Formation of a four-electron donor carbonyl group in the decarbonylation of the unsaturated $H_2C_2Fe_2(CO)_6$ tetrahedrane as an alternative to an iron–iron triple bond

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ABSTRACT

The unsaturated Fe_2C_2 tetrahedrane derivatives $R_2C_2Fe_2(CO)_6$ (R = Ph, ^tBu) are among the many products obtained from reactions of the alkynes RC≡CR with iron carbonyls. In this connection theoretical studies have been performed on the simplest such compounds $H_2C_2Fe_2(CO)_n$ (n = 6, 5) for comparison with the experimentally known structure of the t-butyl derivative t-$Bu_2C_2Fe_2(CO)_6$ and in order to predict the decarbonylation pathways for such (alkyne)$Fe_2(CO)_6$ derivatives. These theoretical studies predict an Fe_2C_2 tetrahedrane structure for $H_2C_2Fe_2(CO)_6$ with a formal Fe=Fe double bond very similar to the experimental structure for t-$Bu_2C_2Fe_2(CO)_6$. Decarbonylation of $H_2C_2Fe_2(CO)_6$ is predicted to give an $H_2C_2Fe_2(CO)_5$ isomer retaining the Fe_2C_2 tetrahedrane structure, with an Fe=Fe double bond but with the unprecedented feature of a four-electron donor bridging carbonyl group in an M_2C_2 tetrahedrane structure. The formation of formal Fe≡Fe triple bonds appears to be avoided in even the higher energy $H_2C_2Fe_2(CO)_5$ structures. These include three triplet Fe_2C_2 tetrahedrane structures with formal Fe=Fe double bonds as well as a coordinately unsaturated singlet structure, still with an Fe=Fe double bond.

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1. Introduction

The chemistry of acetylene derivatives of metal carbonyls dates back to the 1956 discovery [1] that reactions of $Co_2(CO)_8$ with a variety of alkynes lead to stable red (alkyne)$Co_2(CO)_6$ derivatives in good yields under mild reaction conditions. Since this original discovery the chemistry of (alkyne)$Co_2(CO)_6$ derivatives has developed extensively [2,3]. Furthermore, such compounds have proven to be useful in organic synthesis [2,3] for reactions such as the Pauson–Khand synthesis of cyclopentenone derivatives [4].

The structure of (alkyne)$Co_2(CO)_6$ derivatives can be described as a Co_2C_2 tetrahedrane with formal single bonds along each of the six edges of the tetrahedron (Fig. 1). With such a structure the cobalt atoms achieve the favored 18-electron configuration and the carbon atoms achieve the stable octet. The experimental Co–Co distance [5] of 2.462 Å in $^tBu_2C_2Co_2(CO)_6$ is indicative of the formal single bond.

The next major development in acetylene metal carbonyl chemistry was the extensive research by Hübel and coworkers [6] on reactions of iron carbonyls with alkynes under diverse conditions to give a complicated variety of products including not only acetylene derivatives but also cyclobutadiene, cyclopentadienone, tro-

pone, and ferrole iron carbonyl derivatives. Because of the unusually complicated product mixtures obtained from many such reactions the full details of much of this work have never been fully described in the literature. However, among this plethora of iron carbonyl complexes were dark green compounds claimed to have the general formula $R_2C_2Fe_2(CO)_7$ (R = Ph, ^tBu) and inferred to have only terminal carbonyl groups on the basis of the infrared v(CO) frequencies. This original formulation was subsequently shown to be incorrect by an X-ray diffraction structure determination on the t-butyl derivative, which was shown to contain a central Fe_2C_2 tetrahedrane unit with only six carbonyl groups, i.e. t-$Bu_2C_2Fe_2(CO)_6$ (Fig. 1), rather than the originally suggested seven carbonyl groups [7,8]. Application of the 18-electron rule suggests a formal Fe=Fe double bond in this tetrahedrane structure. This is supported by the experimental Fe=Fe distance of 2.316 Å, which is ~0.15 Å shorter than the experimental Co–Co single bond distance of 2.462 Å [5] in the analogous ($^tBu_2C_2$)$Co_2(CO)_6$.

