Iron−Ruthenium−Osmium Mixed Trimetallic Carbonyl Clusters: Theoretical Studies and Structural Trends

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The family of $M_3(CO)_{12}$ (M = Fe, Ru, Os) clusters, where M_3 is any possible combination of Fe, Ru, and Os, was theoretically studied using DFT methods (ADF program). The optimized geometries were compared with the those of the clusters for which structures are available, and the agreement was quite good, especially when the metals were Fe and/or Ru. This allowed the prediction that the structure of the known, but not yet structurally characterized, $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$ clusters should be of the D_3 type, with only terminal carbonyls. On the other hand, the still unknown $FeRuOs(CO)_{12}$ cluster appears to prefer the C_2 form with two bridging carbonyls over the Fe−Ru edge, but the energy differs only by 2.7 kJ mol^{-1} from that of the D_3 arrangement. The calculated enthalpy changes for the formation of mixed $M_3(CO)_{12}$ clusters, a process favored by entropy, are positive except for the formation of $Ru_2Os(CO)_{12}$and $RuOs_2(CO)_{12}$ from the parent clusters, where the reaction is slightly exothermic.

Introduction

The family of $M_3(CO)_{12}$ (M = Fe, Ru, Os) is one of the best known groups of mixed-metal clusters.[1] All possible metal combinations except $FeRuOs(CO)_{12}$ have been synthesized.[2] Structural characterization by X-ray diffraction has been reported for the heteronuclear $FeRu_2(CO)_{12}$, $Fe_2Ru(CO)_{12}$, $Fe_2Os(CO)_{12}$, and $Fe_2Os(CO)_{12}$ clusters.[3] In Scheme 1 the structurally characterized species are indicated in bold face and the unknown cluster in italics. The structures of the homonuclear clusters $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ have been important in the understanding of the carbonyl bonding in metal clusters. Iron-containing clusters prefer carbonyl bridges, while ruthenium and osmium clusters favor terminal carbonyls. The iron−ruthenium−osmium mixed-metal clusters allow us to study systematically the influence of the metal composition on the cluster structure and bridging preferences.[4] Since there are no experimental structure determinations for $RuOs_2(CO)_{12}$ and $Ru_2Os(CO)_{12}$ and no reports of $FeRuOs(CO)_{12}$, we have undertaken a theoretical study to predict the unknown structures and explore the existence and the most favored geometry of $FeRuOs(CO)_{12}$.

Scheme 1

$Os_3(CO)_{12}$

$FeOs_2(CO)_{12}$ $RuOs_2(CO)_{12}$

$Fe_2Os(CO)_{12}$ *$FeRuOs(CO)_{12}$* $Ru_2Os(CO)_{12}$

$Fe_3(CO)_{12}$ **$Fe_2Ru(CO)_{12}$** **$FeRu_2(CO)_{12}$** **$Ru_3(CO)_{12}$**

Density functional theory has been demonstrated to give reasonably accurate structures for the homonuclear iron triad clusters.[5] The same accuracy can be expected to be achievable for the mixed metal clusters as well. The known structures can be used to assess the accuracy and the reliability of the structure predictions.

Results

The trimetallic clusters can be grouped in a triangle having as vertexes the $M_3(CO)_{12}$ species (Scheme 1).

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(1) (a) Wei, C.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351. (b) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155. (c) Braga, D.; Farrugia, L.; Grepioni, F.; Johnson, B. F. G. *J. Organomet. Chem.* **1994**, *C39*, 464. (d) Braga, D.; Grepioni, F.; Farrugia, L.; Grepioni, F.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1994**, 2911. (e) Mason, R.; Rae, A. I. *J. Chem. Soc. (A)* **1968**, 778. (f) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655. (g) Corey, E. R.; Dahl, L. F. *Inorg. Chem.* **1962**, *1*, 521. (h) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(2) (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry;* Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, UK, 1983; Vol. 8, Chapter 42. (b) Farrugia, L. J. In *Comprehensive Organometallic Chemistry II;* Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, UK, 1995; Vol. 10, Chapter 4.

