Terminal *versus* bridging cyclobutadiene rings in binuclear nickel carbonyl derivatives: A cube-antiprism twist of the cyclobutadiene rings in the perpendicular structures†

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Cyclobutadiene–nickel derivatives are accessible from reactions of dichlorocyclobutenes with nickel carbonyl. In this connection the binuclear cyclobutadiene–nickel carbonyls $(C_4H_4)_2Ni_2(CO)_n$ (n = 3, 2, 1) have been examined theoretically as possible sources of new dimetallocene structures and new structures with metal–metal multiple bonds. The lowest energy $(C_4H_4)_2Ni_2(CO)$ isomer is predicted to have a perpendicular structure with two bridging C_4H_4 rings forming an elongated square antiprism enclosing the pair of nickel atoms. The $Ni{\equiv}Ni$ distance of $\sim$2.25 Å corresponds to the formal triple bond required to give both nickel atoms the favored 18-electron configuration, with all eight carbon atoms of the two C_4H_4 rings involved in M–C bonding. A related low energy structure is found for $(C_4H_4)_2Ni_2(CO)_2$ except that the two bridging C_4H_4 rings form an elongated cube enclosing a pair of nickel atoms at a somewhat longer bonding distance ($\sim$2.33 Å). In this case only a $Ni{=}Ni$ double bond is required to give both nickel atoms the 18-electron configuration. Other low energy $(C_4H_4)_2Ni_2(CO)_n$ (n = 1, 2, 3) structures include a monocarbonyl $(\eta^4\text{-}C_4H_4)_2Ni_2(\eta^2\text{-}\mu\text{-}CO)$ with a four-electron donor bridging carbonyl group, a coaxial doubly bridged dicarbonyl $(\eta^4\text{-}C_4H_4)_2Ni_2(\mu\text{-}CO)_2$, and *cis* and *trans* isomers of a bent singly bridged tricarbonyl $(\eta^4\text{-}C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$.

1. Introduction

Cyclobutadiene is an important example of an unstable hydrocarbon in the free state that can be stabilized by formation of metal complexes. An early example of such a stable cyclobutadiene–metal complex is tetramethylcyclobutadiene nickel dichloride, $(\eta^4\text{-}Me_4C_4)_2Ni_2Cl_2(\mu\text{-}Cl)_2$, which was first synthesized from tetramethyldichlorocyclobutene by an oxidative addition reaction using $Ni(CO)_4$ as the nickel source.[1] The discovery of this tetramethylcyclobutadiene nickel complex in 1959 by Criegee and Schroeder predates by several years the critical 1965 discovery of unsubstituted cyclobutadiene–iron carbonyl, $(\eta^4\text{-}C_4H_4)Fe(CO)_3$, by Emerson, Watts and Pettit[2] by the related reaction of dichlorocyclobutene with $Fe(CO)_5$.

Even though a full half-century has elapsed since the first report of the original cyclobutadiene–nickel complex, no cyclobutadiene–nickel carbonyl derivatives have yet been reported. Simple electron counting suggests a possible analogy between cyclobutadiene–nickel carbonyls and cyclopentadienylcobalt carbonyls. Thus a mononuclear $(\eta^4\text{-}C_4H_4)Ni(CO)_2$ would be analogous to the experimentally well-known[3] $(\eta^5\text{-}C_5H_5)Co(CO)_2$.

The binuclear cyclobutadiene–nickel carbonyls $(C_4H_4)_2Ni_2(CO)_n$ (n = 3, 2, 1) are potentially even more interesting. Possible structures for the unsaturated derivatives $(C_4H_4)_2Ni_2(CO)_n$ (n = 2, 1) can contain nickel–nickel multiple bonds and/or four-electron donor bridging carbonyl groups. The isoelectronic binuclear cyclopentadienylcobalt carbonyls $(\eta^5\text{-}C_5R_5)_2Co_2(CO)_n$ (R = H, Me; n = 3[4] and 2[5]) were synthesized in 1995 by Bengali, Bergman and Moore.[6] Furthermore, Vollhardt, Bercaw and Bergman[4] first showed $(\eta^5\text{-}C_5H_5)_2Co_2(CO)$ to be a likely intermediate[4,7] in the pyrolysis of $(\eta^5\text{-}C_5H_5)_3Co_3(CO)_3$ to give $(\eta^5\text{-}C_5H_5)_4Co_2(CO)_2$.

