtained as red-brown crystals from the fourth chromatographed fraction in the case of phenyl(ethylthio)ethyne. The maximum peak at *m/z* 1196 deduced from mass spectrometry suggested a pentaruthenium compound, with a possible molecular formula $[Ru_5(CO)_{13}L_2]$, where L is $C_6H_5C{\equiv}CSC_2H_5$. The infrared spectrum exhibited a band at 1837 cm^{-1} consistent with a bridging carbonyl group. The ^1H NMR spectrum presented, besides multiplets typical of phenyl groups (around 7 ppm), peaks related to two nonequivalent ethyl groups. An X-ray analysis was then carried out with very tiny crystals which unfortunately limited the precision of interatomic distances.

Structure VII is built on a ruthenium triangle with two $Ru(CO)_3$ moieties attached via bridging groups (Figure 5). Both alkyne molecules were broken, giving two ethylthio μ_2-bridging groups and two acetylide groups which combined into a $C(C_6H_5)CC(C_6H_5)C$ ligand in a head to tail mode. The ligand thus may be described as deriving from an ethynylvinylidene. The structure is highly unsymmetrical. Each ethylthio group is ligated to one of the $Ru(CO)_3$ groups. One ethylthio ligand bridges two bonded Ru(1)–Ru(2) atoms (2.788(3) Å), while the other is ligated to two nonbonded Ru(3) and Ru(5) atoms (3.691(3) Å). Note that a CO group bridges the Ru(4)–Ru(2) bond, in agreement with the infrared band at 1837 cm^{-1}.

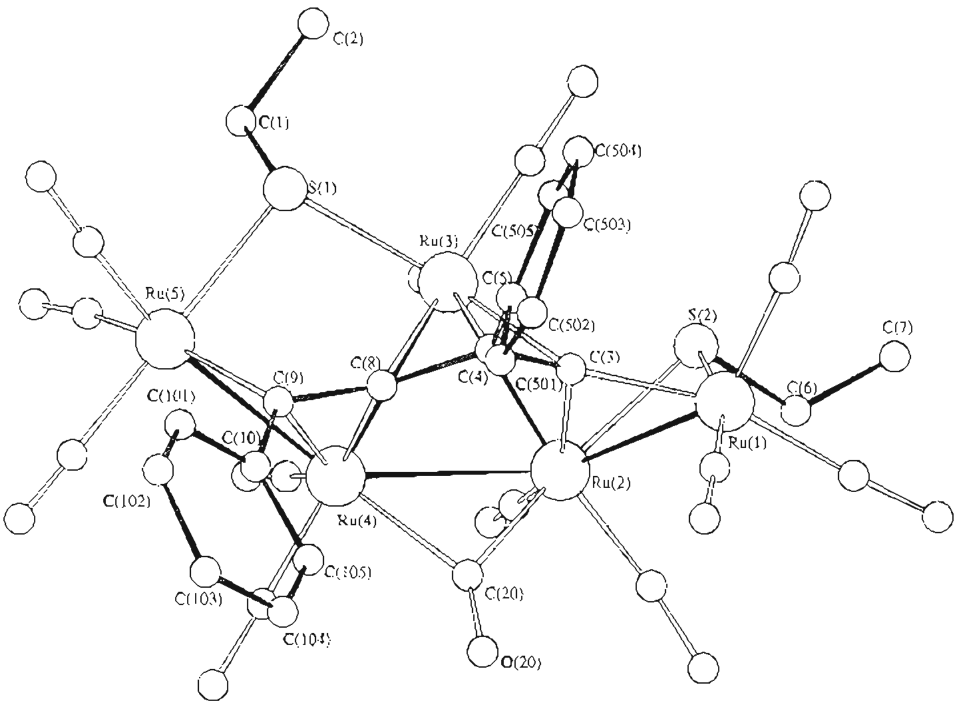
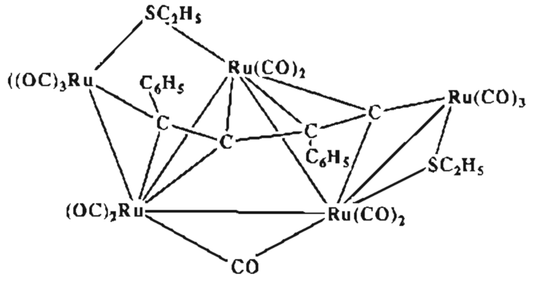


Figure 5. Molecular structure of compound **VII**, $[Ru_5(CO)_{13}(\mu\text{-}SC_2H_5)_2\{\mu_5\text{-}C(C_6H_5)CC(C_6H_5)C\}]$.

Compound VII



$[Ru_5(CO)_{13}(\mu\text{-}SC_2H_5)_2\{\mu_5\text{-}C(C_6H_5)CC(C_6H_5)C\}]$

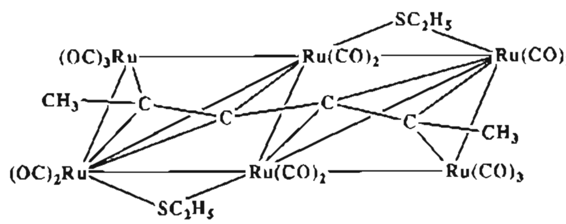
The ligand $C(C_6H_5)CC(C_6H_5)C$ is σ,π-ligated to the five ruthenium atoms. It is first triyl ligated by its terminal carbon atoms, being bonded to Ru(5) by its C(9) end (2.04(2) Å) and to Ru(1) and Ru(2) by its C(3) end (1.98(2), 2.16(2) Å). Second, the ligand skeleton C(9)–C(8)–C(4)–C(3), with C–C distances equal to 1.35(3), 1.48(4), and 1.36(3) Å, respectively, may be described as π-bonded to Ru(4) by C(9)–C(8) (Ru–C = 2.25(2) and 2.05(3) Å) and to Ru(3) by C(4)–C(3) (Ru–C = 2.20(3) and 2.17(2) Å). Indeed, it is preferred to describe the C(8)–Ru(3) bond as a σ bond, as is supported by the longer C(4)–C(8) distance. Compound **VII** is a 80-electron compound, in agreement with the structure.