The decarbonylation of these M_2C_2 tetrahedranes is of particular interest. In this connection the photochemical decarbonylation of $R_2C_2Co_2(CO)_6$ derivatives in frozen Nujol at 90 K was found to give two isomers of $R_2C_2Co_2(CO)_5$ derivatives, differing by the location of the carbonyl group lost from the $R_2C_2Co_2(CO)_6$ starting material [9]. The infrared v(CO) spectra of these $R_2C_2Co_2(CO)_5$ isomers confirmed the presence of only terminal carbonyl groups but provide no direct information on the geometry of the central Co_2C_2 unit. Recent theoretical studies [10] on the simplest of the (alkyne)$Co_2(CO)_5$ derivatives, namely those derived from unsubstituted
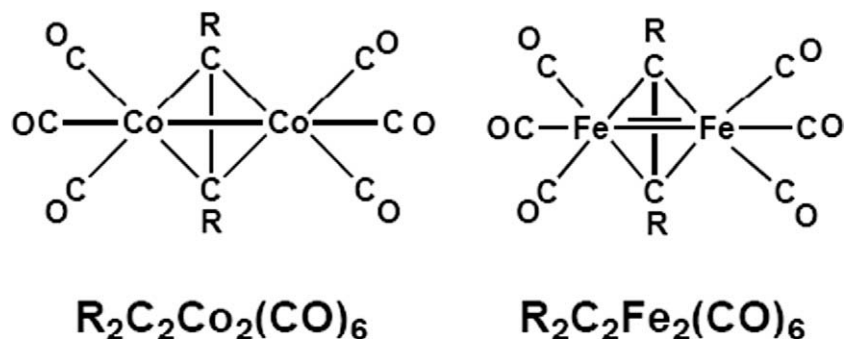
Fig. 1. A comparison of the structures of $R_2C_2Co_2(CO)_6$ with a formal Co–Co single bond and $R_2C_2Fe_2(CO)_6$ with a formal Fe=Fe double bond.
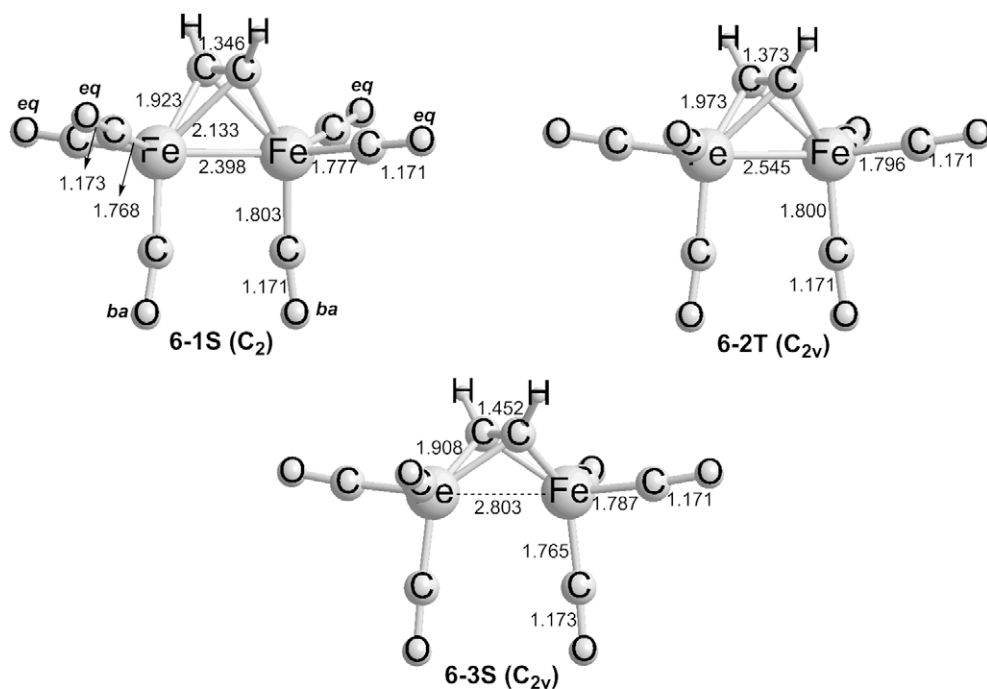

