Theoretical Aspects of the Bonding in Organometallic Clusters Containing Exposed Dicarbon (C_2) Entities. 2. High-Nuclearity Systems

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Received December 18, 1996⊗

The electronic and geometrical structures of a variety of $L_mM_n-C_2$ organometallic systems ($n \geq 5$) in which the dicarbon unit is solely bonded to metal atoms are analyzed and compared by use of molecular orbital calculations. It is shown that the arrangement of the M_5 and M_6 cores can be derived from a square-pyramidal and a trigonal-prismatic geometry, respectively. The bonding of the C_2 ligand with its metallic host follows the Dewar-Chatt-Duncanson model, resulting from an important forward electron donation from occupied C_2 orbitals toward acceptor metallic orbitals, accompanied by a back-donation from occupied metallic orbitals into vacant C_2 π^* orbitals.

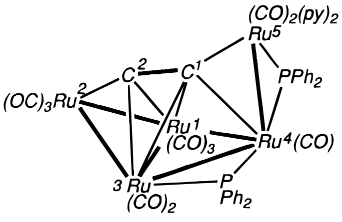
Introduction

C_2 is a simple diatomic entity which has been widely studied.[1] Having been encountered for a long time in organic chemistry on one side and inorganic solid-state chemistry on the other side, C_2 can now be easily observed in molecular organometallic compounds.[2] Among them, cluster compounds are beginning to be intensively investigated,[3] being thought of as models for adsorbed surface carbides. As part of a general study of the bonding and reactivity of these polymetallic−C_2 species,[4−6] we have recently undertaken a theoretical analysis of those containing supported (or *exposed*) C_2 units. Following a previous study on tetrametallic−C_2 compounds,[6,7] we present here the results obtained on higher nuclearity $L_mM_n-C_2$ systems ($n \geq 5$) with the aid of calculations made using the extended Hückel (EH) method (see the Appendix).

Electron Counting and Structural Arrangements

Several examples of high-nuclearity cluster compounds containing an exposed dicarbide entity, i.e. in which the C_2 ligand leans out of one metallic face of the cluster, have been characterized. They are listed in Table 1.

The few clusters exhibiting an $M_5(\mu_5\text{-}C_2)$ core show that the M_5 cage is rather flexible and can accommodate itself to the electron count and the steric demands of the other ligands present. An Ru_4 butterfly metalated at a wingtip forms the metallic core of $Ru_5(CO)_{11}(py)_2(\mu\text{-}PPh_2)_2(C_2)$ (**1**).[8] The C_2 ligand is linked to all five metal atoms, sitting asymmetrically in the groove of the metallic butterfly. With a C_2^{2-} ligand acting as an 8-electron donor,[19] a count of 78 metallic valence electrons (MVEs) is achieved for compound **1**. Such an electron count is in agreement with the polyhedral



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[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1997.

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[3] See for instance: (a) Akita, M.; Moro-oka, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 420. (b) Bruce, M. I. *J. Cluster Sci.*, in press. (c) Bruce, M. I. *Coord. Chem. Rev.*, in press.

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S0276-7333(96)01071-0 CCC: $14.00

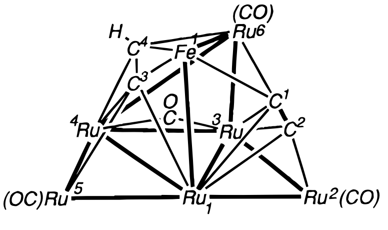
Table 1. High-Nuclearity Transition-Metal Clusters $L_mM_n(C_2)$ Containing an Exposed Dicarbon (C_2) Unit Characterized by X-ray Diffraction[a]

compd	MVE[b]	d_{C-C} (Å)	ref
	$M_5(\mu_5\text{-}C_2)$ Core		
$Ru_5(CO)_{11}(py)_2(\mu\text{-}PPh_2)_2(C_2)$ (**1**)	78	1.301(5)	8
$FeRu_6(CO)_{16}(Cp)(\mu_5\text{-}C_2H)(C_2)$ (**2**)	104 (78)[b]	1.334(9)	9
$Ru_5(CO)_{11}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (**3**)	80	1.305(5)	10
$Ru_5(CO)_{11}(\mu\text{-}Cl)_2(\mu\text{-}PPh_2)_2(C_2)$ (**3′**)	80	1.32(1)	11
$[Ru_5(CO)_{11}(CNBu^t)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)]$ (**4**)	80[d]	1.22(1)	12
$Ru_5(CO)_{10}(\mu\text{-}SMe)_4(\mu\text{-}PPh_2)_2(C_2)$ (**5**)	82[d]	1.28(1)	13
$Ru_5(CO)_{12}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (**6**)	82	1.26(2)/1.31(2)	10
$Fe_2Ru_5(CO)_{17}(Cp)_2(C_2)_2$ (**7**)	112 (82)	1.32(2)/1.34(2)	9
	$M_6(\mu_6\text{-}C_2)$ Core		
$Co_6(CO)_{14}(\mu_4\text{-}S)(C_2)$ (**8**)	92	1.37(2)	14
$Fe_2Ru_6(CO)_{17}(Cp^*)_2(C_2)_2$ (**9**)	120 (92)	1.35(4)/1.37(3)	15
$[Fe_3Co_3(CO)_{18}(C_2)]^-$ (**10**)	94	1.362(8)	16
$FeRu_5(CO)_{14}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (**12**)	94	1.355(9)	17
$Co_6(CO)_{18}(C_2)$ (**11**)	96	1.426(9)	18
	$M_8(\mu_8\text{-}C_2)$ Core		
$[Co_4Ru_5(CO)_{18}(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)]$ (**13**)	134	1.41(4)	17

[a] Abbreviations used: $Bu^t = C(CH_3)_3$, $Me = CH_3$, $Ph = C_6H_5$, $Cp = C_5H_5$, $Cp^* = C_5Me_5$, $py = C_5H_5N$. [b] Metallic valence electron count. [c] MVE count of the $M_n(\mu_n\text{-}C_2)$ core. [d] The $(C_2)^{2-}$ ligand provides only six electrons to the metallic framework (see text).

condensation rules, which allow evaluation of the cluster valence electron count for clusters regarded as the aggregation of polyhedra sharing a vertex, an edge, or a face.[20] Indeed, compound **1** can be seen as resulting from the condensation of a butterfly and an edge via a common vertex (62 + 34 - 18 = 78 MVEs as experimentally observed).

An alternative M_5C_2 arrangement is contained in the heptanuclear species $FeRu_6(CO)_{16}(Cp)(\mu_5\text{-}C_2H)(C_2)$ (**2**).[9]

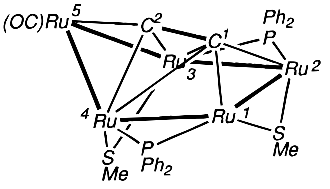


Fe = FeCp Ru = Ru(CO)₂

2

The metal core of compound **2** consists of an Ru_5 raft fused with a nearly perpendicular $FeRu_3$ square. A puckered capped square $FeRu_5$ array is then formed, on top of which sits the C_2 ligand interacting asymmetrically in a π-fashion with the metal atoms of the square. If we consider compound **2** as the condensation of triangular and square units sharing edges, an MVE count of 104 is expected. This is the observed electron count if we assume that the $C_2{}^{2-}$ and $(C_2H)^-$ ligands participate in the cluster bonding with 8 and 6 electrons, respectively. Note that a count of 78 MVEs, as expected for a cluster containing six metal-metal bonds, is achieved for the $FeRu_4(\mu_5\text{-}C_2)$ part of compound **2**. This is obtained by the 71 electrons of the $FeRu_4(Cp)(CO)_{10}(\mu_5\text{-}C_2)$ moiety added to the 7 electrons brought by the $Ru_2(CO)_5(C_2H)$ fragment, which is considered as a ligand attached to the M_5C_2 core ($Ru(CO)_2$ (3 electrons), $Ru(CO)_3$ (1 electron), and C_2H (3 electrons)). This makes it a "skeletal isomer" of compound **1** (vide infra).