(3) (a) Maksakov, V. A.; Kirin, V. P.; Virovets, A. V.; Podberezskaya, N. V.; Semyannikov, P. P. *J. Organomet. Chem.* **1997**, *54*, 57. (b) Braga, D.; Farrugia, L. J.; Gillon, A. L.; Grepioni, F.; Tedesco, E. *Organometallics* **1996**, *15*, 4684. (c) Churchill, M. R.; Fettinger, J. C. *Organometallics* **1990**, *9*, 446. (d) Braga, D.; Farrugia, L. J.; Grepioni, F.; Senior, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1219. (e) Farrugia, L. J.; Senior, A. M.; Braga, D.; Grepioni, F.; Orpen, A. G.; Crossley, J. G. *J. Chem. Soc., Dalton Trans.* **1996**, 631.

(4) (a) Braga, D.; Grepioni, F.; Tedesco, E.; Calhorda, M. J.; Lopes, P. E. M. *J. Chem. Soc., Dalton Trans.* **1995**, 3297. (b) Braga, D.; Grepioni, F.; Wadepohl, H.; Gebert, S.; Calhorda, M. J.; Veiros, L. F. *Organometallics* **1995**, *14*, 5330.

(5) Hunstock, E.; Mealli, C.; Calhorda, M. J.; Reinhold, J. *Inorg. Chem.* **1999**, *38*, 5038, and references therein.

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Table 1. Relative Energies (kJ mol^{-1}) and Selected Distances (Å) in Trimetallic Clusters $M_{3-x}M'_x(CO)_{12}$ and $MM'M''(CO)_{12}$ (M, M′, M″ = Fe, Ru, Os).

	relative energy		M−M distance		M−C distance
cluster	C_2	D_3	C_2	D_3	C_2
Fe_2Ru	0.0	12.7	2.792[a]	2.820[a]	2.041, 1.965
			2.795	2.821	2.034, 1.956
			2.589	2.717	
$FeRu_2$	0.8	0.0	2.719[g,d]	2.891[b]	1.974, 2.062[j]
			2.826[g]	2.821	2.165, 2.096[k]
			2.911	2.824	
Fe_2Os	0.0	15.5	2.593[a]	2.745[a]	2.033, 1.965
			2.828	2.833	2.029, 1.959
			2.829	2.835	
$FeOs_2$	9.2	0.0	2.764[h,e]	2.943[c]	1.972, 2.078[j]
			2.854[h]	2.869	2.245, 2.154[l]
			2.965	2.845	
Ru_2Os	0.29	0.0	2.839[b]	2.932[b]	2.174, 2.115
			2.937	2.958	2.175, 2.118
			2.936	2.952	
$RuOs_2$	16.2	0.0	2.903[i,f]	2.957[c]	2.129, 2.204[k]
			2.949[i]	2.967	2.248, 2.182[l]
			2.978	2.968	
FeRuOs	0.0[d]	2.7	2.725[g]	2.840[g]	2.041, 1.990[j]
			2.850[h]	2.852[h]	2.165, 2.111[k]
			2.917[i]	2.923[i]	
	13.5[e]		2.756[h]		2.068, 1.980[j]
			2.844[g]		2.241, 2.162[l]
			2.922[i]		
	27.3[f]		2.886[i]		2.198, 2.129[k]
			2.846[h]		2.255, 2.176[l]
			2.826[g]		

[a] Fe−Fe. [b] Ru−Ru. [c] Os−Os. [d] Bridge over Fe−Ru. [e] Bridge over Fe−Os. [f] Bridge over Ru−Os. [g] Fe−Ru. [h] Fe−Os. [i] Ru−Os. [j] Fe−C. [k] Ru−C. [l] Os−C.