Fig. 2. Three optimized structures of $H_2C_2Fe_2(CO)_6$. All structures are genuine minima with all real vibrational frequencies.

acetylene, suggest that the initially produced $H_2C_2Co_2(CO)_5$ isomer retains a Co–Co distance of 2.48 Å, which is essentially identical to the 2.49 Å Co–Co distance predicted for the $H_2C_2Co_2(CO)_6$ starting material. This suggests that the initially produced $R_2C_2Co_2(CO)_5$ isomer retains the Co–Co single bond of the $H_2C_2Co_2(CO)_6$ starting material so that the cobalt atom bearing just two terminal carbonyl groups has only a 16-electron configuration. However, the second and lower energy $H_2C_2Co_2(CO)_5$ isomer, produced experimentally by heating the original 90 K matrix to 140 K, is predicted to have a Co=Co distance of only 2.36 Å, which is very similar to the experimentally determined Fe=Fe double bond distance [7,8] of 2.316 Å in t-$Bu_2C_2Fe_2(CO)_6$. Thus this more stable $H_2C_2Co_2(CO)_5$ isomer is inferred to have a formal Co=Co double bond so that both cobalt atoms in the Co_2C_2 tetrahedrane unit have the favored 18-electron configuration.

A similar photochemical decarbonylation of an $R_2C_2Fe_2(CO)_6$ derivative in a low temperature matrix has never been carried out. In order to assess the possibilities for interesting decarbonylation products from such experiments, the possible structures for both $R_2C_2Fe_2(CO)_6$ and its $R_2C_2Fe_2(CO)_5$ decarbonylation product have been studied by density functional theory. Analogy with the

$R_2C_2Co_2(CO)_n$ system discussed above suggests that the original Fe=Fe double bond in the $R_2C_2Fe_2(CO)_6$ might become a formal Fe≡Fe triple bond in the most stable structure of its $R_2C_2Fe_2(CO)_5$ decarbonylation product. However, our theoretical studies on the $H_2C_2Fe_2(CO)_n$ systems (n = 6, 5), reported in detail in this paper, suggest a different course of this decarbonylation reaction, namely conversion of one of the terminal carbonyl groups into a four-electron donor η^2-μ-CO bridging carbonyl group retaining the Fe=Fe double bond in the lowest energy $H_2C_2Fe_2(CO)_5$ structure. Apparently M≡M triple bonds are not favorable in M_2C_2 tetrahedrane structures, although they are found in many stable binuclear cyclopentadienylmetal carbonyls such as $(\eta^5$-$R_5C_5)_2V_2(CO)_5$ [11,12], $(\eta^5$-$R_5C_5)_2Cr_2(CO)_4$ (R = H, [13] Me [14,15]), and $(\eta^5$-$R_5C_5)_2M'_2(CO)_3$ (M' = Mn, [16] Re [17]).