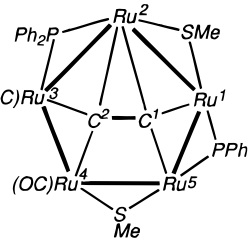
The geometry of the $FeRu_4C_2$ part of **2** somewhat resembles that found in the species $Ru_5(CO)_{11}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (**3**)[10] and $Ru_5(CO)_{11}(\mu\text{-}Cl)_2(\mu\text{-}PPh_2)_2(C_2)$ (**3′**).[11] The same type of "open-envelope" conformation is observed, but with the two Ru atoms which form the hinge now outside bonding distance. As in **2**, the C_2 unit is asymmetrically attached to the M_5 puckered ring. Transition-metal-ring compounds formed of n metal centers are generally characterized by an MVE count of $16n$.[21] This corresponds to 80 MVEs for compounds **3** and **3′**, as experimentally observed if the $C_2{}^{2-}$ ligand contributes 8 electrons.



Ru = Ru(CO)₂

3

The cluster core of $Ru_5(CO)_{11}(CNBu^t)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (**4**) consists of a nearly flat pentagon with the C_2 ligand ensconced in the middle, parallel to an edge.[12] Each carbon atom is strongly bonded to two metal atoms. Such a bonding mode has been previously



Ru = Ru(CO)₂

4

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(19) There are different ways to formally count electrons of the dicarbon moiety. We choose here to consider C_2 as a dianionic species rather than a neutral species so that it agrees with the octet rule. Note that the number of frontier molecular orbitals of C_2 which may participate in the M−C bonding is independent of this electron-counting convention.[6]

(20) Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1983**, 706.

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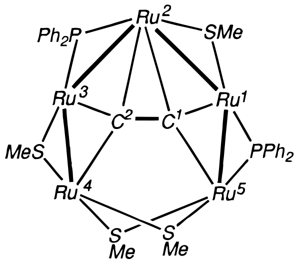
reported by Akita and co-workers in the permetalated ethene compound $Fe_2Ru_2(CO)_{10}(Cp^*)_2(C_2)$.[6,15] As expected, the transition-metal-ring cluster **4** is an electron-precise system with 80 MVEs. This assumes that the C_2^{2-} ligand provides only 6 electrons to the metallic framework instead of 8, as in the isoelectronic M_5C_2 ring species **3** and **3′**. This is in agreement with the rather short C−C bond compared to those measured in **3** and **3′** (see Table 1). The fact that the C_2^{2-} unit brings 6 electrons to the cluster leads to a loss of 2 cluster electrons, compensated by the 2 electrons of the additional $CNBu^t$ ligand.

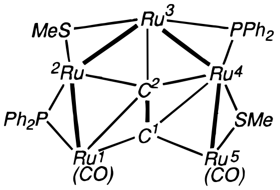
An open pentagonal metal core is observed in $Ru_5(CO)_{10}(\mu\text{-SMe})_4(\mu\text{-PPh}_2)_2(C_2)$ (**5**).[13] The geometry around the C_2 ligand is almost identical with that in compound **4**, with the carbon atoms nearly in the plane of the metal array. Again, if the C_2^{2-} unit gives only 6 electrons to the metallic part, cluster **5** is an electron-precise molecule with 82 MVEs, in agreement with four Ru−Ru bonds.



Ru = Ru(CO)$_2$

5

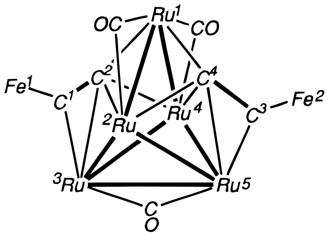
A distorted-open-pentagonal metal array is also contained in $Ru_5(CO)_{12}(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(C_2)$ (**6**).[10] The asymmetric disposition of the C_2 moiety with respect to the Ru_5 open ring somewhat recalls that found in $Ru_4(CO)_{12}(\mu\text{-PPh}_2)_2(C_2)$.[6,22] With the C_2^{2-} unit bringing 8 electrons to the cluster, compound **6** contains 82 MVEs, as expected for an M_5 cluster with four M−M bonds. Therefore, **6** is isoelectronic with **5**.



Ru = Ru(CO)$_2$

6

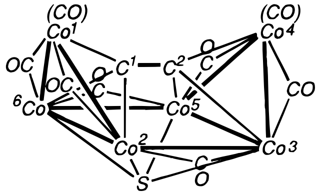
An alternative $M_5(\mu_5\text{-}C_2)$ geometry is encountered in the heptanuclear bis(dicarbide) complex $Fe_2Ru_5(CO)_{17}(Cp)_2(C_2)_2$ (**7**).[9] The five Ru atoms form an arrowhead-shaped cage with the μ_4-acetylide $Fe(Cp)(CO)_2C_2$ groups interacting with the Ru_4 butterfly parts. The polyhedral skeletal electron pair (PSEP) theory predicts a count of 76 MVEs for an arrowhead-type M_5 cluster.[20,21] This is the observed count if the C_2^{2-} ligands contribute 8 electrons. Alternatively, compound **7** can be viewed as the condensation through an open Ru_3 triangle of two $FeRu_4(\mu_5\text{-}C_2)$ systems comprising a butterfly Ru_4 part linked to an $Fe(Cp)(CO)_2$ group via a C_2 bridge. A formal count of 82 MVEs, consistent with the presence of four M−M bonds, is obtained for each $FeRu_4(\mu_5\text{-}C_2)$ moiety. This is achieved by adding the 77 electrons of the $FeRu_4(Cp)(CO)_{13}(C_2)$ fragment to the 5 electrons brought by the $FeRu(Cp)(CO)_4(C_2)$ unit considered as a ligand. Therefore, each $Ru_4Fe(\mu_5\text{-}C_2)$ part of compound **7** can then be considered as a skeletal isomer of the 82-MVE species **5** and **6**.



Fe = Fe(CO)$_2$Cp Ru = Ru(CO)$_2$

7

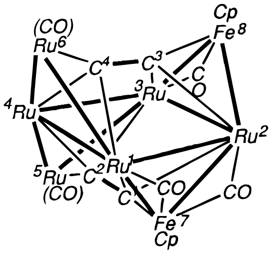
In the hexanuclear cluster $Co_6(CO)_{14}(\mu_4\text{-S})(C_2)$ (**8**) the C_2 unit is inserted in an open-trigonal-prismatic metal array.[14] With the C_2^{2-} ligand acting as an 8-electron donor, compound **8** has 92 MVEs, as expected from the PSEP rules (vide infra). The same arrangement is observed in the isoelectronic species $Ni_2Ru_4(Cp)_2(CO)_8(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(C_2)$.[23]



Co = Co(CO)

8

A similar coordination mode of the C_2 unit tethered to a boatlike metal array is encountered in the octametallic cluster $Fe_2Ru_6(CO)_{17}(Cp^*)_2(C_2)_2$ (**9**).[15] This compound results from the condensation of two boatlike M_6 systems rotated by 90° with respect to each other via a square face. In agreement with the condensation rules, a count of 120 MVEs ((92 × 2) − 64) is observed for **9** if the C_2^{2-} entities participate with 8 electrons in the cluster bonding.



Ru = Ru(CO)$_2$

9

A comparable bonding mode of the C_2 ligand is observed in the 94-MVE cluster $[Fe_3Co_3(CO)_{18}(C_2)]^-$ (**10**)[16] and the 96-MVE cluster $Co_6(CO)_{18}(C_2)$ (**11**).[18] In both cases, the structural arrangement of the cluster core consists of two metal triangles bonded at either end

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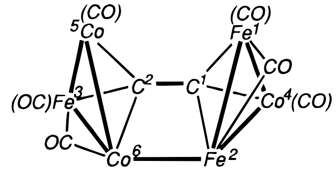
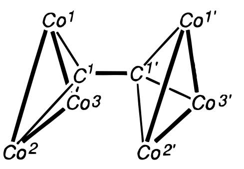
(22) Bruce, M. I.; Snow, M. R.; Tiekink, E. R.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1987**, 701.

(23) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H., unpublished results.