All of the large number of known binuclear cyclopentadienyl metal carbonyls and the much more limited number of known binuclear cyclobutadiene–metal carbonyls, *e.g.* $(\eta^4\text{-}C_4R_4)_2Fe_2(\mu\text{-}CO)_3$ (R = H,[8] Me[9]) and $(\eta^4\text{-}Me_4C_4)_2Co_2(CO)(\mu\text{-}CO)_2$,[10] can also be regarded as carbonylated dimetallocenes. In all cases they have coaxial or bent dimetallocene structures (Fig. 1) in which each $\eta^n\text{-}C_nH_n$ ring (n = 4 or 5) is bonded to only one metal atom but uses all of its ring carbon atoms for such bonding. In this respect they are related to the original (2004) groundbreaking dimetallocene, namely $(\eta^5\text{-}Me_5C_5)_2Zn_2$, which has a coaxial structure consisting of two $(\eta^5\text{-}Me_5C_5)Zn$ units joined solely by a formal Zn–Zn bond.[11]

A 2005 theoretical study[12] predicts the existence of not only coaxial dimetallocene structures but also perpendicular dimetallocene structures for the late transition metal dimetallocenes, particularly $(C_5H_5)_2Cu_2$ (Fig. 1). In the perpendicular dimetallocene structures, the rings function as bridging ligands across a metal–metal bond, rather than as terminal ligands, bonded solely to a single metal atom. Experimentally realized

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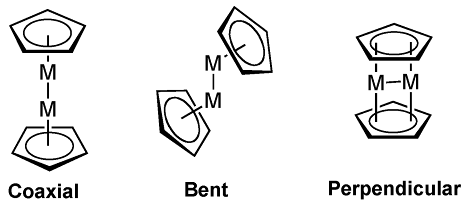


Fig. 1 Types of dimetallocenes.

examples of a perpendicular dimetallocene-type structure are the benzenepalladium(II) complexes $(\mu\text{-}C_6H_6)_2Pd_2(AlCl_4)_2$ and $(C_6H_6)_2Pd_2(Al_2Cl_7)_2$, first synthesized by Allegra and coworkers.[13]

The possibility of perpendicular $(\mu\text{-}C_5H_5)_2Co_2(CO)_n$ (n = 2, 1) structures has been investigated theoretically.[14] However, such structures have been found to be energetically unfavorable. Thus for $(C_5H_5)_2Co_2(CO)_2$ the perpendicular structure is predicted to lie 36 ± 3 kcal mol^{-1} above the global minimum coaxial structure. For $(C_5H_5)_2Co_2(CO)$ the perpendicular structure is more favorable, but still lies ~9 kcal mol^{-1} above the coaxial global minimum.

This paper reports theoretical studies on the binuclear cyclobutadienenickel carbonyls $(C_4H_4)_2Ni_2(CO)_n$ (n = 3, 2, 1) for comparison with the isoelectronic $(C_5H_5)_2Co_2(CO)_n$. Some significant differences between the nickel and cobalt systems are found. Thus a perpendicular structure is predicted to be the global minimum for $(C_4H_4)_2Ni_2(CO)$, lying more than 10 kcal mol^{-1} below the lowest energy coaxial structure. In this structure the two C_4H_4 rings form a distorted square antiprism. Furthermore, in the perpendicular structure for $(C_4H_4)_2Ni_2(CO)_2$, which lies less than 10 kcal mol^{-1} above the coaxial global minimum, the two C_4H_4 rings form an elongated cube. Thus, in the decarbonylation of perpendicular $(C_4H_4)_2Ni_2(CO)_2$ to $(C_4H_4)_2Ni(CO)$, there is an interesting twist of the two C_4H_4 rings from an elongated cube to a similarly elongated square antiprism.

2. Theoretical methods

For carbon and oxygen the double-ς plus polarization (DZP) basis set used here adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ to the Huzinaga–Dunning standard contracted DZ sets, and is designated (9s 5p 1d / 4s 2p 1d).[15,16] For H, a set of p polarization functions $\alpha_p(H) = 0.75$ is added to the Huzinaga–Dunning DZ sets. For Ni, in our loosely contracted DZP basis set, the Wachters' primitive set is used but is augmented by two sets of p functions and one set of d functions, contracted following Hood *et al.*, and designated (14s 11p 6d / 10s 8p 3d).[17,18] Thus, for $(C_4H_4)_2Ni_2(CO)$, $(C_4H_4)_2Ni_2(CO)_2$, and $(C_4H_4)_2Ni_2(CO)_3$, our basis sets included 288, 318, and 348 contracted Gaussian functions, respectively.