2. Theoretical methods

Electron correlation effects were included by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic

compounds [18–32]. The specific theoretical approaches employed herein were same as those in previous work on the $H_2C_2Co_2(CO)_n$ system [10]. Briefly, the $H_2C_2Fe_2(CO)_n$ complexes were examined using the DFT method at the B3LYP and BP86 levels. The B3LYP method is an HF/DFT hybrid method using Becke's three-parameter functional (B3) [33] and the Lee–Yang–Parr generalized gradient correlation functional (LYP) [34], whereas the BP86 method is a pure DFT method combining Becke's 1988 exchange functional (B) [35] with Perdew's 1986 gradient correlation functional (P86) [36]. All-electron double zeta plus polarization (DZP) basis sets were used. The DZP basis sets for C and O, which are designated (9s5p1d/4s2p1d), begin with Dunning's standard double zeta contraction [37] of Huzinaga's primitive sets (DZ) [38] and add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$. For H, a set of p polarization functions $\alpha_p(H) = 0.75$ is added to the Huzinaga–Dunning DZ set. For Fe, the DZP basis set, designated as (14s11p6d/10s8p3d), uses the Wachters' primitive set [39] augmented by two sets of p functions and one set of d functions and contracted following Hood et al. [40]. For $H_2C_2Fe_2(CO)_6$, there are 318 contracted Gaussian functions with the present DZP basis set.

Various initial structures for the $H_2C_2Fe_2(CO)_n$ ($n = 6, 5$) complexes were fully optimized using both B3LYP and BP86 methods. Both singlet and triplet states were investigated. The B3LYP method predicts lower energies for some triplet states of $H_2C_2Fe_2(CO)_5$. However, the BP86 method predicts singlets for the ground states of $H_2C_2Fe_2(CO)_n$ ($n = 6, 5$). Considering that the BP86 functional is more reliable for organometallic systems [41–43], only the BP86 results are reported in present paper.

All of the computations were carried out with the GAUSSIAN 03 program [44] in which the fine grid (75, 302) is the default for evaluating integrals numerically, and the tight (10^{-8} hartree) designation is the default for the SCF convergence. The optimized geometries are depicted in Figs. 2 and 3 with all bond distances given in angstroms. Table 1 lists their electronic states, symmetries, relative energies, the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular (LUMO), S^2 spin expectation values and important bond distances, while Table 2 shows their $\nu(CO)$ frequencies.

3. Results and discussion

3.1. $H_2C_2Fe_2(CO)_6$

Two singlet structures and one triplet structure (shown in Fig. 2 and Table 1) were found for $H_2C_2Fe_2(CO)_6$, namely **6-1S**, **6-2T** and **6-3S**, where **S** indicates singlet and **T** indicates triplet. Indeed, all three structures have similar stereochemistry, differing only in their geometrical parameters, namely bond lengths and bond angles. That is, two carbonyls are in approximately *basal* positions (CO_{ba}) to the Fe–Fe bond, and the remaining four carbonyls in approximate *equatorial* positions (CO_{eq}).

The lowest energy $H_2C_2Fe_2(CO)_6$ structure is the singlet **6-1S**, which is a genuine minimum with no imaginary vibrational frequencies. In **6-1S** a small twist of the HC–CH axis relative to the Fe–Fe bond lowers the symmetry of the central Fe_2C_2 tetrahedrane from C_{2v} to C_2, which is in agreement with the structure determined by X-ray diffraction for t-Bu$_2$C$_2$Fe$_2$(CO)$_6$ [7,8]. Consequently, the three carbonyls on each iron atom are neither strictly in eclipsed positions nor staggered positions to those on another iron atom. This is different from the global minimum predicted for $H_2C_2Co_2(CO)_6$ [10], in which the two sets of carbonyls are in an eclipsed position relative to each other, and the arrangement of CO groups provides a distorted octahedral structure of six bonds about each cobalt atom. Cotton et al. [8] have explained in detail the differences between the known iron and cobalt complexes.

In the $H_2C_2Fe_2(CO)_6$ structure **6-1S**, the predicted Fe–Fe bond distance of 2.398 Å suggests the double bond necessary to give both iron atoms the favored 18-electron configuration. The two *basal* Fe–CO$_{ba}$ bonds in **6-1S** are longer than the four *equatorial* Fe–CO$_{eq}$ bonds by ~0.03 Å. The predicted bond distances for **6-1S** can be compared with the corresponding experimental bond distances for $(t$-Bu$_2$C$_2)$Fe$_2$(CO)$_6$ [14], which are 2.316 Å for the Fe–Fe bond, 2.044–2.130 Å for the Fe–CH bonds, ~1.80 Å for the Fe–CO$_{ba}$ bonds, ~1.78 Å for the Fe–CO$_{eq}$ bonds, and 1.311 Å for the HC–CH bond. Our theoretical results thus agree well with experiment.