It must be underlined that a similar structure has not yet been identified when the synthesis has been carried out with (ethylthio)propyne, and similarly the pentanuclear structure of compound **V** has not been found with (ethylthio)phenylethyne.

Compound VIII, $[Ru_6(CO)_{14}(\mu_2\text{-}SC_2H_5)_2\{\mu_6\text{-}C(CH_3)CCC(CH_3)\}]$. The chromatographic separation of the reaction mixture of $[Ru_3(CO)_{12}]$ with $CH_3C{\equiv}CSC_2H_5$ yielded a third fraction which gave very dark brown crystals of compound **VIII**. The molecular peak of the mass spectrum was located at *m/z* 1200, suggesting a hexanuclear compound. A possible formula would be $[Ru_6(CO)_{14}L_2]$, where L is $CH_3C{\equiv}CSC_2H_5$.

The ^1H NMR spectrum exhibited peaks characteristic of one methyl group and one ethyl group. To be consistent with the results of mass spectrometry, one had to assume two equivalent methyl and two equivalent ethylthio groups.

Compound VIII



$[Ru_6(CO)_{14}(\mu\text{-}SC_2H_5)_2\{\mu_6\text{-}C(CH_3)CCC(CH_3)\}]$

The X-ray analysis (Figure 6) of **VIII** showed a hexaruthenium structure in agreement with mass spectrometry. The metal skeleton has a rhombic six-atom-raft geometry. Dihedral angles between the four coupled ruthenium triangles have the following values: Ru(1)Ru(2)Ru(6) with Ru(2)Ru(5)Ru(6) = 150.5°, Ru(2)Ru(5)Ru(6) with Ru(2)Ru(3)Ru(5) = 160.7°, and Ru(2)Ru(3)Ru(5) with Ru(3)Ru(4)Ru(5) = 149.7°.

Each of the two internal triangles has an external edge bridged by an ethylthio group; these ethylthio groups result from C–S alkyne cleavage. The dihedral angles between these Ru_3 triangles and the corresponding Ru_2S triangles are 70.5° for the $S(1)C_2H_5$ group and 70.3° for the $S(2)C_2H_5$ group, respectively. The two acetylide fragments coupled to yield a hexa-2,4-diyne, the four central C(2)C(3)C(4)C(5) carbon atoms of which are respectively σ-bonded to Ru(1), Ru(2), Ru(5), and Ru(4). In addition, this ligand is π-bonded to Ru(6) by C(2)–C(3) and to Ru(3) by C(4)–C(5). All Ru–C distances support this description quite well.

Note that the coupling of the acetylide fragments occurred in the opposite manner with respect to that observed for compound **VII**, i.e. C(R)CCC(R) for compound **VIII** and C(R)CC(R)C for compound **VII**.

The electron count for the rhombic-raft-geometry is known to be 90 electrons.[7] Compound **VIII** is a 90-electron compound.

Other examples of such rhombic geometry are known. Some of them correspond to 90 electrons.[7,10] For instance, $[HCuRu_5(CO)_8\{P(C_6H_5)_3\}]$ has been described by Evans et al.;[10a] the dihedral angles between triangles are equal to 159.1, 155.2, and 154.8°, which is not very different from those observed in

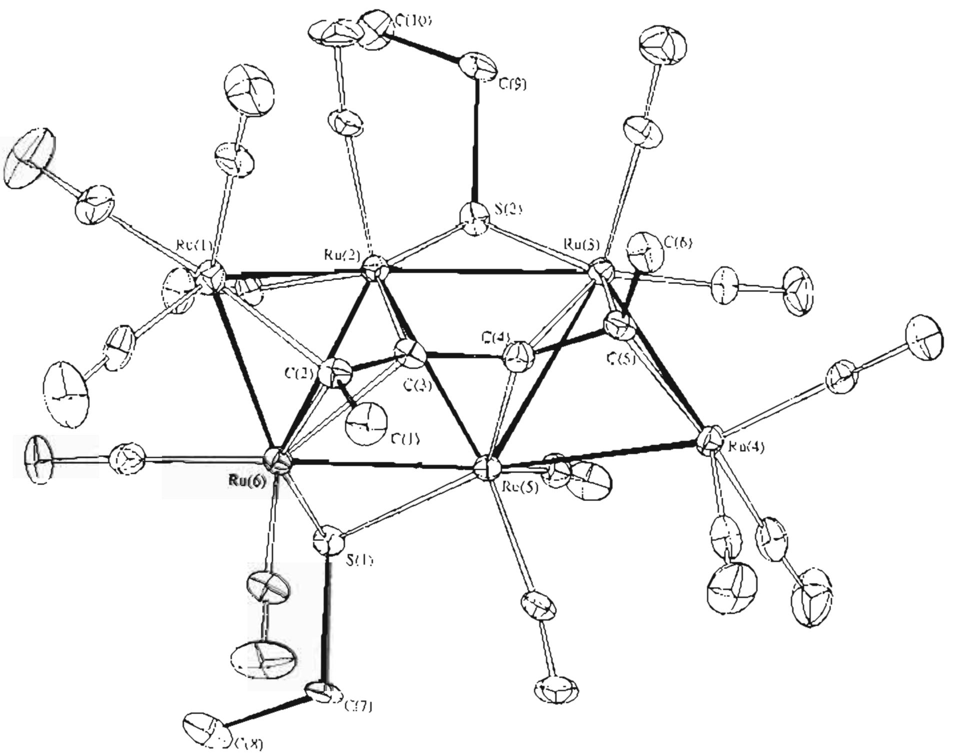


Figure 6. Molecular structure of compound VIII, $[Ru_6(CO)_{14}(\mu\text{-}SC_2H_5)_2\{\mu_6\text{-}C(CH_3)CCC(CH_3)\}]$.

compound VIII. In the case of $[Os_6S(CO)_{19}]$,[10b] the four triangles have a common vertex, and the dihedral angle of the two internal triangles is 102.2°. Some other six-atom-raft geometries correspond to 92 valence electrons. This is the case for $[Os_5(CO)_{20}(CCHC_6H_5)]$,[10c] which is constituted of four osmium triangles fused as in compound VIII. However, three of them are coplanar and the fourth makes a dihedral angle of 146° with this plane. Another example of a raft hexanuclear compound is $[H_{16}Cu_2Re_4\{P(CH_3)_2(C_6H_5)\}_8]^{2+}$.[10d] The metallic skeleton of this cation is completely planar, and the compound has only 80 valence electrons.