These have been studied by theoretical methods in detail before,[5] so that in this work the mixed clusters $M_{3-x}M'_x(CO)_{12}$ and $MM'M''(CO)_{12}$ (M, M′, M″ = Fe, Ru, Os) will be mainly addressed. Although DFT calculations[6] were performed in the absence of symmetry constraints (see Experimental Section), the labels C_2 and D_3 will be used, as they describe the basic features of the structures: C_2 refers to the structure of $Fe_3(CO)_{12}$, with two CO asymmetric bridges spanning an Fe−Fe bond, while D_3 will be a structure with only terminal carbonyls, as in $Ru_3(CO)_{12}$, but lacking a mirror plane containing the metallic triangle. For convenience, the same labels are used for the mixed clusters as well, to indicate the carbonyl arrangement, although the true symmetry is lower, owing to the mixed metal composition (no 3-fold axis). The relative energies and main structural parameters are collected in Table 1. As this study refers to clusters with 12 carbonyl ligands, only the metals will be used to identify them. The most stable calculated isomer of each complex is shown in Figure 1.

Before discussing these values in more detail, distances and angles in calculated and in experimentally determined structures will be compared, for those compounds whose structures are available, namely, the Fe_2Ru, $FeRu_2$, Fe_2Os, and $FeOs_2$ derivatives. This procedure is useful for checking the quality of the calculation method and how reliable it will be for making predictions. A similar comparison has been done for the homometallic clusters before,[5] but some details must be brought into attention. The crystal structures for the seven compounds are shown in Figure 2, in the same triangular format as above.

Many of the crystal structures of these clusters show disorder at room temperature. For $Fe_3(CO)_{12}$, the structure determined at 120 K was chosen (GAFMEF04) and one set of coordinates (from the Cambridge Crystallographic Data Base)[7] taken for the drawing. Two independent molecules existed in the unit cell of $Ru_3(CO)_{12}$ (FOKNEY) and $Os_3(CO)_{12}$ (FOKBUC01), and one of them was arbitrarily taken. When available, data from low-temperature X-ray diffraction determinations were chosen.

The structures fall into two main groups, namely, those with bridging carbonyls, where the bridge always spans an Fe−Fe bond and which are all very similar, and those with only terminal carbonyls. $Ru_3(CO)_{12}$ (FOKNEY), $Os_3(CO)_{12}$ (FOKBUC01), and $FeOs_2(CO)_{12}$ (POYCIP) exhibit a symmetry very close to D_{3h}, with all the axial carbonyls almost parallel to one another. Interestingly, in the remaining example, $FeRu_2(CO)_{12}$