Fe = Fe(CO)$_2$ Co = Co(CO)$_2$

10

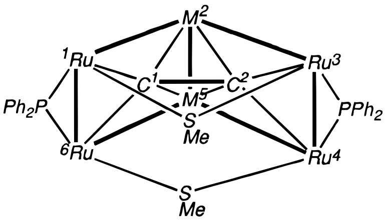


Co = Co(CO)$_3$

11

of the C_2 unit. In agreement with the electron count, the two metal triangles are parallel and are nonbonded to each other in **11**. On the other hand, they are tipped toward each other in **10** in such a way that a long intertriangle metal−metal bond length (2.90 Å) is created.[16]

A different structural arrangement is noted in $FeRu_5(CO)_{14}(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(C_2)$ (**12**).[17] The metal cage

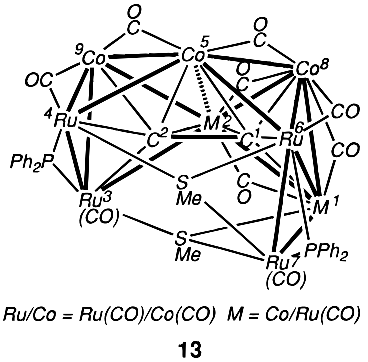


Ru = Ru(CO)$_2$ M = Fe/Ru(CO)$_3$

12

resembles a gabled roof with the C_2 unit symmetrically sitting in the groove perpendicular to the M(2)−M(5) bond. Compound **12** can be viewed as two metallic squares sharing an edge. The application of the condensation rules leads to an expected count of 94 MVEs ((2 × 64) − 34). This is the observed electron count if the C_2^{2-} ligand acts as an 8-electron donor. Consequently, cluster **12** is a skeletal isomer of the isoelectronic compound **10**.

The structural arrangement of the compound $Co_4Ru_5(CO)_{18}(\mu_3\text{-SMe})_2(\mu\text{-PPh}_2)_2(C_2)$ (**13**)[17] can be derived from that of **12**. Each square of the gabled roof is now capped

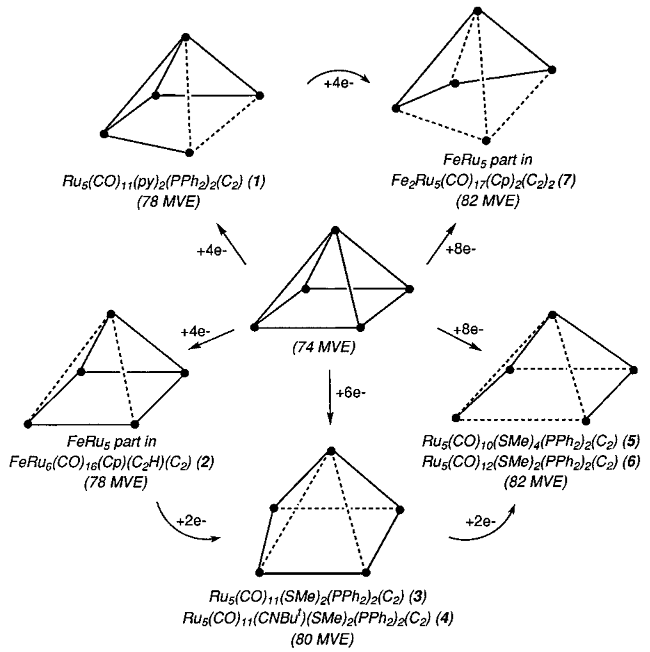


Ru/Co = Ru(CO)/Co(CO) M = Co/Ru(CO)

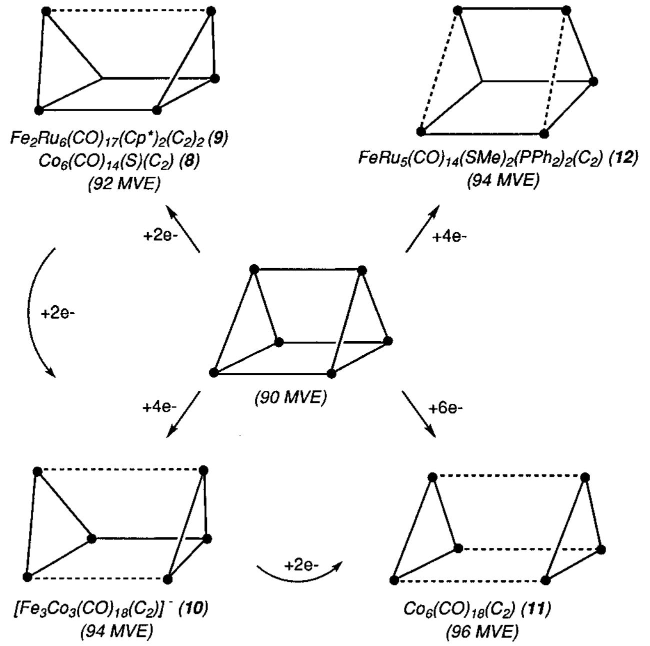
13

by an additionnal metal atom, leading to an M_8 cluster core made of two edge-sharing square-pyramidal polyhedra, one of which is also metalated at an edge. In this case, the count of 134 MVEs for **12** does not agree with that predicted by the condensation rules (130 MVEs) if the C_2^{2-} unit, bound to 8 metal atoms, contributes 8 electrons.

Scheme 1



Scheme 2



In transition-metal cluster chemistry atoms from the iron and cobalt triads frequently aggregate to build square-pyramidal, octahedral, or triangular-prismatic compounds. In main-group-element-containing transition-metal clusters, an accurate fitting between the atomic radius of the interstitial element and the cavity size of the metallic host is a prerequisite for their formation.[4,5] The incorporation of large elements or large units often obliges the metal atoms to reorganize in a more open structure, as illustrated by the C_2-containing compounds mentioned here. Indeed, the structural arrangements of the $M_5(\mu_5\text{-}C_2)$ and $M_6(\mu_6\text{-}C_2)$ clusters listed in Table 1 can be derived upon formal addition of electrons from the square-pyramidal and trigonal-prismatic structures, respectively. This is shown in Schemes 1 and 2. Since they are too large to be completely encapsulated, the C_2 units insert after having forced the opening of the M_5 or M_6 cages.

The open-envelope conformation of the 78-MVE $FeRu_4$ part of compound **2**, for instance, can be obtained from

Table 2. Computed Characteristics for Different $M_5(\mu_5\text{-}C_2)$ Compounds

	1	2	3	4	5	6	7[a]
HOMO/LUMO Gap (eV)							
	1.22	0.96	1.38	1.00	1.45	1.32	1.13
Atomic Net Charges							
Ru(1)	−0.17	−0.10	−0.22	−0.21	−0.13	−0.05	−0.02
Ru(2)	−0.16	+0.05	−0.23	−0.00	−0.02	−0.20	−0.01
Ru(3)	−0.23	−0.09	−0.07	−0.19	−0.07	−0.11	−0.05
Ru(4)	−0.26	−0.12	−0.09	−0.05	−0.14	+0.03	−0.01
Ru(5)	−0.08	+0.03	−0.11	−0.15	−0.10	−0.10	−0.04
Ru(6)		−0.01					
Fe(1)		+0.17					+0.53
Fe(2)							+0.50
C(1)	−0.29	−0.18	−0.22	−0.32	−0.40	−0.30	−0.07
C(2)	−0.29	−0.33	−0.31	−0.35	−0.36	−0.27	−0.36
C_2 FMO Occupations							
σ_u	1.51	1.48	1.50	1.54	1.54	1.54	1.47
π_u	1.62/1.59	1.52/1.61	1.69/1.48	1.98/1.46	1.75/1.69	1.84/1.46	1.57/1.47
σ_g	1.29	1.30	1.30	1.33	1.34	1.27	1.34
$\pi_g{}^*$	0.36/0.25	0.33/0.33	0.23/0.36	0.10/0.28	0.22/0.25	0.15/0.32	0.26/0.38
Overlap Populations[b]							
C(1)−C(2)	1.39 [1.30]	1.32 [1.33]	1.38 [1.31]	1.69 [1.22]	1.59 [1.28]	1.54 [1.26]	1.37 [1.33]
C(1)−Ru(1)	0.17 [2.31]	0.15 [2.28]	0.41 [2.13]	0.41 [2.11]	0.38 [2.15]	0.19 [2.30]	
C(1)−Ru(2)			0.42 [2.13]	0.10 [2.35]	0.15 [2.25]		
C(1)−Ru(3)	0.09 [2.43]	0.08 [2.48]	0.08 [2.41]				0.32 [2.14]
C(1)−Ru(4)	0.40 [2.12]		0.11 [2.47]		0.25 [2.30]	0.16 [2.27]	
C(1)−Ru(5)	0.38 [2.19]			0.23 [2.29]		0.51 [2.06]	
C(1)−Ru(6)		0.34 [2.19]					
C(1)−Fe(1)		0.60 [1.88]					0.60 [1.93]
C(2)−Ru(1)	0.18 [2.21]	0.16 [2.26]				0.09 [2.36]	0.35 [2.15]
C(2)−Ru(2)	0.66 [1.96]	0.68 [1.94]		0.07 [2.38]	0.10 [2.33]	0.44 [2.10]	0.25 [2.25]
C(2)−Ru(3)	0.25 [2.17]	0.25 [2.18]	0.20 [2.26]	0.44 [2.10]	0.31 [2.25]	0.21 [2.41]	0.16 [2.25]
C(2)−Ru(4)			0.18 [2.23]	0.28 [2.19]	0.38 [2.14]	0.10 [2.45]	0.35 [2.16]
C(2)−Ru(5)			0.71 [1.94]				