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.[19–25] Two DFT methods were used in this study. The first functional is the hybrid B3LYP method, which incorporates Becke's three-parameter exchange functional (B3)[26] with the Lee, Yang and Parr (LYP) correlation functional.[27] The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B)[28] with Perdew's 1986 correlation functional.[29] It has been noted that the BP86 method may be somewhat more reliable than the B3LYP method for the type of organometallic systems considered in this paper.[30,31]

The geometries of all of the structures were fully optimized using both the DZP B3LYP and DZP BP86 methods. The harmonic vibrational frequencies were determined at the same levels of theory by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities are evaluated analytically as well. All of the computations were carried out with the Gaussian 94 program[32] 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 energy convergence.[33]

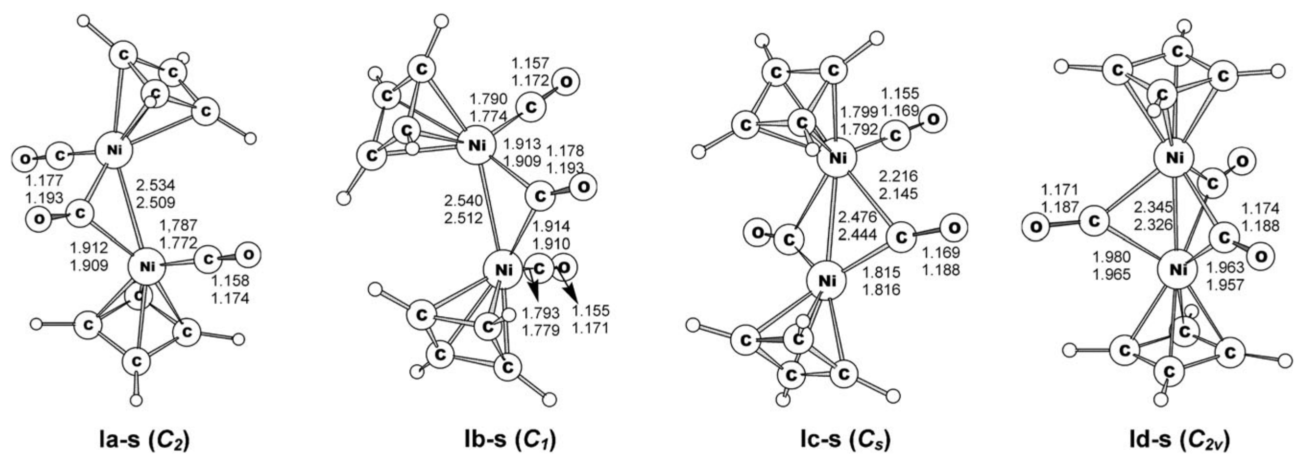
In the search for minima, low magnitude imaginary vibrational frequencies are suspect, because the numerical integration procedures used in existing DFT methods have significant limitations. Thus, an imaginary vibrational frequency of magnitude less than 50*i* cm^{-1} should imply that there is a minimum with energy very similar to that of the stationary point in question. In most cases we do not follow the eigenvectors corresponding to imaginary frequencies less than 50*i* cm^{-1} in search of other minima.[34]