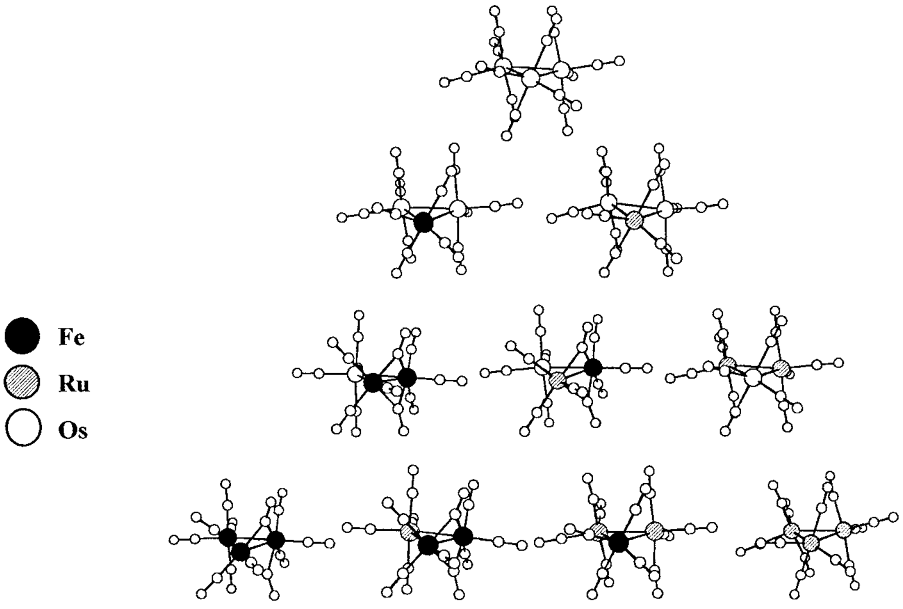

Figure 1. Representation of the most stable isomers of the $M_3(CO)_{12}$ clusters (DFT calculations), where M can be any combination of Fe, Ru, and Os.

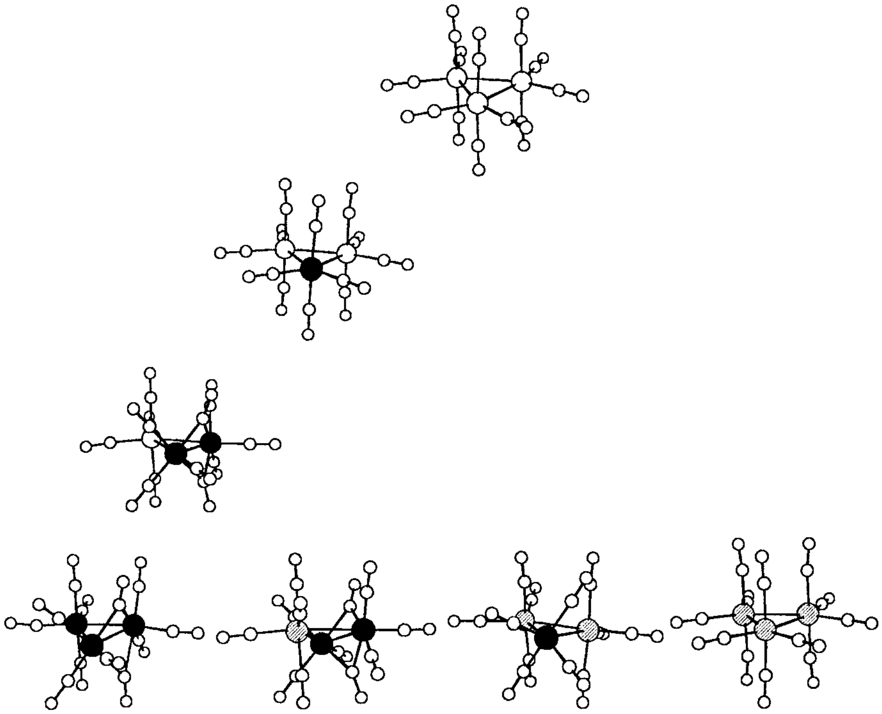

Figure 2. Representation of the experimental structures of the $M_3(CO)_{12}$ clusters, where M can be any combination of Fe, Ru, and Os.

Table 2. Selected Distances (Å) and Angles (deg) in the X-ray Structures of the $M_2M'(CO)_{12}$ Clusters (M_2M' = Fe_2Ru, $FeRu_2$, Fe_2Os)

	structure type	M−M$_{br}$	M−M	M−C$_{br}$	M−C	M−C$_{br}$−M	ref REFCODE
Fe_2Ru	C_2	2.578[a]	2.734				3b
		2.575[a]	2.735				RAQVUA
			2.733				
			2.736				
$FeRu_2$	D_3		2.806		1.764−1.833[b]		3b
			2.775		1.923−1.968[c]		RAQWIP
			2.763				
Fe_2Os	C_2	2.566[a]	2.739	2.09, 1.92			3d
		2.575[a]	2.744	1.94, 2.07			SELHAS01
			2.744	2.04,1.97			
			2.739	2.00, 2.05			
$FeOs_2$	D_3		2.846		1.878−1.912[b]		3a
			2.833		1.830−1.925[d]		POYCIP
			2.834				

[a] Two independent molecules. [b] Fe−C. [c] Ru−C. [d] Os−C.