The triplet structure **6-2T** for $H_2C_2Fe_2(CO)_6$ (Fig. 2 and Table 1), unlike the singlet structure **6-1S**, has full C_{2v} symmetry and lies 8.4 kcal/mol above **6-1S**. The Fe–Fe distance of 2.545 Å in **6-2T** is
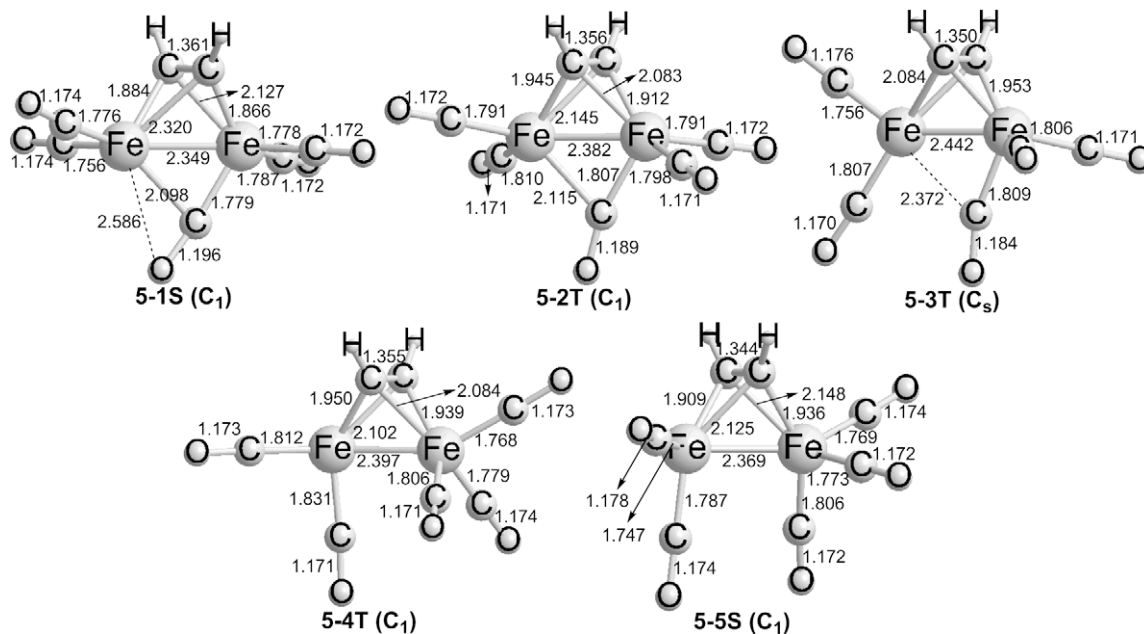

Fig. 3. The five optimized structures of $H_2C_2Fe_2(CO)_5$.

Table 1
The singlet and triplet structures of $(H_2C_2)Fe_2(CO)_n$ (n = 6, 5) at the BP86/DZP level of theory. All structures are genuine minima with all real vibrational frequencies.