Remark about the Electron Count for Compounds III and IV. Compounds such as $[Fe_4(CO)_{11}\{P(C_6H_4CH_3)\}_2]$[7,8a,b] or $[Ru_4(CO)_{11}\{P(C_6H_5)\}_2]$[8c] are usually described as M_4P_2 octahedra. They have two phosphinidene ligands, one on each side of the square plane. The PSEP rule[11] may be applied as follows: two 4-electron donors PR, three 2-electron donors $Fe(CO)_3$ or $Ru(CO)_3$, and one 0-electron donor $Fe(CO)_2$ or $Ru(CO)_2$; that is 7 pairs typical of a six vertex closo M_4P_2 structure. On another hand, they all correspond to 62 valence electrons. If those compounds are considered as based on a M_4 square plane, they have 2 electrons fewer than 64 required by the EAN rule.[7] Similarly, with application of the PSEP rule to $[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)\{\mu_2\text{-}P(C_6H_5)_2\}]$,[1e,5] there is one $C{\equiv}CC_6H_5$ 5-electron donor, one $P(C_6H_5)_2$ 3-electron donor, and three $Ru(CO)_3$ 2-electron donors. Seven pairs fit with a six vertex closo Ru_5C structure. The valence electron count leads to 74, which is in agreement with the EAN rule for a Ru_5 square pyramid. The formal transformation of closo Ru_5C into nido Ru_4C structure should imply the withdrawal of $Ru(CO)_2$ without changing the number of skeletal electron pairs. Actually, the two-electron donor μ_4-$Ru(CO)_3$ of $[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)\{\mu_2\text{-}P(C_6H_5)_2\}]$[1e,5] is replaced by two CO, leading to III and IV, $[Ru_4(CO)_{12}(\mu_4\text{-}C{\equiv}CR)(\mu_2\text{-}SC_2H_5)]$. This increases the number of skeletal electron pairs by one and the PSEP rule is no longer applicable. However, the inert gas rule for compounds III and IV is fulfilled. The cluster is indeed characterized by 64 valence electrons, and the metal atoms obey the EAN rule. Square planar compounds such as $[Ag_2Au_2(C{\equiv}CC_6H_5)_4\{P(C_6H_5)_3\}_2]$,[7,8d] $[Os_4S(CO)_{12}(C{=}CHC_6H_5)]$,[7,8e] $[Co_2Fe_2(CO)_{11}\{(PC_6H_5)\}_2]$,[7,8a] and $[Fe_4(CO)_{11}\{P(OCH_3)_3\}(PC_6H_4CH_3)_2]$[7,8f,g] cannot be described by the PSEP rule, but they all have 64 valence electrons following the EAN rule for a square planar structure.

The two compounds $[Ru_4(CO)_{12}(\mu_4\text{-}C{\equiv}CC_6H_5)(\mu_2\text{-}SC_2H_5)]$ (compound IV) and $[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)\{\mu_2\text{-}P(C_6H_5)_2\}]$[1e,5] are rather unique. The first has a nido Ru_4C structure, which does not follow PSEPT but ruthenium atoms obey the EAN rule. The second one has a closo Ru_5C structure which fulfills the PSEP electron count and the EAN rule. It appears that these structures as well as those of compounds I, II, and V–VIII are better rationalized using the EAN rule.

Extended Hückel computations have been carried out for compound IV (see Experimental Section). In the case of $[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CH)(\mu_2\text{-}PH_2)]$, it turned out that the LUMO was 0.88 eV above the HOMO. This large gap would explain the stability of this pentaruthenium compound with 7 pairs of skeleton electrons. Then the case of $[Ru_4(CO)_{12}(\mu_4\text{-}C{\equiv}CH)(\mu_2\text{-}SH)]$ was considered. The LUMO is 2.16 eV above the HOMO, which is itself 0.22 eV above the next occupied energy level. This result is consistent with 12 CO, making a total number of 64 electrons, instead of 11 CO which would then satisfy the PSEP rule, but which would have left empty one energy level 0.12 eV above the last occupied one. Nevertheless there is a difference between these two compounds, i.e. the nature of the heteroatom. In order to take into account this difference, the calculations were carried out from the model $[Ru_4(CO)_{12}(\mu_4\text{-}C{\equiv}CH)(\mu_2\text{-}SH)]$ by replacing the SH group by a PH_2 group. No significant variations occurred since the LUMO is 2.22 eV above the HOMO (instead of 2.16 eV), itself 0.34 eV above the next occupied energy level (instead of 0.22 eV). The electronegativity of the heteroatom does not seem to have any influence.

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(10) (a) Evans, J.; Street, A. C.; Webster, M. *J. Chem. Soc., Chem. Commun.* 1987, 637. (b) Adams, R. D.; Horvath, I. T.; Mathur P. *Organometallics* 1984, *3*, 623. (c) Jeffrey, J. G.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Welch, D. A. *J. Chem. Soc., Chem. Commun.* 1986, 318. (d) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* 1983, *105*, 5137.

(11) Mingos, D. M. P.; Wales, D. J. *Introduction to cluster chemistry*; Prentice Hall International Edition, Prentice Hall: Englewood Cliffs, NJ, 1990.