(RAQWIP), the $Fe(CO)_4$ unit has rotated relative to the M3 plane and the D_{3h} symmetry has been lost. This arrangement has been found in all the calculations for this type of geometry, because no symmetry constraint was kept. Indeed, for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, the energy of the optimized structure calculated with D_{3h} symmetry dropped by 5.2 and 5.3 kJ mol^{-1}, respectively, when no symmetry constraints were kept. This was the reference structure for later discussions. Selected data from the experimental structures are given in Table 2.

The root-mean-square deviation (rms) in Å was calculated for the seven compounds in Figure 2, and the results are given in Table 3, the first column giving the rms for the metal triangles and the second for the complete cluster (calculated from the atomic positions).

Table 3. Root Mean Square Deviations (Å) between Calculated and X-ray Structures of $M_2M'(CO)_{12}$ and $M_3(CO)_{12}$ Clusters (M_2M' = Fe_2Ru, $FeRu_2$, Fe_2Os, $FeOs_2$, Fe_3, Ru_3, Os_3; M = Fe, Ru, Os)

cluster	structure type	rms M_3	rms $M_3(CO)_{12}$
Fe_2Ru	C_2	0.030	0.064
$FeRu_2$	D_3	0.039	0.085
Fe_2Os	C_2	0.045	0.164
$FeOs_2$	D_3	0.040	0.754
Fe	C_2	0.023	0.225
Os_3	D_3	0.071	0.122
Ru_3	D_3	0.039	

Discussion

The agreement between experimental and calculated structures is relatively good, except when Os is present ($FeOs_2$ compared to $FeRu_2$, for instance), and is better for the metal triangle than for the whole structure. Concerning the homonuclear clusters, the agreement is poor for $Fe_3(CO)_{12}$ as a consequence of the problems of

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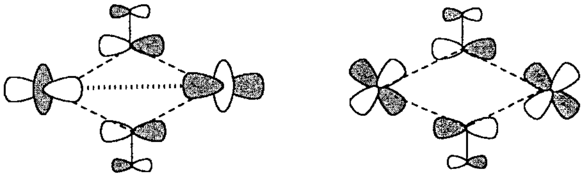
(6) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(7) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Watson, D. G. *J. Chem. Inf. Comput. Sci.*, **1991**, *31*, 204.

Scheme 2



disorder in the structure,[1a−c] and for $Os_3(CO)_{12}$ because the carbonyls in one group are rotated relative to the Os_3 core, as a consequence of having optimized the geometry without symmetry constraints (the same happens for Ru). On the whole, the agreement is quite satisfactory.

It is well known that the lighter metals show a stronger preference for coordinating carbonyl groups in a bridging mode in binary carbonyl clusters. As one moves from 3d metals to 4d and 5d, this tendency disappears and the structure containing only terminal carbonyls becomes more stable. This has been rationalized in several works dealing with different clusters types.[4,8] The origin of this feature can be traced to the back-donation component of the metal−(μ-CO) bond, as, in order to overlap the π^* orbital of the bridging CO, the orbitals of the metals are out of phase. This anti bonding interaction is much more repulsive when more diffuse orbitals (5d, 4d, compared to 3d) are involved. When two bridging carbonyls span only one metal−metal bond, this effect applies to both the in-phase and the out-of-phase combinations of the two π^* orbitals of the CO's, increasing the magnitude of the effect (Scheme 2).

From a thermodynamic point of view, one might expect that bridging carbonyls, leading to a larger number of metal−C bonds, could be preferred, despite the weakening of the C≡O and M−M bonds. In view of these arguments, it is challenging to analyze how these conflicting factors will balance when several metals are present, as in the mixed clusters under study.