[a] Carbon net charges, C−C and C−M overlap populations, and distances are averaged on the two C_2 ligands. [b] Distances (Å) are given in brackets.

the 74-MVE square-pyramidal M_5 cluster by the breaking of two adjacent M(basal)−M(apical) bonds (see Scheme 1). Subsequent two-electron addition accompanied by the cleavage of one M(basal)−M(basal) bond opposite to the two already broken M(basal)−M(apical) bonds affords the M_5 ring observed in the 80-MVE species **3**, **3′**, and **4**. The open-ring structure of the 82-MVE compounds **5** and **6** is obtained with the breaking of an additional M(basal)−M(basal) bond upon addition of two more electrons. The cleavage of an M(basal)−M(apical) bond and an M(basal)−M(basal) bond adjacent to each other leads to the isomeric M_5 geometry present in **2**, analogous to that of the metalated butterfly core present in the 78-MVE complex **1**. Additional breaking of nonadjacent M(basal)−M(apical) and M(basal)−M(basal) bonds upon further 4-electron addition gives rise to the metal arrangement present in compound **7**, a skeletal isomer of that encountered in the 82-MVE species **5** and **6**.

The PSEP rules predict a count of 90 MVEs for a trigonal-prismatic metal cluster.[20,21] Adding two electrons may result in the breaking of one intertriangle bond, leading to the boatlike metal array observed in the 92-MVE compounds **8** and **9** (see Scheme 2). Additional cleavage of one or two intertriangle M−M bonds due to further 2- and 4-electron additions, respectively, gives rise to the structural arrangements encountered for the 94-MVE and 96-MVE compounds **10** and **11**, respectively. Alternatively, the gabled-roof structure reported for the 94-MVE species **12**, a skeletal isomer of the isoelectronic complex **10**, can be obtained by rupture of two parallel intratriangle M−M bonds (see Scheme 2).

Although such a description allows a rationale of the metallic arrangements present in these metal−dicarbide clusters within the framework of the PSEP rules, it says nothing concerning the isomerism induced by the different coordination modes of the C_2 ligand. For instance, it conceals the fact that the $C_2{}^{2-}$ ligand formally acts as an 8-electron donor in the 80-MVE species **3** and as a 6-electron donor in the isoelectronic compound **4**, in which it lies perpendicular and parallel to an M−M bond, respectively. As noticed previously for the M_4-(μ_4-C_2) complexes,[6] both the metal arrangements *and* the coordination modes of the C_2 unit must be considered for a full description of the M_5C_2 and M_6C_2 systems.

In order to clarify the similarities and the differences in electronic structure and electron count, extended Hückel calculations were carried out on the different C_2-containing compounds listed in Table 1. The experimental X-ray structures were chosen for the calculations (see the Appendix).

Electronic Structure of Compounds Containing an M_5C_2 Core

Some computed characteristics for different M_5C_2 clusters are summarized in Table 2. Before discussing these numbers, let us repeat Schaefer's words, which express a consensus among theorists: "Any scheme (such as population analysis) for assigning charges to atoms in a molecule is arbitrary. However, comparison of population analyses for a series of molecules does allow one to make qualitative conclusions concerning changes in electron distribution."[24] With this in mind, let us examine Table 2.

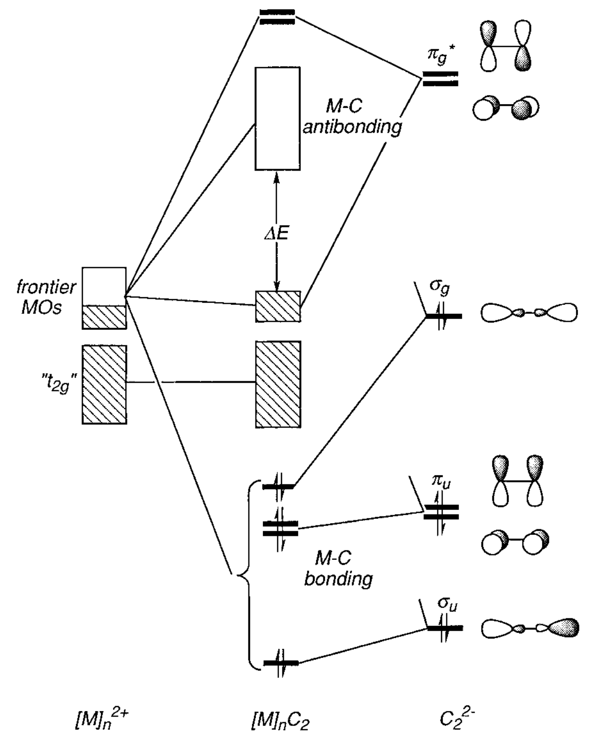
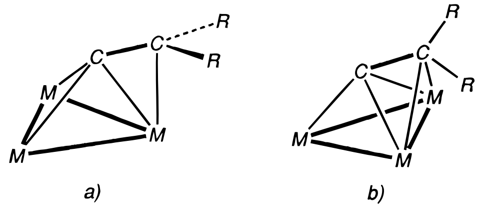


Figure 1. Qualitative interaction MO diagram for $[M]_nC_2$ compounds.

As expected, the results suggest that the *exposed* C_2 unit enters into a synergic bonding interaction with molecular orbitals of the metal cage. Important electron donation occurs primarily from the σ_u(s), σ_g(p), and π_u orbitals of the C_2^{2-} ligand to empty metallic molecular orbitals and is supplemented by back-donation from filled metallic molecular orbitals to the π_g* orbitals of the C_2^{2-} moiety (see Figure 1). It is noteworthy that this forward and backward donation is rather similar for compounds $Ru_5(CO)_{11}(py)_2(\mu\text{-}PPh_2)_2(C_2)$ (**1**), $FeRu_6(CO)_{16}(Cp)(\mu_5\text{-}C_2H)(C_2)$ (**2**), and $Ru_5(CO)_{11}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (**3**), indicating that the bonding of the C_2 unit with the metal framework is highly comparable in these compounds. This is not too surprising for **2** and **3**, since the C_2 ligand is bound in the same way to the metal framework. However, at first sight the C_2 coordination mode in **1** differs from that observed in **2** and **3**. Nevertheless, a close examination of the carbon−metal overlap populations (OP), which reflect the structural data, indicates that in all of these three clusters C(1) is normally σ-bonded to two metal atoms (strong OP: from 0.34 to 0.60) and very weakly π-bonded to two other metal atoms (weak OP: from 0.08 to 0.17), whereas C(2) is strongly σ-ligated to one metal atom (strong OP: from 0.66 to 0.71) and π-bonded to two metal atoms (medium OP: from 0.16 to 0.25).

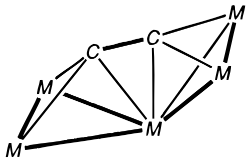
Such a bonding mode may lead us to describe these compounds as containing a metalated vinylidene ligand $CC(ML_m)_2$ spanning a metal triangle. Regardless of the orientation of the C(1)−$(ML_m)_2$ group, either perpendicular (in **1**) or parallel (in **2** and **3**) to the plane of the metal triangle, the metalated vinylidene cap is oriented toward a metal−metal vector. This somewhat contrasts with experimental[25] and theoretical[26] works on vinylidene−trimetallic compounds $L_mM_3(\mu_3\text{-}CCR_2)$, which indicate that the CCR_2 ligand generally prefers to bend toward a metal vertex with the CR_2 plane parallel to the basal plane and toward a metal−metal vector with the R groups oriented in an upright manner relative to the basal plane (see **14a** and **14b**, respectively). Note



a) b)

14

that with two metal fragments as R groups, arrangement **14a** may lead to an alternative and hypothetical 78-MVE skeletal isomer of **1** and **2**, in which the metal atoms depict a bow-tie framework (two metal triangles sharing a vertex) (see **15**).