Table 1. Crystallographic Data for Compounds **II**, **IV**, and **V**

	II	**IV**	**V**
chem formula	$Ru_3C_{19}O_9SH_{10}$	$Ru_4C_{22}O_{12}SH_{10}$	$Ru_5C_{22}O_{12}S_2H_{16}$
a, Å	15.951(9)	17.282(6)	10.014(1)
b, Å	12.520(4)	9.587(6)	10.464(2)
c, Å	12.881(4)	9.674(4)	16.179(3)
α, deg		61.38(5)	91.50(3)
β, deg	113.20(2)	100.36(3)	101.52(2)
γ, deg		94.63(5)	111.37(1)
V, Å^3	2364	1385	1546.6
Z	4	2	2
mol weight	717	902	1041
space group	*Cc*	*P*1	$P\bar{1}$
temp		room temperature	
radiation (λ, Å)		Mo Kα (0.710 69)	
ρ_{calc}, g·cm^{-3}	2.023	1.082	2.25
μ(Mo Kα), cm^{-1}	19.937	11.147	25.413
abs corr		difabs[a]	
R^b	0.026	0.039	0.035
$R_w{}^b$	0.027	0.046	0.043

[a] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, 3156. [b] *R* and R_w are defined as follows: $R = \sum(F_o - F_c)/\sum F_o$. $R_w = [\sum w(F_o - F_c)^2/\sum(F_o)^2]^{1/2}$.

Table 2. Crystallographic Data for Compounds **VI–VIII**

	VI	**VII**	**VIII**
chem formula	$Ru_3C_{37}O_7S_3H_{30}$	$Ru_5C_{33}O_{13}S_2H_{20}$	$Ru_6C_{24}O_{14}S_2H_{16}$
a, Å	20.447(6)	9.279(3)	20.815(3)
b, Å	17.924(8)	12.318(8)	19.254(8)
c, Å	10.619(3)	17.921(11)	8.692(8)
α, deg		84.31(4)	
β, deg	100.86(4)	83.15(4)	92.49(2)
γ, deg		69.43(4)	
V, Å^3	3822	1896	3480
Z	4	2	4
mol weight	985	1193	1198
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
temp		room temperature	
radiation (λ, Å)		Mo Kα (0.710 69)	
ρ_{calc}, g·cm^{-3}	1.661	2.051	2.29
μ(Mo Kα), cm^{-1}	13.489	20.709	26.67
abs corr		difabs[a]	
R^b	0.084	0.070	0.035
$R_w{}^b$	0.0996	0.075	0.039

[a] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, 3156. [b] *R* and R_w are defined as follows: $R = \sum(F_o - F_c)/\sum F_o$. $R_w = [\sum w(F_o - F_c)^2/\sum(F_o)^2]^{1/2}$.

Table 3. Selected Interatomic Distances (Å) and Bond Angle (deg) for Compound **II**

Ru(1)–Ru(3)	2.8391(8)	Ru(2)–Ru(3)	2.8524(8)
Ru(1)–S(1)	2.424(2)	Ru(1)–C(1)	2.239(7)
Ru(1)–C(2)	2.317(7)	Ru(2)–S(1)	2.416(2)
Ru(2)–C(1)	2.213(7)	Ru(2)–C(2)	2.300(7)
Ru(3)–C(1)	1.927(7)	C(1)–C(2)	1.280(9)
Ru(2)–Ru(3)–Ru(1)	72.30(2)		

Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) for Compound **IV**

Ru(1)–Ru(2)	2.803(2)	Ru(1)–Ru(4)	2.884(2)
Ru(2)–Ru(3)	2.877(2)	Ru(3)–Ru(4)	2.796(2)
Ru(1)–S(30)	2.398(4)	Ru(1)–C(1)	2.14(1)
Ru(2)–S(30)	2.391(4)	Ru(2)–C(1)	2.12(1)
Ru(3)–C(1)	2.11(1)	Ru(3)–C(2)	2.12(2)
Ru(4)–C(1)	2.14(1)	Ru(4)–C(2)	2.17(1)
C(1)–C(2)	1.37(2)		
Ru(4)–Ru(1)–Ru(2)	90.13(5)	Ru(3)–Ru(2)–Ru(1)	89.74(5)
Ru(4)–Ru(3)–Ru(2)	90.39(5)	Ru(3)–Ru(4)–Ru(1)	89.73(5)
S(30)–Ru(1)–Ru(2)	54.1(1)	S(30)–Ru(1)–Ru(4)	87.3(1)
C(1)–Ru(1)–Ru(2)	48.5(4)	C(1)–Ru(1)–Ru(4)	47.5(4)
C(1)–Ru(1)–S(30)	80.7(4)	S(30)–Ru(2)–Ru(1)	54.3(1)
S(30)–Ru(2)–Ru(3)	86.4(1)	C(1)–Ru(2)–Ru(1)	49.1(4)
C(1)–Ru(2)–Ru(3)	47.1(4)	C(1)–Ru(2)–S(30)	81.2(4)
C(1)–Ru(3)–Ru(2)	47.2(4)	C(1)–Ru(3)–Ru(4)	49.2(4)
C(2)–Ru(3)–Ru(2)	79.5(4)	C(2)–Ru(3)–Ru(4)	50.0(4)
C(2)–Ru(3)–C(1)	37.9(6)	C(1)–Ru(4)–Ru(1)	47.6(4)
C(1)–Ru(4)–Ru(3)	48.5(3)	C(2)–Ru(4)–Ru(1)	79.9(4)
C(2)–Ru(4)–Ru(3)	48.5(5)	C(2)–Ru(4)–C(1)	37.2(6)
Ru(2)–S(30)–Ru(1)	71.6(1)	Ru(4)–C(1)–Ru(1)	84.9(5)
Ru(2)–C(1)–Ru(1)	82.4(5)	Ru(4)–C(1)–Ru(2)	142.3(8)
Ru(3)–C(1)–Ru(1)	141.1(8)	Ru(4)–C(1)–Ru(3)	82.3(5)
Ru(3)–C(1)–Ru(2)	85.7(5)	Ru(4)–C(2)–Ru(3)	81.4(6)

Conclusion

The results reported in this paper show that mono(alkylthio)-alkynes have the same behavior toward iron carbonyl and ruthenium carbonyl. In both cases, the coupling of two thioalkyne molecules has been observed, as for aminoalkynes, and also facile C–heteroatom cleavage, as for phosphinoalkynes. However, no metallacyclopentadiene moieties have been found using phosphinoalkynes. From these points of view, i.e. coupling and cleavage, the influence of sulfur seems to be intermediate between that of nitrogen and that of phosphorus.