n	isomer	State (symmetry)	Rel. energy[a] (kcal/mol)	HOMO-LUMO gap (a.u.)	$\langle S^2 \rangle$	Fe–Fe (Å)	HC–CH[b] (Å)	Fe–CH (Å)
6	6-1S	^1A (C_2)	0.0	0.048	0.00	2.398	1.346	1.923, 2.133
	6-2T	$^3A_2$ (C_{2v})	8.4	-	2.02	2.545	1.373	1.973
	6-3S	$^1A_1$ (C_{2v})	9.8	0.035	0.00	2.803	1.452	1.908
5	5-1S	^1A (C_1)	0.0	0.051	0.00	2.349	1.361	1.866, 2.127, 1.884, 2.320
	5-2T	^3A (C_1)	2.4	-	2.03	2.382	1.356	1.912, 2.083, 1.945, 2.145
	5-3T	$^3A'$ (C_s)	5.5	-	2.03	2.442	1.350	1.953, 2.084
	5-4T	^3A (C_1)	7.3	-	2.04	2.397	1.355	1.939, 2.084, 1.950, 2.102
	5-5S	^1A (C_1)	9.9	0.039	0.00	2.369	1.344	1.936, 2.148, 1.909, 2.125

[a] The total energies of structure **6-1S** and **5-1S** are −3285.57764 and −3172.18143 a.u., respectively.
[b] The CC bond distance in the free HC≡CH molecule is 1.225 Å (BP86/DZP).

Table 2
v(CO) frequencies (in cm^{-1}) and infrared intensities (in km/mol, given in parentheses) of the $(H_2C_2)Fe_2(CO)_n$ complexes at the BP86/6-311G(d) level of theory. Bridging v(CO) frequencies are give in **bold** type.

n	Structure	v(CO) frequencies
6	**6-1S**	1964 (8), 1975 (52), 1983 (1526), 1991 (938), 2012 (1825), 2047 (141)
	6-2T	1963 (6), 1978 (0), 1978 (1698),1990 (951),1992 (2244), 2041 (137)
	6-3S	1969 (117), 1976 (0), 1983 (1760), 1989 (1021), 2014 (1622), 2048 (92)
5	**5-1S**	**1831 (433)**, 1963 (436), 1977 (1149), 1995 (1842), 2026 (72)
	5-2T	**1863 (452)**, 1964 (524), 1976 (1113), 1985 (2368), 2027 (85)
	5-3T	**1897 (259)**, 1967 (771), 1976 (904), 2000 (1887), 2033 (163)
	5-4T	1956 (186), 1972 (938), 1977 (576), 1987 (1821), 2038 (380)
	5-5S	1948 (270), 1966 (406), 1976 (1165), 1988 (1433), 2035 (414)

~0.15 Å longer than that in **6-1S** and thus corresponds to a single bond rather than a double bond. From comparison, the experimental Fe–Fe single bond distances determined by X-ray diffraction are 2.54 Å [45,46] for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ and 2.523 Å [47] for $Fe_2(CO)_6(\mu\text{-}CO)_3$. Thus the iron atoms in the $H_2C_2Fe_2(CO)_6$ structure **6-2T** have 17-electron configurations consistent with the triplet state. The bond distances of HC–CH (1.373 Å) and Fe–CO$_{eq}$ (1.796 Å) in **6-2T** are also longer than those in **6-1S**, whereas the Fe–CO$_{ba}$ distance of 1.800 Å is similar to that in **6-1S**. On the other hand, the Fe–CH distance of 1.973 Å is ~0.05 Å shorter than the average of the four Fe–CH distances in **6-1S**.

The C_{2v} singlet $H_2C_2Fe_2(CO)_6$ structure **6-3S** (Fig. 2 and Table 1) is another local minimum, with a geometry similar to the triplet structure **6-2T**, but lying at slightly higher energy (~1 kcal/mol) than **6-2T**. However, structure **6-3S** has a significantly longer Fe–Fe distance (2.803 Å), indicating a very weak iron–iron interaction so that the iron atoms have only 16-electron configurations. Compared with those in **6-1S** and **6-2T**, in **6-3S** the HC–CH distance (1.452 Å) is significantly longer, the Fe–CO$_{ba}$ distances (1.765 Å) are shorter, and the Fe–CH distances (1.908 Å) are much shorter.