15

Due to the different stoichiometries and the lack of symmetry of compounds **1** and **2**, we were not able to compare their total energies in order to understand the preferred M_5C_2 arrangement for a count of 78 MVEs. We note only that the computed bonding energy between the C_2^{2-} ligand and the metallic moiety is slightly more important in **2** than in **1** (8.04 *vs* 7.30 eV). Let us mention that a rotation of the Ru(4)−Ru(5) vector from perpendicular to parallel to the Ru(1−3) plane accompanied by the rupture of the Ru(3)−Ru(4) bond and the formation of the Ru(3)−Ru(5) bond in **1** gives rise to an M_5C_2 arrangement identical with that contained in **2**.

In **1**, a localized bonding picture with Ru atoms having an 18-electron configuration suggests an asymmetrically bound C_2 moiety being electron-poor at C(1) and electron-rich at C(2) and metal atoms being charged differently.[8] Surprisingly enough, our calculations show that each carbon atom of the C_2 ligand bears the same negative charge (ca. −0.29), although they bind differently to the metal cluster, reflecting an efficient "sharing" of electrons over the whole M_5C_2 cluster. The sum of the C(1)−M overlap populations is roughly equal to the sum of the C(2)−M overlap populations (1.04 *vs* 1.09). We think that the long C(1)−Ru(1,3) bonding contacts (2.31 and 2.43 Å), which are not taken into account within a localized bonding description, lead to an equalization of the carbon charges. The M−M and M−C bonding is rather delocalized overall in compound **1**.

As said previously, the bonding between the C_2 unit and the metallic core is nearly identical in the "open-envelope" compounds **2** and **3**, having 78 and 80 MVEs,

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(24) Schaefer, H. F. *The Electronic Structure of Atoms and Molecules*; Addison-Wesley: Reading, MA, 1972; p.384.

(25) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197 and references therein.

(26) (a) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, 101, 3456. (b) McGlinchey, M. J. In *Topics in Physical Organometallic Chemistry*; Gielen, M., Ed.; Freund: London, 1992; Vol. 4, p 41.

respectively (see Table 2). The electronic structure of species **3** has already been investigated by Adams and co-workers using an idealized geometry.[27] Comparable results were obtained with the experimental structure. In contrast to compound **1**, the computed net charges on the carbon atoms reflect the asymmetric linkage of the C_2 ligand over the M_5 ring. The carbon atom C(2), which sits in a relatively exposed position above the metal ring, is more electron-rich than the carbon atom C(1) (−0.18 and −0.22 *vs* −0.33 and −0.31 in **2** and **3**, respectively). This suggests that electrophilic attack on the C_2 entity is likely to occur at C(2), as evidenced by the reactivity of complex **3**.[27] The C(1)−Ru(1,3) and C(1)−Ru(3,4) bonding contacts in **2** and **3**, respectively, which here again are not taken into account within a localized bonding scheme, are longer than the corresponding ones in **1**, and consequently back-donation of electron density to C(1) is less efficient. This may explain why C(1) is less negatively charged than C(2).

Although isoelectronic with compound **3**, the 80-MVE compound $Ru_5(CO)_{11}(CNBu^t)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (**4**) deserves particular attention. Application of the EAN formalism requires the C_2^{2-} ligand to act here as a 6-electron donor vis-à-vis the metallic cluster, with no formal C(1,2)−Ru(2) bonds. Calculations performed on **4** support such a bonding description. As shown in Table 2, the C_2 ligand is more electron-rich, and both π-donation and π^*-back-donation are smaller than in **3**, reflecting a weaker interaction with the metal framework. This is illustrated in Figure 2, which shows the pertinent interactions between the metallic fragment and the dicarbon unit in **4**. Basically, the $[Ru_5(CO)_{11}(\mu\text{-}CO)_2(CNBu^t)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2]^{2+}$ fragment of **4** consists of five ML_4 entities. Each ML_4 unit possesses two frontier orbitals,[28] and their assemblage to form the metallic ring gives rise to five M−M bonding hybrid FMOs above a nest of low-lying (mainly d) orbitals. These are shown in Figure 3. Counting C_2 as a dianionic ligand, two FMOs are formally occupied before interaction.

Among the five metallic FMOs, four interact rather strongly with those of the dicarbon moiety (see Figure 2). The dominant interactions occur between the metallic 3a, 4a, and 5a orbitals and the C_2 2a ("in-plane" π_u), 1a (σ_u), and 4a (σ_g) orbitals, respectively. The metallic FMOs lie nearly in the ring plane. Consequently, the "out-of-plane" π_u (3a) and π_g* (6a) orbitals of the C_2 ligand hardly interact with the metal framework. The occupation of FMO 3a is nearly two electrons, and back-donation to FMO 6a is rather weak. As the C_2 ligand in **4** is less involved in M−C bonding than are those in **1**−**3**, the carbon−carbon distance is shorter in the former. This is also reflected by the computed bonding interaction energy between the C_2^{2-} and $[Ru_5]^{2+}$ fragments, which is weaker than the corresponding ones in compounds **1**−**3** (4.67 *vs* ca. 7.5 eV). Despite the fact that the C−C separation is closer to a triple bond than a double bond, compound **4** can indeed be described as a kind of distorted permetalated ethene, in which the C_2 ligand is σ-bonded to Ru(1) and Ru(3) and σ-/π-bonded to Ru(4) and Ru(5). This is reflected by the strong *vs* medium Ru−C OPs (0.41, 0.44 *vs* 0.23, 0.28, respectively). It turns out that a combination of reduced electron donation from the C_2 ligand toward the rest of the molecule and reduced back-donation from the rest of the molecule into the C_2 π^* FMOs results in a short C−C bond in complex **4**, compared to that of ethylene. This is due to the different nature of the groups borne by the C_2 unit (organometallic *vs* organic groups) and different bonding angles. Comparable results were obtained on the planar tetrametallic complex $Fe_2Ru_2(CO)_{10}(Cp^*)_2(\mu_4\text{-}C_2)$.[6,15]

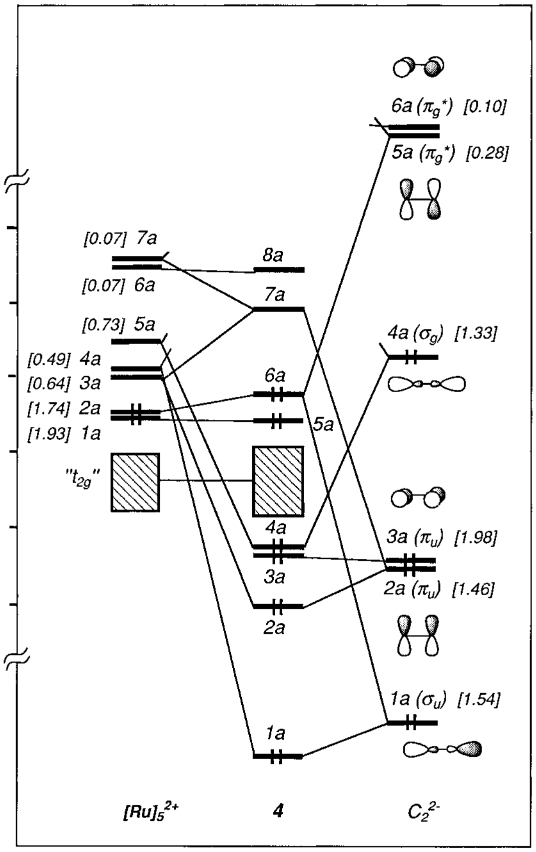

Figure 2. Molecular orbital diagram of the 80-MVE compound **4**, $Ru_5(CO)_{11}(CNBu^t)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (Bu^t, Me and Ph groups have been replaced by H atoms). The numbers in brackets indicate the electron occupation of FMOs after interaction.