3. Results

3.1 Molecular structures

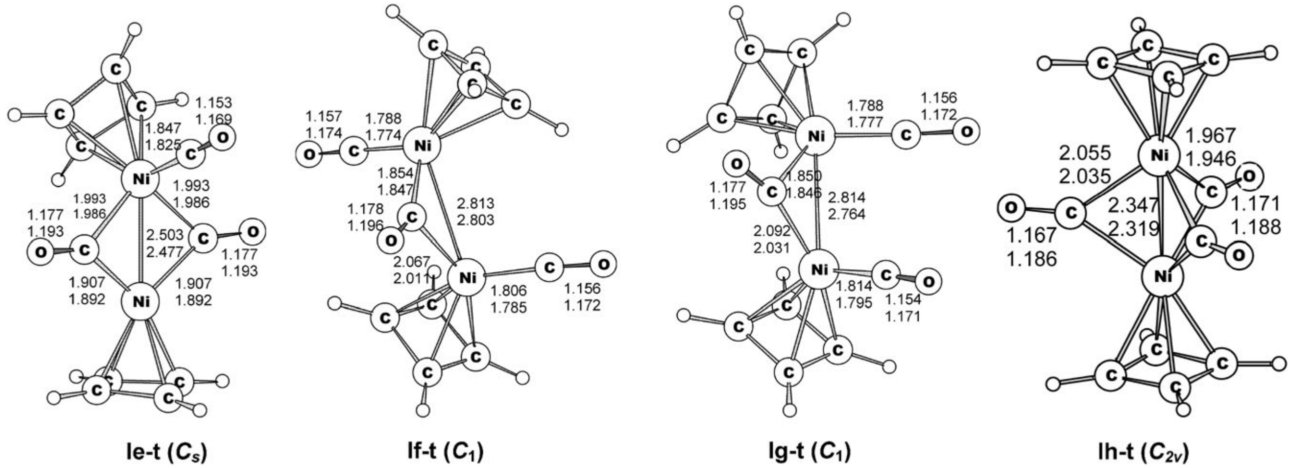
3.1.2 $(C_4H_4)_2Ni_2(CO)_3$. Singlet and triplet structures of $(C_4H_4)_2Ni_2(CO)_3$ having one, two, or three bridging CO groups have been studied (Fig. 2 and 3). The singlet and triplet *trans*-$(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ and *cis*-$(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ structures are stationary points with the energies of the singlet structures lower than those of the corresponding triplet structures. The singlet singly bridged *trans*-$(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ structure (**Ia-s**) is the global minimum, and it is lower than *cis*-$(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ (**Ib-s**) by 2.1 kcal mol^{-1} (B3LYP) or 2.5 kcal mol^{-1} (BP86) in energy (Tables 1 and 2). The doubly bridged singlet structure $(C_4H_4)_2Ni_2(CO)(\mu\text{-}CO)_2$ (**Ic-s**) has a substantial imaginary vibrational frequency of 121*i* cm^{-1} (B3LYP) or 44*i* cm^{-1} (BP86). Following the corresponding normal mode leads to the singly bridged *trans*-$(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ (**Ia-s**) global minimum structure. The doubly bridged triplet structure $(C_4H_4)_2Ni_2(CO)(\mu\text{-}CO)_2$ (**Ie-t**) is a genuine minimum lying 24.4 kcal mol^{-1} (B3LYP) or 22.8 kcal mol^{-1} (BP86) above the global minimum *trans*-$(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ (**Ia-s**). Structure **Ie-t** has the lowest energy of the triplet structures by the BP86 method. The triply bridged $(C_4H_4)_2Ni_2(\mu\text{-}CO)_3$ structures **Id-s** and **Ih-t** are transition states with imaginary vibrational frequencies of 231*i* cm^{-1} and 595*i* cm^{-1} (B3LYP) or 127*i* cm^{-1} and 475*i* cm^{-1} (BP86), respectively. Following the appropriate normal modes leads to the corresponding singly bridged *cis*-$(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ structures **Ib-s** and **Ig-t**, respectively.

The Ni–Ni distances predicted for the singlet singly bridged $(\eta^4\text{-}C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ structures, namely **Ia-s** and **Ib-s**,



Ia-s (C_2) **Ib-s (C_1)** **Ic-s (C_s)** **Id-s (C_{2v})**

Fig. 2 Optimized geometries for the four singlet $(C_4H_4)_2Ni_2(CO)_3$ structures. Note that structures **Ic-s** and **Id-s** have large imaginary vibrational frequencies and thus are transition states rather than genuine minima.



Ie-t (C_s) **If-t (C_1)** **Ig-t (C_1)** **Ih-t (C_{2v})**

Fig. 3 Optimized geometries for the four triplet $(C_4H_4)_2Ni_2(CO)_3$ structures. Note that the triply bridged structure **Ih-t** has a large imaginary vibrational frequency and thus is a transition state rather than a genuine minimum.

fall in the range 2.51 to 2.54 Å, which are consistent with the single bonds required to give each Ni atom the favored 18-electron configuration in both structures. For comparison, the doubly carbonyl bridged Ni–Ni single bond in $(\eta^5\text{-}C_5H_5)_2Ni_2(\mu\text{-}CO)_2$ is determined experimentally by X-ray diffraction[35] to be 2.36 Å. However, a doubly bridged Ni–Ni bond would be expected to be shorter than a singly bridged Ni–Ni bond.

The Ni–Ni bond distances in the triplet **If-t** (2.813 Å by B3LYP or 2.803 Å by BP86) and **Ig-t** (2.814 Å by B3LYP or 2.764 Å by BP86) are significantly longer than those in **Ia-s** and **Ib-s**. This implies a much weaker Ni–Ni interaction in the triplet relative to the singlet structures, consistent with 18-electron nickel configurations in the singlet structures but only 17-electron nickel configurations in the triplet structures.