3.2. $H_2C_2Fe_2(CO)_5$

The five structures found for $H_2C_2Fe_2(CO)_5$ (Fig. 3 and Table 1) have all real vibrational frequencies, indicating genuine minima. The two lowest energy $H_2C_2Fe_2(CO)_5$ structures **5-1S** and **5-2T** both have a single unsymmetrical CO bridge, and can be derived from the $H_2C_2Fe_2(CO)_6$ structure of corresponding spin multiplicity, namely **6-1S** or **6-2T**, respectively, by removal of a *basal* carbonyl group. The absence of the CO$_{ba}$ group on one iron atom (the "left" one in Fig. 3) causes the CO$_{ba}$ group on other iron atom (the "right" one in Fig. 3) to bend towards the vacant position on the other iron atom (the "left" one in figure), thereby forming the bridging CO group. The $H_2C_2Fe_2(CO)_5$ structure **5-1S** is a singlet, whereas struc-

ture **5-2T** is a triplet, with **5-2T** lying 2.4 kcal/mol (BP86) in energy above **5-1S**. The predicted Fe=Fe distances of 2.349 Å in **5-1S** and 2.382 Å in **5-2T** are both slightly shorter than the Fe=Fe double bond distance of 2.398 Å in **6-1S** and can likewise be considered to be formal double bonds. The short Fe–O distance of 2.586 Å to the bridging CO group in **5-1S** indicates a four-electron donor bridging $\eta^2\text{-}\mu\text{-}CO$ carbonyl group. Such a four-electron bridging carbonyl group combined with the formal Fe=Fe double bond gives each iron atom in **5-1S** the favorable 18-electron configuration for a binuclear singlet. However, in the triplet $H_2C_2Fe_2(CO)_5$ structure **5-2T** the Fe···O distance to the bridging carbonyl group of 2.920 Å is too long to indicate a direct interaction and thus a four-electron donor bridging carbonyl group. Hence, in the triplet $H_2C_2Fe_2(CO)_5$ structure the combination of a normal two-electron donor bridging carbonyl group and an Fe=Fe double bond gives both iron atoms 17-electron configurations, consistent with a binuclear triplet. The four-electron donor bridging carbonyl group in **5-1S** is predicted to exhibit a v(CO) frequency at 1831 cm^{-1}, which is appreciably lower than the 1863 cm^{-1} v(CO) frequency predicted for the two-electron donor bridging group in **5-2T** (Table 2).

A triplet $H_2C_2Fe_2(CO)_5$ structure **5-3T** with a semibridging carbonyl group was found at 5.5 kcal/mol above the global minimum **5-1S** (Fig. 3 and Table 1). The semibridging carbonyl group in **5-3T** has a short M–C distance of 1.809 Å and a long M–C distance of 2.372 Å and is predicted to exhibit a v(CO) frequency of 1897 cm^{-1}, which is 70 cm^{-1} below the lowest terminal v(CO) frequency of 1967 cm^{-1} (Table 2). Structure **5-3T** can be derived from **5-2T** by twisting one Fe(CO)$_2$ unit relative to the other so that the two Fe(CO)$_2$ planes are perpendicular to each other. The Fe=Fe distance of 2.442 Å in **5-3T** is the longest found in the five $H_2C_2Fe_2(CO)_5$ structures (Fig. 3) but nevertheless can correspond to the formal double bond needed to give each iron atom the 17-electron configuration for a binuclear triplet.

An unbridged triplet $H_2C_2Fe_2(CO)_5$ structure **5-4T** is found at 7.3 kcal/mol above the global minimum **5-1S**. In structure **5-4T**, the three carbonyls on one iron atom (the "right" one in Fig. 3) combined with two Fe–C bonds to the C_2H_2 unit and the Fe=Fe bond provide a quasi-octahedral structure of six bonds about this iron atom. The Fe=Fe distance of 2.397 Å in **5-4T** is very close to that in $H_2C_2Fe_2(CO)_6$ (**6-1S**) and may thus similarly be regarded as a double bond. If this double bond is assumed to be a "dative" double bond with the Fe(CO)$_3$ group donating three of the four Fe=Fe double bond electrons and the Fe(CO)$_2$ group donating only a single electron, then each iron atom has the 17-electron configuration for a binuclear triplet.