Such a bonding description of the C_2 ligand with the metal ring in **4** agrees with the EAN formalism. Of course, the M−M and M−C bonding is delocalized overall. Weak but bonding M−C contacts, not taken into account within the EAN formalism, are present between the carbon atoms and the Ru(2) center (see Table 2). This might increase somewhat the electronic density on the metal framework, partially explaining the relatively long Ru-Ru separations, some of which are greater than 3 Å.[13] Nevertheless, we think that to a first approximation a tautomeric form with a μ_4-C_2 bonding mode is more appropriate than that with a μ_5-C_2 bonding mode to describe the linkage of the C_2 moiety in the planar compound **4**.

As noted earlier, compounds **3** and **4** are isoelectronic. Because of a different orientation of the C_2 unit with respect to the metal pentagon, perpendicular to a metal edge in one case and parallel to a metal edge in the other case, **3** and **4** can be considered as skeletal isomers. A change from **3** to **4** can theoretically be obtained by a rotation of 90° of the C_2 ligand above the metal ring.

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[27] Adams, C. J.; Bruce, M. I.; Liddell, M. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1314.

[28] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 358.

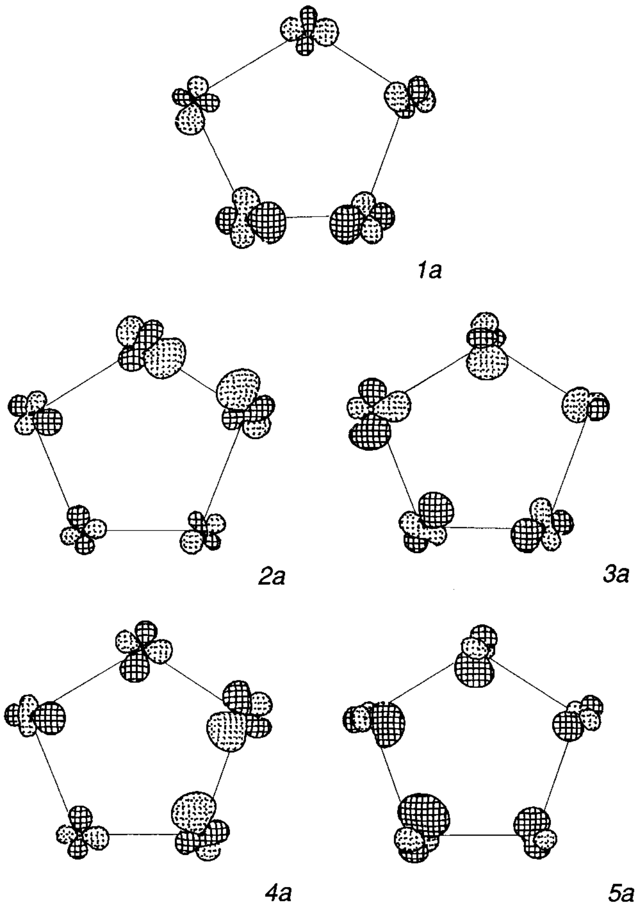

Figure 3. Frontier molecular orbitals of the metallic fragment $[Ru_5(CO)_{11}(CNBu^t)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2]^{2+}$ of **4**.

The number of M−C bonds is reduced in the latter, this rotation being accompanied by a loss of two electrons from C_2 to the metal cluster, compensated by the addition of a two-electron ligand ($CNBu^t$) to a metal center.

The different characteristics computed for compound **5** indicate that the C_2 ligand is slightly more involved in the M−C bonding than is the case in **4**. The interaction energy between the C_2 ligand and the metallic fragment is more important (5.00 *vs* 4.67 eV) and the Ru(2)−C OPs in **5** are slightly larger than in **4** (0.15 and 0.10 *vs* 0.10 and 0.07), suggesting that the C_2 unit is not as weakly attached to Ru(2). The larger M−C back-bonding is reflected in the C−C distance (1.26 *vs* 1.22 Å), and the atomic net charges are slightly larger than the corresponding net charges in **4** (see Table 2). Nevertheless, the metal−carbon bonding in compound **5** is very similar to that in cluster **4**, involving the C_2^{2-} ligand acting as a six- rather than an eight-electron donor, i.e. neglecting to a first approximation the Ru(2)−C interaction. The two additional electrons of the cluster compared to **4** lie in an Ru−Ru antibonding molecular orbital.

The bonding of C_2 with the metallic open ring in the compound $Ru_5(CO)_{12}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (**6**) is intermediate between that observed in **1**−**3** on the one hand and **4** and **5** on the other hand. The weaker bonding interaction energy between the C_2^{2-} and $[Ru_5(CO)_{12}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2]^{2+}$ moieties (5.42 *vs* ca. 7.5 eV in complexes **1**−**3**) indicates that the C_2 unit is also less involved in the M−C bonding in **6**, explaining the rather strong C−C bond. The M−C overlap populations support the formal description of the M−C bonding involving σ-interactions with Ru(2) and Ru(5) (strong OP: 0.51 and 0.44) and rather weak π-interactions with Ru(1), Ru(3), and Ru(4) (weak or medium OP: from 0.09 to 0.21). Application of the EAN formalism is not fully appropriate to account for the bonding in compound **6**, since it takes into account the weak C(2)−Ru(1,4) interactions and neglects the stronger C(2)−Ru(3) interaction (see Table 2). Here again the M−C bonding is highly delocalized. Nevertheless, a comparison can be made with the M_4C_2 complex $Ru_4(CO)_{12}(\mu\text{-}PPh)_2(C_2)$.[6,22] Metal−metal and metal−carbon σ- and π-bonds and carbon net charges, for instance, are comparable. In both compounds the long M−C π-contacts prevent an important donation from C_2 to the metal atoms and therefore contribute to strengthen the C−C bond and to diminish the electron density on the metal framework. The electron-poor character of the open metal ring is reflected by the net charges on the metal atoms (see Table 2) and the rather short Ru−Ru distances.[10,22] As noted for $Ru_4(CO)_{12}(\mu\text{-}PPh)_2(C_2)$,[6] a nonplanar Ru(1)−Ru(2)−Ru(4)−Ru(5) arrangement around the C_2 ligand (as experimentally observed) must increase the M−C bonding and consequently the stability of complex **6**.

The net charges on the carbon atoms of the C_2 moiety are similar (−0.30 and −0.27), though C(1) and C(2) are bound to three and four metal atoms, respectively, but we note that the C(1)−M and C(2)−M overlap populations are nearly equal (0.86 *vs* 0.84, respectively). Although these charges are comparable to those computed for cluster **1**, reduced donation from the C_2 orbitals toward metallic MOs and back-donation from filled metallic MOs to C_2 acceptor orbitals are found in **6**, compared to those computed in **1** (see Table 2).

Although the electron donation and back-donation between the C_2 ligands and the $FeRu_4$ cores in the compound $Fe_2Ru_5(CO)_{17}(Cp)_2(C_2)_2$ (**7**) look similar to those observed in compounds **1**−**3** (see Table 2), the bonding between the two fragments is different. For instance, the M−C overlap populations suggest that C(1) is firmly σ-bonded to Fe(1) (strong OP: 0.60) and to a lesser extent to Ru(3) (medium OP: 0.32), whereas C(2) is σ-/π−bonded to Ru(1,3) (medium OP: 0.35 and 0.16) and π-bonded to Ru(2,4) (medium OP: 0.25 and 0.35). The hypervalent character of the carbon atoms of the C_2 ligands, particularly C(1) and C(3), precludes a satisfactory description of the bonding in complex **7** with the EAN rule. Indeed, the bonding of C(1), sitting in the groove of the distorted metal butterfly recalls somewhat that observed in butterfly-cluster carbides such as $[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$.[29] The computed net charges on the carbon atoms indicate that the C_2 moieties in **7** form dipolar ligands, being largely more electron-rich at C(1,3) (average −0.07) than at C(2,4) (average −0.36). When the C_2 unit is asymmetrically linked to a metal framework such as in compounds **1**−**3**, the carbon atom having the higher connectivity is generally the more electron-poor atom. Surprisingly, the situation is different in **7**, where it is the carbon atoms attached to only two metal atoms which are more electron-poor than those bound to four metal atoms. We think that the charge on the former may be sensitive to the electron-

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(29) Bradley, J. S.; Ansell, G. B.; Leonowicz, M. E.; Hill, E. W. *J. Am. Chem. Soc.* **1981**, *103*, 4968.