However, some differences exist between ruthenium and iron. In the case of ruthenium, trinuclear compounds I and II have structures which were not found for iron. Complex VI contains a ligand resulting from two thioalkynes and one acetylide, a situation not yet observed with iron. Pentanuclear complexes V and VII have ruthenium skeletons different from those of pentanuclear compounds observed for iron. No iron hexanuclear compound has been yet obtained with thioalkyne as a ligand.

Experimental section

General Procedures. Standard Schlenk techniques were used for syntheses, and all reactions were carried out in an atmosphere of argon. Solvents used for synthesis and chromatography were distilled under nitrogen from sodium prior to use. Ruthenium carbonyl was purchased from Strem Chemicals. $RC\equiv CSC_2H_5$ was prepared in the laboratory following the methods of Pourcelot et al. for R = CH_3[12] and of Makosza et al. for R = C_6H_5.[13] Reactions were monitored by thin-layer chromatography. Separation of products was performed by column chromatography using silica gel 60 (70–230 mesh ASTM) under an atmosphere of dry nitrogen.

IR spectra were recorded with a Perkin-Elmer 457 or a Nicolet spectrometer using either KBr pellets or a hexane solution. ^1H and ^{13}C NMR spectra were recorded on Bruker 250- and 500-MHZ spectrometers, and chemical shifts were referenced to $Si(CH_3)_4$. Mass spectra were recorded with a Nermag R1010, usually by chemical ionization with NH_3.

X-ray Structure Analysis. All measurements were carried out at room temperature using either a Nonius CAD4 or a Philips PW 1100 diffractometer. Details concerning the crystallographic data collection and structure determinations are given in Tables 1 and 2. Suitable crystals, sometimes very tiny, were chosen and placed in a Lindeman glass capillary tube. Cell dimensions were determined from 25 reflections dispersed in reciprocal space. Two standard reflections were monitored every 2 h during data collection to check the crystal orientation and the absence of decomposition. The usual correction for Lorentz and polarization effects was carried out. Direct methods and successive Fourier maps were used to locate the positions of all atoms. Full matrix least squares refinement of atomic parameters and isotropic (compounds **III**, **VI**, **VII**) or anisotropic (compounds **I**, **II**, **IV**, **V**, **VIII**) thermal parameters were carried out using the program CRYSTALS[14] and a DEC Microvax II. The size of the crystals and the number of recorded reflections for compounds **VI** and **VII** did not allow the refinement of anisotropic thermal parameters. The atomic scattering factors, including anomalous dispersion corrections, were provided by CRYSTALS. Only hydrogen atoms located in a difference Fourrier map were included, in fixed positions with an overall isotropic thermal parameter. Selected bond lengths and bond angles are given in Tables 3–8, respectively, for compounds **II** and **IV**–

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Table 5. Selected Interatomic Distances (Å) and Bond Angles (deg) for Compound **V**

Ru(1)–Ru(2)	2.863(1)	Ru(1)–Ru(4)	2.972(1)
Ru(1)–Ru(5)	2.983(1)	Ru(2)–Ru(3)	2.782(1)
Ru(3)–Ru(4)	2.899(2)	Ru(4)–Ru(5)	3.051(1)
S(1)–Ru(2)	2.401(3)	S(1)–Ru(3)	2.384(3)
S(1)–Ru(5)	2.442(3)	S(2)–Ru(1)	2.425(3)
S(2)–Ru(5)	2.389(3)	C(1)–Ru(1)	2.14(1)
C(1)–Ru(2)	2.15(1)	C(1)–Ru(3)	2.14(1)
C(1)–Ru(4)	2.15(1)	C(2)–Ru(1)	2.15(1)
C(2)–Ru(4)	2.14(1)	C(1)–C(2)	1.35(2)
C(6)–Ru(5)	2.04(1)	C(6)–Ru(4)	2.29(1)
C(7)–Ru(4)	2.45(1)		

Ru(2)–Ru(1)–Ru(4)	89.10(4)	Ru(4)–Ru(1)–Ru(5)	61.64(3)
Ru(3)–Ru(2)–Ru(1)	91.57(4)	Ru(2)–Ru(3)–Ru(4)	92.20(4)
Ru(3)–Ru(4)–Ru(1)	87.11(4)	Ru(1)–Ru(4)–Ru(5)	59.35(3)
Ru(4)–Ru(5)–Ru(1)	59.01(3)	Ru(1)–S(2)–Ru(5)	76.57(9)
Ru(2)–S(1)–Ru(3)	71.10(8)	Ru(3)–S(1)–Ru(5)	114.3(1)
Ru(2)–S(1)–Ru(5)	113.7(1)	Ru(1)–C(1)–Ru(2)	83.6(4)
Ru(2)–C(1)–Ru(3)	80.8(4)	Ru(3)–C(1)–Ru(4)	85.0(4)
Ru(4)–C(1)–Ru(1)	87.7(4)	Ru(4)–C(2)–Ru(1)	87.6(4)
Ru(4)–C(6)–Ru(5)	89.5(4)	Ru(5)–C(6)–C(7)	168.1(12)
C(6)–C(7)–C(8)	166.1(15)		