The final $H_2C_2Fe_2(CO)_5$ structure, namely singlet **5-5S** at 9.9 kcal/mol above **5-1S**, is also an unbridged structure, which can be derived from the $H_2C_2Fe_2(CO)_6$ structure **6-1S** by removing a *equatorial* carbonyl group (Fig. 3 and Table 1). The absence of one carbonyl group makes the Fe=Fe bond in **5-5S** shorter at 2.369 Å, but still in the range of a double bond, thereby giving one iron

atom an 18-electron configuration and the other iron atom only a 16-electron configuration.

3.3. Carbonyl dissociation energies

The bond dissociation energies for the loss of one carbonyl group from the global minimum $H_2C_2Fe_2(CO)_6$ is 38.1 kcal/mol (B3LYP) or 43.3 kcal/mol (BP86). This carbonyl dissociation energy is in approximate agreement with the experimental [48] carbonyl dissociation energies of 37 kcal/mol for $Cr(CO)_6$ and 41 kcal/mol for $Fe(CO)_5$. However, it is significantly higher than the experimental carbonyl dissociation energy of 27 kcal/mol for $Ni(CO)_4$.

3.4. Vibrational frequencies

Table 2 summarizes our theoretical $v(CO)$ frequencies for the compounds using the BP86 functional. The results in Table 2 indicate that the $H_2C_2Fe_2(CO)_n$ ($n = 6, 5$) complexes exhibit infrared $v(CO)$ frequencies in the range 2048 to 1948 cm^{-1} for terminal carbonyl groups, similar to other metal carbonyl derivatives. For the semibridging carbonyl group, the $v(CO)$ frequency can be somewhat lower (e.g., 1897 cm^{-1} in structure **5-3T**). The $v(CO)$ frequencies for bridging carbonyl groups are significantly lower (as is generally found for other metal carbonyl derivatives [49]) and fall in the range of 1863–1831 cm^{-1} for the $H_2C_2Fe_2(CO)_5$ structures discussed in this paper. The predicted $v(CO)$ vibrational frequencies for the stable structures are of particular interest, since any future experimental work to detect these species is likely to rely on relatively strong $v(CO)$ vibrational frequencies for initial product characterization.

4. Summary

Our density functional theory studies predict an Fe_2C_2 tetrahedrane structure for $H_2C_2Fe_2(CO)_6$ with a formal Fe=Fe double bond very similar to the experimental structure [7,8] for the *t*-butyl derivative *t*-$Bu_2C_2Fe_2(CO)_6$. Decarbonylation of $H_2C_2Fe_2(CO)_6$ is predicted to give an $H_2C_2Fe_2(CO)_5$ isomer retaining the Fe_2C_2 tetrahedrane structure with an Fe=Fe double bond. However, the latter structure incorporates a four-electron donor bridging carbonyl group, which is an unprecedented structural feature in M_2C_2 tetrahedrane metal carbonyl derivatives. The formation of formal Fe≡Fe triple bonds is avoided in even the higher energy $H_2C_2Fe_2(CO)_5$ structures. These include three triplet Fe_2C_2 tetrahedrane structures with formal Fe=Fe double bonds, as well as a coordinately unsaturated singlet structure still with an Fe=Fe double bond.

Acknowledgments

Appendix A. Supplementary material

Table S1: The vibrational frequencies (in cm^{-1}) and infrared intensities (in km/mol, given in parentheses) of the $H_2C_2Fe_2(CO)_n$ ($n = 6, 5$) complexes at the B3LYP/DZP and BP86/DZP levels; Table S2: The Cartesian coordinates of the optimized $H_2C_2Fe_2(CO)_n$ ($n = 6, 5$) structures at the B3LYP/DZP and BP86/DZP levels; complete GAUSSIAN 03 reference (Ref. [44]). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.005.

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