Table 3. Computed Characteristics for Different Polymetallic-C_2 Compounds Containing an $M_6(\mu_6\text{-}C_2)$ or an $M_8(\mu_8\text{-}C_2)$ Core

	8	**9**[a]	**10**	**11**[b]	**12**	**13**
			HOMO/LUMO Gap (eV)			
	1.33	1.38	2.09	2.27	1.32	0.59
			Atomic Net Charges			
M(1)	−0.13	+0.04	−0.01	−0.13	−0.15	−0.14 (Ru)
M(2)	−0.10	+0.38	−0.17	−0.10	+0.16 (Fe)	+0.44 (Co)
M(3)	−0.13	+0.19	−0.01	−0.13	−0.15	+0.06
M(4)	−0.13	+0.15	−0.13		−0.15	−0.24
M(5)	−0.10	−0.10	−0.10		−0.05 (Ru)	+0.27
M(6)	−0.13	−0.01	+0.08		−0.12	+0.08
M(7)		+0.62				−0.14
M(8)		+0.36				+0.11
M(9)						+0.34
C(1)	−0.16	−0.21	−0.22	−0.34	−0.32	−0.17
C(2)	−0.19	−0.36	−0.19	−0.34	−0.32	−0.19
			C_2 FMO Occupations			
σ_u	1.37	1.43	1.36	1.38	1.45	1.39
π_u	1.37/1.38	1.46/1.48	1.38/1.38	1.35/1.35	1.39/1.45	1.31/1.32
σ_g	1.33	1.36	1.35	1.39	1.47	1.40
π_g*	0.46/0.50	0.45/0.43	0.51/0.48	0.64/0.64	0.47/0.46	0.49/0.50
			Overlap Populations[c]			
C(1)−C(2)	1.15 [1.37]	1.20 [1.36]	1.15 [1.36]	1.01 [1.43]	1.20 [1.36]	1.08 [1.41]
C(1)−M(1)	0.60 [1.81]	0.31 [1.88]	0.47 [1.96]	0.49 [1.95]	0.38 [2.11]	0.39 [2.06]
C(1)−M(2)	0.34 [1.99]	0.32 [2.19]	0.43 [1.95]	0.49 [1.94]	0.26 [2.07]	0.19 [2.05]
C(1)−M(3)				0.50 [1.93]		
C(1)−M(4)			0.47 [1.92]			
C(1)−M(5)					0.28 [2.06]	0.17 [2.12]
C(1)−M(6)	0.34 [2.03]				0.37 [2.12]	0.32 [2.20]
C(1)−M(7)		0.62 [1.88]				
C(1)−M(8)						0.41 [1.94]
C(2)−M(2)					0.27 [2.07]	0.21 [2.05]
C(2)−M(3)	0.33 [2.01]	0.32 [2.13]	0.43 [1.99]		0.38 [2.12]	0.31 [2.20]
C(2)−M(4)	0.61 [1.81]	0.31 [2.17]			0.37 [2.12]	0.36 [2.10]
C(2)−M(5)	0.35 [2.02]	0.61 [2.00]	0.48 [1.93]		0.29 [2.07]	0.18 [2.09]
C(2)−M(6)			0.41 [1.94]			
C(2)−M(9)						0.40 [1.94]

[a] Carbon net charges, C−C and C−M overlap populations, and distances are averaged on the two C_2 ligands. [b] The structure described in ref 18b was used for calculations. [c] Distances (Å) are given in brackets.

withdrawing properties of the Fe(Cp)(CO)$_2$ group attached to them.

Electronic Structure of Compounds Containing an M_6C_2 Core

Some computed characteristics for different clusters containing M_6C_2 cores are summarized in Table 3. Here again, as for the M_5C_2 compounds, a strong covalent interaction occurs between the C_2 entities and their metallic hosts (see Figure 1). This is reflected both by important M−C overlap populations and the occupation of the C_2^{2-} FMOs. A glance at these computed characteristics indicates right away that the C_2 ligands are more strongly bound to the M_6 metallic cages than they were to the M_5 cages (compare Tables 2 and 3). Indeed, both forward and backward electron donations are more important in the case of the M_6C_2 clusters. The consequence is a diminution of the electron density between the carbon atoms of the C_2 units, leading to C−C bonds ca. 0.05 Å longer than those found in the M_5C_2 complexes. This does not prevent the carbon atoms from having net atomic charges comparable to those computed for the M_5C_2 species (ca. −0.2, −0.3). The greater electron loss from the C_2^{2-} donor orbitals in the former is compensated by a greater electron acceptance by the C_2^{2-} acceptor orbitals.

The bonding modes between C_2 and the metallic cage are remarkably similar in compounds **8**−**11**. The compounds $[Fe_3Co_3(CO)_{18}(C_2)]^-$ (**10**) and $Co_6(CO)_{18}(C_2)$ (**11**) have already been theoretically studied.[16] EH calculations that we carried out on the experimental structures lead to results comparable to those obtained by Shriver et al. on somewhat idealized structures. These authors studied the MO diagram of **11** formed by interaction between the FMOs of the C_2^{2-} and $[Co_6(CO)_{18}]^{2+}$ fragments. Among the 12 FMOs expected for 2 noninteracting, eclipsed triangular $Co_3(CO)_9$ units,[26] the 6 highest FMOs interact strongly with the donor and acceptor FMOs of the C_2 unit, leading to the formation of 6 occupied M−C bonding orbitals.[16] These MOs correspond formally to the 6 σ M−C bonds. It turns out that a 2-electron−2-center localized bonding scheme can account for the M−C bonding in species **11**. Such a cluster can be described as a permetalated ethane. The nature of the metallic substituents and the M−C−C angles larger than the H−C−C angles in ethane partially explain the shorter C−C bond distance in **11** (1.43 *vs* 1.54 Å). Our calculations using the experimental structure of **11**, in which the two Co_3 triangles are slightly twisted,[16] indicate a large HOMO/LUMO gap (more than 2 eV) for the observed count of 96 EVMs, in agreement with the PSEP electron-counting rules.

The HOMOs are nearly degenerate and are fully occupied for a count of 96 MVEs. With 2 electrons fewer, i.e. for a count of 94 MVEs, the system becomes Jahn-Teller unstable and a distorted structure is expected. With the help of EH calculations on an idealized structure of **11**, Shriver et al. have shown that if the two Co_3 planes tilt in such a way that two metal atoms get close to each other, the HOMO/LUMO gap for the count of 94 MVEs increases, due to the destabilization of the LUMO. This is what happens in the 94-MVE compound $[Fe_3Co_3(CO)_{18}(C_2)]^-$ (**10**), in which a long intertriangle Fe(2)−Co(6) bond has been formed by a tilt of the two M_3 triangles of ca. 18°.[16] This intertriangle M−M contact is rather long compared to the intratriangle M−M distances (2.90 *vs* 2.52 Å), but it corresponds to a bonding M−M interaction (weak Fe(2)−Co(6) OP: 0.07) sufficient to induce a large HOMO/LUMO gap for the observed count of 94 MVEs (a HOMO/LUMO gap of 2.09 eV is computed for the experimental compound **10**).

The electronic structure of the 92-MVE boatlike compounds $Co_6(CO)_{14}(\mu_4\text{-S})(C_2)$ (**8**) and $Fe_2Ru_6(CO)_{17}(Cp^*)_2(C_2)_2$ (**9**) can also be derived from that of the 96-EVM species **11**. In compound **8**, for instance, two M−M nonbonding MOs of the HOMO region become M−M σ-antibonding and are destabilized when two intertriangle metal−metal bonds are formed. A HOMO/LUMO gap of 1.33 eV is computed for the expected count of 92 MVEs. The same conclusions can be drawn for the octanuclear $M_8(C_2)_2$ species **9**, for which a comparable HOMO/LUMO gap is calculated.