The clusters containing two iron atoms (Fe_2Ru, Fe_2Os) exhibit the same structure as $Fe_3(CO)_{12}$, with two CO bridges over the Fe−Fe bond, the energy being 12.7 and 15.5 kJ mol^{-1} lower than in the alternative D_3 geometry, respectively. At the other extreme, the clusters containing two osmium atoms ($FeOs_2$, $RuOs_2$) adopt the geometry with only terminal carbonyls, as any bridging carbonyl would have to bind at least one osmium atom, and this situation would require much energy. The D_3 geometry is favored by 9.2 and 16.2 kJ mol^{-1}, respectively. The mixed FeRuOs cluster also shows bridging carbonyls, spanning the Fe−Ru bond, as expected. This structure is only slightly favored by 2.7 kJ mol^{-1} relative to the D_3, but is much more stable than the other bridged alternatives (13.5 kJ mol^{-1} with bridges over Fe−Os and 27.3 kJ mol^{-1} with bridges over Ru−Os). This leaves two other clusters where ruthenium is a major component ($FeRu_2$, Ru_2Os). In Ru_2Os a bridging carbonyl must also coordinate to two ruthenium atoms, in the least disfavored arrangement, a situation similar to that in the parent compound $Ru_3(CO)_{12}$, where the structure containing only terminal carbonyls is preferred. In this case, however, the energy difference between isomers is extremely small (0.3 kJ mol^{-1}), the D_3 form having the lowest energy. For the $FeRu_2$ cluster, the D_3 geometry is stabilized by 0.8 kJ mol^{-1} relative to the one with CO bridges over the Fe−Ru bond. The energy differences are relatively small, reflecting the intermediate situation of Ru in what concerns the formation of structures with carbonyl bridges spanning metal−metal bonds.

To understand the relative stabilities of the hetero- and homonuclear clusters, the change in enthalpy associated with reactions described by eq 1 was calculated.

$$M_3(CO)_{12} + 2\,M'_3(CO)_{12} \rightarrow 3\,MM'_2(CO)_{12} \qquad (1)$$

$$\Delta H_r = 3E_{MM'2(CO)12} - (E_{M3(CO)12} + 2E_{M'3(CO)12})$$

The results are the following (kJ mol^{-1}):

1. $Fe_3(CO)_{12} + 2\,Ru_3(CO)_{12} \rightarrow 3\,FeRu_2(CO)_{12}$ $\Delta H_1 = 51.7$

2. $2\,Fe_3(CO)_{12} + Ru_3(CO)_{12} \rightarrow 3\,Fe_2Ru(CO)_{12}$ $\Delta H_2 = 88.8$

3. $Fe_3(CO)_{12} + 2\,Os_3(CO)_{12} \rightarrow 3\,FeOs_2(CO)_{12}$ $\Delta H_3 = 42.6$

4. $2\,Fe_3(CO)_{12} + Os_3(CO)_{12} \rightarrow 3\,Fe_2Os(CO)_{12}$ $\Delta H_4 = 67.0$

5. $Ru_3(CO)_{12} + 2\,Os_3(CO)_{12} \rightarrow 3\,RuOs_2(CO)_{12}$ $\Delta H_5 = -5.0$

6. $2\,Ru_3(CO)_{12} + Os_3(CO)_{12} \rightarrow 3\,Ru_2Os(CO)_{12}$ $\Delta H_6 = -3.6$

7. $Fe_3(CO)_{12} + Ru_3(CO)_{12} + Os_3(CO)_{12} \rightarrow 3\,FeRuOs(CO)_{12}$ $\Delta H_7 = 26.6$

With the exception of the mixed RuOs clusters, all the others are thermodynamically unstable relative to homonuclear clusters. For the mixed-metal clusters, entropy favors mixing. It may not overcome large energy barriers, but would make reactions 5 and 6 ($\Delta H < 0$), at least, more favorable.