Table 6. Selected Interatomic Distances (Å) and Bond Angles (deg) for Compound **VI**

Ru(1)–Ru(2)	2.768(6)	Ru(2)–Ru(3)	2.851(6)
Ru(1)–S(2)	2.40(1)	Ru(1)–C(4)	2.08(4)
Ru(2)–S(1)	2.38(1)	Ru(2)–C(3)	2.29(4)
Ru(2)–C(4)	2.26(4)	Ru(2)–C(7)	2.12(4)
Ru(3)–S(1)	2.37(1)	Ru(3)–C(8)	2.28(4)
Ru(3)–C(11)	2.15(4)	Ru(3)–C(12)	2.16(5)
S(2)–C(7)	1.81(4)	C(3)–C(4)	1.47(6)
C(3)–C(7)	1.54(5)	C(3)–C(12)	1.43(5)
C(7)–C(8)	1.44(6)	C(8)–C(11)	1.47(6)
C(11)–C(12)	1.41(5)		

Ru(3)–Ru(2)–Ru(1)	131.3(2)	S(2)–Ru(1)–Ru(2)	75.6(3)
C(4)–Ru(1)–Ru(2)	53.4(12)	C(4)–Ru(1)–S(2)	86.5(12)
S(1)–Ru(2)–Ru(1)	153.5(4)	S(1)–Ru(2)–Ru(3)	53.0(3)
C(3)–Ru(2)–Ru(1)	72.4(10)	C(3)–Ru(2)–Ru(3)	59.4(10)
C(3)–Ru(2)–S(1)	108.4(11)	C(4)–Ru(2)–Ru(1)	47.4(10)
C(4)–Ru(2)–Ru(3)	91.8(10)	C(4)–Ru(2)–S(1)	144.6(11)
C(4)–Ru(2)–C(3)	37.8(14)	C(7)–Ru(2)–Ru(1)	74.8(10)
C(7)–Ru(2)–Ru(3)	64.9(10)	C(7)–Ru(2)–S(1)	88.7(11)
C(7)–Ru(2)–C(3)	40.8(15)	C(7)–Ru(2)–C(4)	69.6(15)
S(1)–Ru(3)–Ru(2)	53.2(3)	C(8)–Ru(3)–Ru(2)	74.5(12)
C(8)–Ru(3)–S(1)	85.6(13)	C(11)–Ru(3)–Ru(2)	98.3(11)
C(11)–Ru(3)–S(1)	124.3(11)	C(11)–Ru(3)–C(8)	38.7(16)
C(12)–Ru(3)–Ru(2)	82.5(12)	C(12)–Ru(3)–S(1)	132.5(13)
C(12)–Ru(3)–C(8)	64.5(17)	C(12)–Ru(3)–C(11)	38.1(14)
Ru(3)–S(1)–Ru(2)	73.8(4)		

Table 7. Selected Interatomic Distances (Å) and Bond Angles (deg) for Compound **VII**

Ru(1)–Ru(2)	2.788(3)	Ru(2)–Ru(3)	2.792(3)
Ru(2)–Ru(4)	2.913(3)	Ru(3)–Ru(4)	2.790(3)
Ru(4)–Ru(5)	2.799(3)	S(1)–Ru(3)	2.367(6)
S(1)–Ru(5)	2.438(6)	S(2)–Ru(1)	2.383(7)
S(2)–Ru(2)	2.373(7)	C(3)–Ru(1)	1.98(2)
C(3)–Ru(2)	2.16(2)	C(3)–Ru(3)	2.17(2)
C(4)–Ru(3)	2.20(3)	C(8)–Ru(3)	2.24(3)
C(8)–Ru(4)	2.05(3)	C(9)–Ru(4)	2.25(2)
C(9)–Ru(5)	2.04(2)	C(20)–Ru(2)	2.15(3)
C(20)–Ru(4)	2.13(3)		

Ru(1)–Ru(2)–Ru(3)	88.72(8)	Ru(3)–Ru(2)–Ru(4)	58.51(7)
Ru(2)–Ru(3)–Ru(4)	62.90(7)	Ru(2)–Ru(4)–Ru(3)	58.59(7)
Ru(3)–Ru(4)–Ru(5)	82.66(8)	Ru(3)–S(1)–Ru(5)	100.4(2)
Ru(1)–S(2)–Ru(2)	71.8(2)	Ru(1)–C(3)–Ru(2)	84.5(9)
Ru(2)–C(3)–Ru(3)	80.4(8)	Ru(3)–C(8)–Ru(4)	80.9(9)
Ru(4)–C(9)–Ru(5)	81.2(8)	C(9)–C(8)–C(4)	152.4(24)
C(8)–C(4)–C(3)	119.1(22)	Ru(4)–C(20)–Ru(2)	85.8(10)
Ru(2)–C(20)–O(20)	136.5(22)	Ru(4)–C(20)–O(20)	137.7(22)

Table 8. Selected Interatomic Distances (Å) and Bond Angles (deg) for Compound **VIII**

Ru(1)–Ru(2)	2.987(2)	Ru(1)–Ru(6)	2.700(2)
Ru(2)–Ru(3)	2.833(2)	Ru(2)–Ru(5)	2.813(2)
Ru(2)–Ru(6)	2.791(2)	Ru(3)–Ru(4)	2.714(2)
Ru(3)–Ru(5)	2.802(2)	Ru(4)–Ru(5)	2.955(2)
Ru(5)–Ru(6)	2.797(2)	S(1)–Ru(5)	2.376(4)
S(1)–Ru(6)	2.364(4)	S(2)–Ru(2)	2.382(4)
S(2)–Ru(3)	2.378(4)	C(2)–Ru(1)	2.00(2)
C(2)–Ru(6)	2.20(1)	C(3)–Ru(2)	2.08(1)
C(3)–Ru(6)	2.24(1)	C(4)–Ru(3)	2.24(1)
C(4)–Ru(5)	2.09(1)	C(5)–Ru(3)	2.20(1)
C(5)–Ru(4)	2.04(2)		