The lowering of symmetry of the structural arrangement of the metallic cage in compounds **8**−**10** compared to that of **11** leads to some geometrical and electronic modifications of the interaction of the C_2 unit with the metallic host. Indeed, the tilt of two metallic triangles implies a change in the M−C−C angles. This affects the M−C overlap populations and consequently the M−C bond distances (see Table 3). In complexes **8** and **9**, the results seem to indicate that the C_2 ligand is σ-bound to the apical metal atoms (strong OP: *ca.* 0.61) and σ-/π-bound to the metal atoms of the square (medium OP: *ca.* 0.33). The occupied MOs in **11**, which become unoccupied in compounds **8**−**10**, possess some C_2 π^* contribution. Therefore, we observe upon depopulation some diminution of the back-donation from the metal cage into the C_2 acceptor orbitals. This results in a slight shortening of the C−C bonds (see Tables 1 and 3). Nevertheless, the description of these species as permetalated ethane molecules remains valid.

Carbon atomic net charges, forward and backward electron donation, and the HOMO/LUMO gap computed for the 94-MVE compound $FeRu_5(CO)_{14}(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(C_2)$ (**12**) are comparable to the corresponding values obtained for complexes **8**−**11** (see Table 3). However, a very different coordination of the C_2 ligand is observed in **12**. The carbon atoms are hypervalent in the latter, each being symmetrically bound to both a metallic square and the other carbon atom. A localized bonding scheme cannot account for the M−C bonding in this complex. Numerous ($\sigma + \pi$)-type interactions between the C_2^{2-} FMOs and the metallic FMOs are responsible for the M−C bonding. Nevertheless, the bonding energy between the C_2 ligand and its metallic host is nearly equal to those calculated for the previous permetalated ethane M_6C_2 complexes, particularly that for the 94-MVE skeletal isomeric compound $[Fe_3Co_3(CO)_{18}(C_2)]^-$ (**10**) (8.80 *vs* 8.57 eV). This further illustrates the flexibility of the C_2 ligand in its bonding to metallic clusters.

A deviation of the carbon atoms from the plane of metal atoms (0.38 Å for C(1) and 0.36 Å for C(2)) is rather important in preventing a strong interaction between the C−C bonding σ_g (s) low-lying orbital and the metallic fragment. No back-donation occurs from the metallic fragment toward the corresponding C_2 σ_u^* high-lying orbital. Two electrons remain formally on the C_2 ligand to ensure the C−C bond. Note that some carbon character is found in HOMO/LUMO frontier MOs.

A similar M−C bonding mode is observed in $Co_4Ru_5(CO)_{18}(\mu_3\text{-SMe})_2(\mu\text{-PPh}_2)_2(C_2)$ (**13**). The bonding energy between C_2^{2-} and $[M_9]^{2+}$ is 8.01 eV, close to that computed for **12** (8.80 eV). Additional M−C bonding σ-interactions with apical metal atoms Co(8,9) leads to a weakening of the electronic density on the C_2 ligand relative to that calculated in **12** (see the C atomic net charges and FMO occupations in Table 3). In accord with this result the C−C bond distance is longer in **13** than in **12** (1.41 *vs* 1.36 Å). These supplementary M−C σ-interactions result in the diminution of the deviation of the C atoms from the metallic squares in **13** relative to **12** (0.30 and 0.28 Å *vs* 0.38 and 0.36 for C(1) and C(2), respectively).[15] Note that the coordination mode of each carbon atom of the C_2 unit reminds one of that encountered in carbide clusters containing a square-pyramidal $M_5(\mu_5\text{-C})$ core such as $Fe_5(CO)_{15}(\mu_5\text{-C})$.[30]

As mentioned earlier, compound **13** has four more electrons than expected from the PSEP electron-counting rules (134 *vs* 130 MVEs). A HOMO/LUMO gap of 0.60 eV is computed for the observed electron count. The HOMO/LUMO frontier MOs are heavily weighted toward the metal atoms (>85%), some of them being slightly M−M antibonding according to our calculations. The excess of electrons seems to be reflected in rather long M−M distances. For instance, some Ru−Ru separations are greater than 2.90−2.95 Å, which may be compared with those in $Ru_3(CO)_{12}$ (*ca.* 2.85 Å). The propensity for transition metal clusters to accept extra electrons in slightly M−M antibonding MOs by expanding the metallic cage has been noted before for electron-rich compounds which do not follow the usual electron-counting rules.[31]

Concluding Remarks

The molecular orbital studies described above have shown that the *exposed* C_2 ligand, in M_5C_2 and M_6C_2 clusters interacts strongly with the metal cage via electron donation from the C_2 σ(p)- and π-bonding FMOs into vacant metallic MOs, supplemented by back-donation from filled metallic MOs to the C_2 π^* orbitals. Our results stress that the M−C bonding therefore follows the Dewar-Chatt-Duncanson model that has been established previously for C_2 moieties fully encapsulated in metallic clusters.[4]

Stable, closed-shell electronic structures with substantial HOMO/LUMO gaps (often larger than 1 eV) are calculated for all the complexes. Regardless of the structural arrangement of the metal cage, we would

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[30] Braye, E. H.; Dahl, L. F.; Hübel, W.; Wampler, D. L. *J. Am. Chem. Soc.* **1962**, *84*, 4633. For a theoretical study see: (a) Halet, J.-F.; Saillard, J.-Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1986**, *5*, 139. (b) Reference 5.

[31] See for instance Halet, J.-F. *Coord. Chem. Rev.* **1995**, *143*, 637 and references therein.

expect that the C_2 ligand, which is generally slightly negatively charged, would be rather nucleophilic if the reactions are charge-controlled. The same conclusions are roughly drawn if the chemical reactions are orbital-controlled, since the carbon atoms generally contribute more to the HOMOs than to the LUMOs. This has been nicely experimentally illustrated by one of us in the case of the 80-MVE compound $Ru_5(CO)_{11}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(C_2)$ (**3**). The reactions of **3** with H_2 or C_2H_4 lead to the new complexes $Ru_5(CO)_{10}(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(\mu_3\text{-}CCHR)$ (R = H, $CH{=}CH_2$), in which one carbon atom of the C_2 ligand (C(2)) has inserted into H—H or C—H bonds.[27] Note, though, that the C_2 ligand is often well-protected, particularly in the hexanuclear species, and consequently eventual chemical attack might affect first the metal cage of the clusters.

Acknowledgment. We express our thanks to Prof. M. Akita and to Prof. J.-Y. Saillard for sending results prior to publication and for helpful comments. G.F. is grateful to the Région Bretagne for financial support.

Appendix

All calculations were carried out within the extended Hückel[32] formalism (using the weighted H_{ij} formula) with the CACAO program.[33] The exponents (ζ) and the valence shell ionization potentials (H_{ii} in eV) were respectively as follows: 1.3, −13.6 for H 1s; 1.625, −21.4 for C 2s; 1.625, −11.4 for C 2p; 2.275, −32.3 for O 2s; 2.275, −14.8 for O 2p; 1.6, −18.6 for P 3s; 1.6, −14.0 for P 3p; 1.817, −20.0 for S 3s; 1.817, −13.3 for S 3p; 1.9, −9.1 for Fe 4s; 1.9, −5.32 for Fe 4p; 2.0, −9.21 for Co 4s; 2.0, −5.29 for Co 4p; 2.078, −8.6 for Ru 5s; 2.043, −5.1 for Ru 5p. H_{ii} values for Fe 3d, Co 3d, and Ru 4d were set equal to −12.6, −13.18, and −12.2 eV, respectively. A linear combination of two Slater-type orbitals of exponents $\zeta_1 = 5.35$, $\zeta_2 = 1.8$, $\zeta_1 = 5.55$, $\zeta_2 = 1.9$, and $\zeta_1 = 5.378$, $\zeta_2 = 2.303$ with the weigthing coefficients $c_1 = 0.5366$, $c_2 = 0.6678$, $c_1 = 0.5551$, $c_2 = 0.6461$, and $c_1 = 0.5340$, $c_2 = 0.6365$ was used to represent the Fe 3d, Co 3d, and Ru 4d atomic orbitals, respectively.

We have chosen to present results carried out on the experimental structures, although we know that such a procedure somewhat prevents a close comparison. However, most of the studied compounds adopt rather distorted structures with low symmetry. Their modeling leads to slightly different results, particularly for the M_5C_2 species in which the numerous long but bonding M−C contacts are difficult to reproduce. The C_5R_5, SR, CNR, and PR_2 groups have been replaced by C_5H_5, SH, CNH, and PH_2 groups for the calculations.

Supporting Information Available: Tables of metal−metal EH overlap populations and distances for different M_5C_2 and M_6C_2 species (3 pages). Ordering information is given on any current masthead page.

OM9610713

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