The two predicted terminal ν(CO) frequencies for the singly bridged $(\eta^4\text{-}C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ structures fall in the narrow ranges 1983 ± 1 and 2007 ± 11 cm^{-1} (Table 3). However, the bridging ν(CO) frequencies for the singlet $(\eta^4\text{-}C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ structures **Ia-s** and **Ib-s** of 1852 ± 2 cm^{-1} are appreciably higher than the bridging ν(CO) frequencies of 1821 ± 3 cm^{-1} for the corresponding triplet structures **If-t** and **Ig-t**. This difference in the bridging ν(CO) frequencies can be related to the longer Ni–Ni distances in the triplets relative to the singlets.

3.1.2 $(C_4H_4)_2Ni_2(CO)_2$.

Four structures were optimized for the unsaturated $(C_4H_4)_2Ni_2(CO)_2$ (Fig. 4 and Table 4), namely singlet and triplet doubly CO-bridged structures as well as structures without bridging CO groups. The lowest energy singlet and triplet structures of $(C_4H_4)_2Ni_2(CO)_2$, namely **IIa-s** and **IIc-t**, respectively, each have a coaxial $(\eta^4\text{-}C_4H_4)Ni{=}Ni(\eta^4C_4H_4)$ arrangement with two bridging CO ligands. An unbridged triplet $(C_4H_4)_2Ni_2(CO)_2$ structure **IId-t** is found at 8.0 kcal mol^{-1} (B3LYP) or 22.7 kcal mol^{-1} (BP86) above the global minimum **IIa-s**.

The theoretical Ni=Ni distance in the singlet $(C_4H_4)_2Ni_2(\mu\text{-}CO)_2$ structure **IIa-s** is only 2.335 Å (B3LYP) or 2.318 Å (BP86), which is ~0.1 Å shorter than the doubly bridged formal Ni–Ni single bond in **Ic-s** and consistent with the doubly bridged formal double bond required to satisfy the 18-electron rare gas configuration. A similar Ni=Ni distance

Table 1 Metal bond distances (in Å), HOMO–LUMO energy gaps (E_{gap} in eV), total energies (E in hartree), relative energies (ΔE in kcal mol^{-1}), and imaginary vibrational frequencies for the singlet $(C_4H_4)_2Ni_2(CO)_3$ structures

	trans-$(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$		*cis*-$(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$		$(C_4H_4)_2Ni_2(CO)(\mu\text{-}CO)_2$		$(C_4H_4)_2Ni_2(\mu\text{-}CO)_3$	
	Ia-s (C_2)		**Ib-s** (C_1)		**Ic-s** (C_s)		**Id-s** (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Ni–Ni	2.534	2.509	2.540	2.512	2.476	2.444	2.345	2.326
E_{gap}	2.95	1.64	2.96	1.63	2.98	1.45	2.56	1.49
$-E$	3666.37260	3666.89343	3666.36920	3666.88949	3666.36056	3666.88537	3666.32060	3666.86359
ΔE	0.0	0.0	2.1	2.5	7.6	5.1	32.6	18.7
Imaginary frequencies	None	None	None	None	121*i*	44*i*	231*i*	127*i*

Table 2 Metal bond distances (in Å), HOMO–LUMO energy gaps (E_{gap} in eV), total energies (E in hartree), relative energies (ΔE in kcal mol^{-1}), imaginary vibrational frequencies, and $\langle S^2\rangle$ expectation values for the triplet $(C_4H_4)_2Ni_2(CO)_3$ structures