Ru(2)–Ru(1)–Ru(6)	58.52(4)	Ru(1)–Ru(2)–Ru(6)	55.60(4)
Ru(1)–Ru(2)–Ru(5)	109.75(5)	Ru(1)–Ru(2)–Ru(3)	138.30(5)
Ru(6)–Ru(2)–Ru(5)	59.88(4)	Ru(6)–Ru(2)–Ru(3)	116.67(6)
Ru(5)–Ru(2)–Ru(3)	59.50(4)	Ru(2)–Ru(3)–Ru(5)	59.89(4)
Ru(2)–Ru(3)–Ru(4)	117.46(5)	Ru(5)–Ru(3)–Ru(4)	64.76(4)
Ru(3)–Ru(4)–Ru(5)	59.06(4)	Ru(4)–Ru(5)–Ru(3)	56.18(4)
Ru(4)–Ru(5)–Ru(2)	110.58(5)	Ru(4)–Ru(5)–Ru(6)	137.69(5)
Ru(3)–Ru(5)–Ru(2)	60.62(4)	Ru(3)–Ru(5)–Ru(6)	117.53(5)
Ru(2)–Ru(5)–Ru(6)	59.68(4)	Ru(5)–Ru(6)–Ru(2)	60.44(4)
Ru(5)–Ru(6)–Ru(1)	119.31(5)	Ru(2)–Ru(6)–Ru(1)	65.88(5)
Ru(5)–S(1)–Ru(6)	72.3(1)	Ru(2)–S(2)–Ru(3)	73.1(1)
Ru(1)–C(2)–Ru(6)	80.0(5)	Ru(2)–C(3)–Ru(6)	80.4(4)
Ru(3)–C(4)–Ru(5)	80.5(5)	Ru(3)–C(5)–Ru(4)	79.5(5)
C(2)–C(3)–C(4)	145.8(14)	C(3)–C(4)–C(5)	144.5(14)

VIII. Since compound **I** (R = CH_3) is identical to compound **II** (R = C_6H_5), and compound **III** (R = CH_3) is identical to compound **IV** (R = C_6H_5), the structural data are not given for those two compounds **I** and **III**.

EHT Calculations. EHT calculations[15] were carried out with the Ru parameters previously described by Thorn and Hoffmann.[16] The geometrical parameters were fixed at the RX values given in the aforementioned structure of compound **IV** (vide supra). Model calculations were performed with SH (S–H = 1.45 Å) instead of SC_2H_5 and PH_2 (P–H = 1.40 Å) instead of $P(C_6H_5)_2$ and the group CCH (C–H = 0.95 Å) instead of C_6H_5, with the valence direction of the actual structure. The calculation yielded the following values (eV): −12.98, −12.75 (HOMO), −10.59 (LUMO) for compound **IV**; −12.90, −12.68 (HOMO), −11.80 (LUMO) for Carty's compound.[1e,5]

Syntheses. Reaction of $CH_3C\equiv CSC_2H_5$. A 1 mmol (0.64 g) amount of $[Ru_3(CO)_{12}]$ was mixed with 1 mmol (0.1 g) of $CH_3C\equiv CSC_2H_5$ in 15 mL of hexane. The solution was refluxed for 3 h, i.e. until complete reaction of $[Ru_3(CO)_{12}]$ using thin-layer chromatography ($R_f = 0.63$). Chromatography was carried out on a silica column prepared with heptane and maintained under nitrogen during separation. Each fraction was collected under argon. A 95/5 heptane/dichloromethane mixture eluted yellow compound **I**, 30% yield, and then orange compound **III**. Brown compound **VIII**, 2% yield, was eluted with a 90/10 heptane/dichloromethane mixture. A 85/15 heptane/dichloromethane mixture eluted red compound **V**, 13% yield. A more polar solvent eluted more fractions, brown and orange, not yet identified.

Compound **I**, $[Ru_3(CO)_9(SC_2H_5)(C\equiv CCH_3)]$, has been obtained as yellow crystals from a hexane solution at −20 °C. Mass spectrometry: $[M + H]^+$, *m/z* 656; $[M + H]^+ - CO$, *m/z* 628. Infrared (KBr pellet): ν(CO) 2070, 2060, 2020, 2000, 1980, 1960 cm^{-1}. ^{1}H NMR (250 MHz, residual H of C_6D_6 set at 7.16 ppm): CH_3CH_2S, t, 3H, 0.72 ppm, ^3J = 9.1 Hz; CH_3CH_2S, q, 2H, 2.01 ppm, ^3J = 9.1 Hz; CH_3, s, 3H, 2.34 ppm. ^{13}C NMR (250 MHz, C_6D_6): *C*O, 199.1, 191.3, 189.9 ppm; $C\equiv C$, 139.5, 55.5 ppm; CH_2S, 39.9 ppm; $CH_3C\equiv$, 18.2 ppm; CH_3CH_2S, 16.4 ppm.

Compound III, $[Ru_4(CO)_{12}(C\equiv CCH_3)(SC_2H_5)]$. Mass spectrometry: $[M + H]^+$, *m/z* = 841. Infrared (KBr pellet): ν(CO) 2077, 2062, 1998, 1942 cm^{-1}.

Compound V, $[Ru_5(CO)_{12}(SC_2H_5)_2(C\equiv CCH_3)_2]$. Mass spectrometry: $[M + H]^+$, *m/z* 1042 $[M + H]^+ + CO$, *m/z* 1070. Infrared (KBr pellet): ν(CO) 2074, 2044, 2007, 1940 cm^{-1}; $\nu(\mu_4\text{-}C\equiv C)$ 1840 cm^{-1}.