Conclusions

The results described above show a good agreement between the calculated structures and those experimentally available for seven clusters. This allows us to predict that the mixed Ru/Os clusters, namely, $RuOs_2(CO)_{12}$ and $Ru_2Os(CO)_{12}$, should have a D_3 type of structure with only terminal carbonyls. It is difficult to distinguish between the asymmetric D_3 geometry and the more idealized D_{3h} structure. As can be seen in Figure 2, the D_3 symmetry is only observed in the mixed $FeRu_2(CO)_{12}$ cluster, all the others exhibiting a perfect D_{3h} symmetry. The energy differences are so small, that factors such as crystal packing may be responsible for it not being observed in other clusters. In what concerns the still nonexistent $FeRuOs(CO)_{12}$ cluster, its formation from the homonuclear clusters is not energetically favored. On the other hand, although the energy of the isomer containing CO bridges over the Fe−Ru bond is lower than that of the nonbridged isomer, the difference (2.7 kJ mol^{-1}) is too small to be confident. It is, however, the most likely structure.

Experimental Section

The density functional calculations[6] were performed using the Amsterdam Density Functional program package.[9] The local spin density (LSD) exchange correlation potential[10] was used with the local density approximation (LDA) of the correlation energy (Vosko, Wilk, Nusair).[11] Becke's nonlocal corrections[12] to the exchange energy and Perdew's nonlocal corrections[13] to the correlation energy were used. Relativistic effects were considered for Ru and Os and were treated by a quasi-relativistic method where Darwin mass and velocity terms are incorporated.[14]

For the metals, carbon, and oxygen, the inner shells were frozen (Fe [1s−2p], Ru [1s−3d], Os [1s−5p], C, O [1s]), while the outer shells of all elements were described by triple-ζ basis sets.

Full geometry optimizations were carried out for all the mixed clusters, without symmetry constraints, but starting from either the typical C_2 geometry (isomers containing two CO bridges spanning one metal−metal bond) or the D_3 one (isomers containing only terminal carbonyls). In this way, it was possible to allow for asymmetric carbonyl bridges, for instance.

The optimized geometries of the homonuclear $M_3(CO)_{12}$ clusters were taken from ref 5 and optimized again in the same conditions used for the mixed trinuclear clusters (different basis set).

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(8) (a) Braga, D.; Grepioni, F.; Calhorda, M. J.; Veiros, L. F. *Organometallics* **1995**, *14*, 1992. (b) Braga, D.; Grepioni, F.; Byrne, J. J.; Calhorda, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 3287. (c) Evans, D. G. *J. Chem. Soc., Chem. Commun.* **1983**, 675. (d) Li, J.; Jug, K. *Inorg. Chim. Acta* **1992**, *196*, 89.

(9) (a) ADF 2.3, Theoretical Chemistry, Vrije Universiteit, Amsterdam, 1997. (b) Baerends, E. J.; Elis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. (c) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84. (d) Fonseca Guerra, C.; Visser, O.; Sniders, J. G.; te Velde, G.; Baerends, E. J. Parallelisation of the Amsterdam Density Functional Programme. In *Methods and Techniques for Computational Chemistry*; Clementi, E., Corongiu, C., Eds.; STEF: Cagliari, 1995; pp 303−395.

(10) Parr, R. G.; Young, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(11) Vosko, S.; Wilk, L.; Nusair, M. J. *Can. Phys.* **1980**, *58*, 1200.

(12) (a) Becke, A. *J. Chem. Phys.* **1986**, *84*, 4524. (b) Becke, A. *Phys. Rev.* **1988**, *A34*, 3098.

(13) (a) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822. (b) Perdew, J. P. *Phys. Rev.* **1986**, *B34*, 7406.

(14) (a) Ziegler, T.; Tschinke, V.; Baerends, E. J.; Snijders, J. G.; Ravenek, W. *J. Phys. Chem.* **1989**, *93*, 3050. (b) Snijders, J. G.; Baerends, E. J. *Mol. Phys.* **1978**, *36*, 1789. (c) Snijders, J. G.; Baerends, E. J.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909.