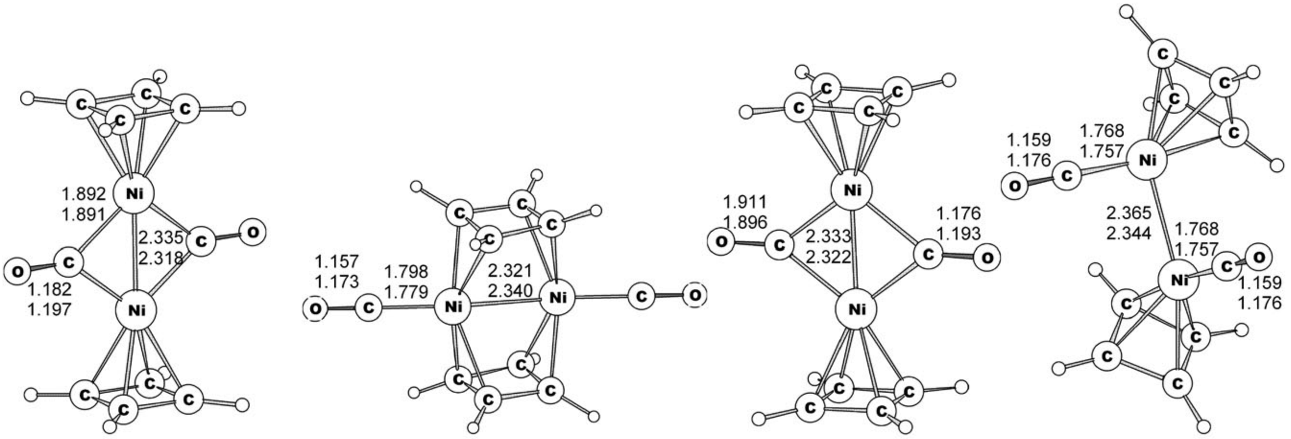
	$(C_4H_4)_2Ni_2(CO)(\mu\text{-}CO)_2$		$(C_4H_4)_2Ni_2(trans\text{-}CO)_2(\mu\text{-}CO)$		$(C_4H_4)_2Ni_2(cis\text{-}CO)_2(\mu\text{-}CO)$		$(C_4H_4)_2Ni_2(\mu\text{-}CO)_3$	
	Ie-t (C_s)		**If-t** (C_1)		**Ig-t** (C_1)		**Ih-t** (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Ni–Ni	2.503	2.477	2.813	2.803	2.814	2.764	2.347	2.319
E_{gap}	2.66	1.12	2.41	1.02	2.36	0.97	2.03	0.56
$-E$	3666.33369	3666.85710	3666.33820	3666.85320	3666.33730	3666.85173	3666.29429	3666.82681
ΔE	24.4	22.8	21.6	25.2	22.2	26.2	49.1	41.8
Imaginary frequencies	None	None	None	None	None	None	595*i*	475*i*
$\langle S^2\rangle$	2.03	2.01	2.03	2.01	2.03	2.01	2.05	2.01

Table 3 Metal carbonyl ν(CO) frequencies (in cm^{-1}) and infrared intensities in parentheses (in km mol^{-1}) predicted for the $(C_4H_4)_2Ni_2(CO)_3$ structures (BP86) (bridging ν(CO) frequencies in **bold**)

	ν(CO) frequencies
Ia-s (C_2)	**1853 (a, 486)**, 1984 (b, 1452), 1996 (a, 15)
Ib-s (C_1)	**1850 (a, 499)**, 1982 (a, 299), 2018 (a, 1223)
Ie-t (C_s)	**1834 (a″, 925)**, **1861(a′,10)**, 2007 (a′, 804)
If-t (C_1)	**1818 (a, 421)**, 1983 (a, 1519), 1992 (a, 5)
Ig-t (C_1)	**1823 (a, 407)**, 1980 (a, 315), 2011 (a, 1283)

of 2.333 Å (B3LYP) or 2.322 Å (BP86) is found in the triplet $(C_4H_4)_2Ni_2(\mu\text{-}CO)_2$ structure **IIc-t**. In this case the Ni═Ni double bond is considered to be a $\sigma + {}^2/_2\pi$ bond similar to that in the known stable triplet[36] $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$ and in isolated dioxygen. This gives the nickel atoms in **IIc-t** the favored 18-electron configuration but leaves two unpaired electrons in the π "half-bond" components of the formal Ni═Ni double bond. A similar Ni═Ni distance is also found in the unbridged $(\eta^4\text{-}C_4H_4)_2Ni_2(CO)_2$ structure **IId-t**, which can also be interpreted as a similar $\sigma + {}^2/_2\pi$ double bond containing the two unpaired electrons of the triplet.

The other singlet $(C_4H_4)_2Ni_2(CO)_2$ structure **IIb-s** at 1.7 kcal mol^{-1} (B3LYP) or 9.2 kcal mol^{-1} (BP86) above the global minimum **IIa-s** is predicted to have a perpendicular metallocene-like structure with two terminal CO ligands similar to that predicted for the carbonyl-free dimetallocenes[12] Cp_2M_2 (M = Cu, Ni) and perpendicular $\perp$-$Cp_2Co_2(CO)_2$, in which each cyclobutadiene ring bridges the cobalt–cobalt



IIa-s(C_{2h}) IIb-s(C_i) IIc-t(D_{2h}) IId-t(C_2)

Fig. 4 Optimized geometries for the four $(C_4H_4)_2Ni_2(CO)_2$ structures.