Compound VIII, $[Ru_6(CO)_{14}(SC_2H_5)_2\{C(CH_3)CCC(CH_3)\}]$. Mass spectrometry: $[M + H]^+$, *m/z* 1199. Infrared (KBr pellet): ν(CO) 2080, 2063, 2046, 2011, 1979, 1962, 1946, 1923 cm^{-1}. ^{1}H NMR (300 MHz, residual H of C_6D_6 set at 7.16 ppm): 2 CH_3CH_2S, t, 0.93 ppm; 2 CH_3CH_2S, 2 diastereotopic H, 2 unresolved multiplets centered on 1.93 and 2.18 ppm; 2 CH_3, s, 2.69 ppm.

Reaction of $C_6H_5C\equiv CSC_2H_5$. A 1 mmol (0.64 g) amount of $[Ru_3(CO)_{12}]$ was mixed with 1 mmol (0.162 g) of $C_6H_5C\equiv CSC_2H_5$ in hexane.

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The solution was refluxed for 3 h. Chromatography was carried out on a silica column prepared and used as above. The 95/5 heptane/dichloromethane mixture separated yellow compound **II** which was crystallized, 46% yield. A 90/10 heptane/dichloromethane eluent provided orange compound **IV**, 4% yield, and red compound **VII**, 4.5% yield. A 85/15 heptane/dichloromethane solution eluted a brown unknown compound. Compound **VI**, 3% yield, was eluted as a dark brown fraction with a 75/25 heptane/dichlomethane mixture. More polar solvents separated another dark red unidentified fraction.

Compound **II** has been identified by infrared spectroscopy (KBr pellet): ν(CO) 2070, 2050, 2020, 2000, 1980, 1960 cm^{-1}. The similarity of this spectrum to the spectrum of compound **I** suggested a similar structure which has been checked by determining by X-ray the structures of compounds **I** and **II**, $[Ru_3(CO)_9(SC_2H_5)(C{\equiv}CC_6H_5)]$. Mass spectrometry: $[M + H]^+$, m/z 718. ^1H NMR (500 MHz, residual H of C_6D_6 set at 7.29 ppm): $C\mathit{H}_3CH_2S$, t, 0.88 ppm, $^3J = 7.6$ Hz; $CH_3C\mathit{H}_2S$, q, 2.36 ppm, $^3J = 7.6$ Hz; $C_6\mathit{H}_5$, 7–7.9 ppm. ^{13}C NMR (500 MHz, C_6D_6): $\mathit{C}O$, 199.3, 192.1, 189.7 ppm; $\mathit{C}{\equiv}\mathit{C}$, 150.6, 63.0 ppm; C_6H_5, 135.1, 131.5, 130.3, 129.2 ppm; $\mathit{C}H_2S$, 41.2 ppm; $\mathit{C}H_3CH_2S$, 17.0 ppm.

Compound IV, $[Ru_4(CO)_{12}(C{\equiv}CC_6H_5)(SC_2H_5)]$. Mass spectrometry: $[M + H]^+$, m/z 903; $[M + H]^+ - CO$, m/z 875. Infrared (KBr pellet): ν(CO) 2097, 2071, 2050, 2024, 1994, 1973, 1962, 1951 cm^{-1}. ^1H NMR (250 MHz, residual H of C_6D_6 set at 7.17 ppm): $C\mathit{H}_3CH_2S$, t, 3H, 0.82 ppm, $^3J = 7.3$ Hz; $CH_3C\mathit{H}_2S$, q, 2H, 2.09 ppm, $^3J = 7.3$ Hz; $C_6\mathit{H}_5$, 6.86–7.53 ppm.

Compound VI, $[Ru_3(CO)_7(SC_2H_5)\{S(C_2H_5)CC(C_6H_5)C(SC_2H_5)C(C_6H_5)CC(C_6H_5)\}]$. Mass spectrometry: $[M + H]^+$, m/z 986, $[M + H]^+ - CO$, m/z 958; $[M + H]^+ - 2CO$, m/z 930. ^1H NMR (500 MHz, residual H of C_6D_6 set at 7.29 ppm): $C\mathit{H}_3CH_2S$, t, 0.46 ppm; $CH_3C\mathit{H}_2S$, 2 diastereotopic H, 2 unresolved multiplets centered on 1.58 and 1.98 ppm; $C\mathit{H}_3CH_2S$, t, 0.82 ppm; $CH_3C\mathit{H}_2S$, 2 diastereotopic H, 2 unresolved multiplets centered on 2.37 and 2.49 ppm; bridging ethylthio group, $C\mathit{H}_3CH_2S$, t, 1.58 ppm; $CH_3C\mathit{H}_2S$, 2 diastereotopic H, 2 unresolved multiplets centered on 3.22 and 3.32 ppm; 3 $C_6\mathit{H}_5$ 6.8–8.1 ppm.

Compound VII, $[Ru_5(CO)_{13}(SC_2H_5)_2\{CC(C_6H_5)CC(C_6H_5)\}]$. Mass spectrometry: $[M + H]^+$, m/z 1194. Infrared (KBr pellet): ν(CO) 2089, 2073, 2044, 2018, 2001, 1990, 1962 cm^{-1}; ν(CO bridging) 1837 cm^{-1}. 1H NMR (500 MHz, residual H of C_6D_6 set at 7.29 ppm): $C\mathit{H}_3CH_2S$, t, 0.65 ppm; $CH_3C\mathit{H}_2S$, 2 diastereotopic, 1 unresolved multiplet centered on 1.90 ppm; $C\mathit{H}_3CH_2S$, t, 0.88 ppm; $CH_3C\mathit{H}_2S$, 2, diastereotopic H, 2 unresolved multiplets centered on 2.35 and 2.52 ppm; $2C_6\mathit{H}_5$, 6.9 and 7.8 ppm.

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Supplementary Material Available: For compounds **II**, **IV**, and **VI–VIII**, tables of data collection details, fractional atomic coordinates, anisotropic thermal parameters, bond distances, and bond angles (35 pages). Ordering information is given on any current masthead page.