Table 4 Metal bond distances (in Å), HOMO–LUMO energy gaps (E_{gap} in eV), total energies (E in hartree), relative energies (ΔE in kcal mol^{-1}), imaginary vibrational frequencies, and $\langle S^2 \rangle$ expectation values for the $(C_4H_4)_2Ni_2(CO)_2$ structures

	$(C_4H_4)_2Ni_2(\mu\text{-}CO)_2$		$(C_4H_4)_2Ni_2(CO)_2$		$(C_4H_4)_2Ni_2(\mu\text{-}CO)_2$		$(C_4H_4)_2Ni_2(CO)_2$	
	IIa-s (C_{2h})		**IIb-s** (C_i)		**IIc-t** (D_{2h})		**IId-t** (C_2)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Ni–Ni	2.335	2.318	2.321	2.340	2.333	2.322	2.365	2.344
E_{gap}	1.86	0.86	3.57	2.25	3.00	1.48	3.20	1.65
$-E$	3553.00234	3553.53070	3552.99969	3553.51602	3552.99360	3553.51080	3552.98956	3553.49451
ΔE	0.0	0.0	1.7	9.2	5.5	12.5	8.0	22.7
Imaginary frequencies	None	None	None	None	None	None	None	None
$\langle S^2 \rangle$	0.00	0.00	0.00	0.00	2.05	2.01	2.02	2.01

Table 5 Metal carbonyl ν(CO) frequencies (in cm^{-1}) and infrared intensities (in parentheses, in km mol^{-1}) predicted for the $(C_4H_4)_2Ni_2(CO)_2$ structures (BP86) (bridging ν(CO) frequencies in **bold**)

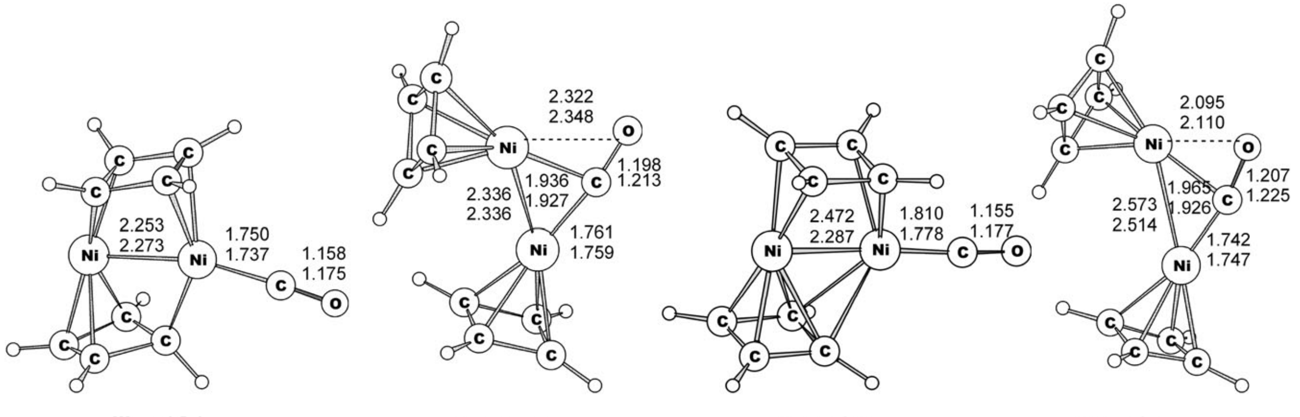
	ν(CO) frequencies
IIa-s (C_{2h})	**1826 (b_u, 1061), 1857 (a_g, 0)**
IIb-s (C_i)	1980 (a_u, 1994), 1995 (a_g,0)
IIc-t (D_{2h})	**1834 (b_{2u}, 935), 1861 (a_g, 0)**
IId-t (C_2)	1971 (b, 857), 1992 (a, 757)

bond.[14] The eight carbon atoms of the two bridging cyclobutadiene ligands form an elongated cube, with two carbon atoms of each C_4H_4 ring being bonded to each nickel atom. Therefore, each cyclobutadiene ring in **IIb-s** can be considered to be a $\eta^{2,2}$ ligand with each nickel atom bonded to one double bond of each C_4H_4 ring and one carbonyl group. Such an $\eta^{2,2}$ bridging cyclobutadiene ligand using two carbons for bonding to each metal atom in an M_2 unit is novel and has not yet been achieved experimentally. A formal Ni=Ni double bond is then required to give each nickel atom in **IIb-s** the favored 18-electron configuration. This is consistent with the predicted Ni=Ni distance of 2.321 Å (B3LYP) or 2.340 Å (BP86) in **IIb-s**.

For the $(C_4H_4)_2Ni_2(CO)_2$ structures the bridging ν(CO) frequencies fall in the range 1826–1861 cm^{-1} and the terminal ν(CO) frequencies fall in the range 1971–1995 cm^{-1} (BP86, Table 5). In transition metal carbonyl chemistry the ν(CO) frequencies of typical symmetrical two-electron donor bridging CO groups are well known to occur 100 to 150 cm^{-1} below the ν(CO) frequencies of terminal CO groups in a given type of metal carbonyl derivative.[37]

3.1.3 $(C_4H_4)_2Ni_2(CO)$.

Optimizations have been carried out on triplet and singlet $(C_4H_4)_2Ni_2(CO)$ structures in which the single CO group is either bridging or terminal. Two types of equilibrium geometries are obtained (Fig. 5 and Table 6). The global minimum $(C_4H_4)_2Ni_2(CO)$ structure is the perpendicular structure **IIIa-s** with a terminal carbonyl group and two bridging C_4H_4 rings. One of the bridging cyclobutadiene rings (the "top" ring in Fig. 5) is a $\eta^{2,2}$-μ-C_4H_4 ring with two carbon atoms bonded to each nickel atom. The second bridging C_4H_4 ring (the "bottom" ring in Fig. 5) is a $\eta^{3,1}$-μ-C_4H_4 ring with three carbon atoms bonded to the carbonyl-free nickel atom (the "left" nickel in Fig. 5) and the fourth carbon atom bonded to the nickel atom bearing the carbonyl group (the "right" nickel in Fig. 5). The different bonding modes of the two C_4H_4 rings in **IIIa-s** lead to a twist of one ring relative to the other so that the eight carbon atoms of the two C_4H_4 rings form an elongated square antiprism. Thus the decarbonylation of the singlet perpendicular $(\mu\text{-}C_4H_4)_2Ni_2(CO)_2$ structure **IIb-s** (Fig. 4) to the likewise singlet perpendicular $(\mu\text{-}C_4H_4)_2Ni_2(CO)$ structure **IIIa-s** (Fig. 5) involves twisting the C_8 elongated cube formed by the two C_4H_4 rings into an elongated square antiprism. In the perpendicular singlet monocarbonyl $(\mu\text{-}C_4H_4)_2Ni_2(CO)$ (**IIIa-s**) each nickel atom thus receives a total of five electrons from the



IIIa-s(C_s) **IIIb-s**(C_1) **IIIc-t**(C_1) **IIId-t**(C_s)

Fig. 5 Optimized geometries for the four $(C_4H_4)_2Ni_2(CO)$ structures.

Table 6 Metal bond distances (in Å), metal carbonyl ν(CO) frequencies (in cm^{-1}), HOMO–LUMO energy gaps (E_{gap} in eV), total energies (E in hartree), relative energies (ΔE in kcal mol^{-1}), imaginary vibrational frequencies, and $\langle S^2\rangle$ expectation values for the optimized $(C_4H_4)_2Ni_2(CO)$ structures. The bridging ν(CO) frequencies are in **bold**.

	$(C_4H_4)_2Ni_2(CO)$		$(C_4H_4)_2Ni_2(\mu\text{-}CO)$		$(C_4H_4)_2Ni_2(CO)$		$(C_4H_4)_2Ni_2(\mu\text{-}CO)$	
	IIIa-s (C_s)		**IIIb-s** (C_1)		**IIIc-t** (C_1)		**IIId-t** (C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Ni–Ni	2.253	2.273	2.336	2.336	2.472	2.287	2.573	2.514
ν(CO)	2086	1992	**1822**	**1758**	2083	1970	**1784**	**1701**
E_{gap}	2.90	1.41	1.83	0.90	2.87	1.46	2.53	0.92
$-E$	3439.62812	3440.12950	3439.59711	3440.10756	3439.61147	3440.10401	3439.59633	3440.09160
ΔE	0.0	0.0	19.5	13.8	10.5	16.0	20.0	23.8
Imaginary frequencies	None	None	None	None	None	None	None	None
$\langle S^2\rangle$	0.00	0.00	0.00	0.00	2.03	2.01	2.03	2.00

two C_4H_4 rings and the carbonyl group. A formal Ni$\equiv$Ni triple bond is necessary to give both nickel atoms the favored 18-electron configuration. This is reasonably consistent with the Ni$\equiv$Ni distance of 2.253 Å (B3LYP) or 2.273 Å (BP86) in **IIIa-s**, which is ~0.07 Å shorter than the Ni=Ni distance in the dicarbonyl **IIb-s**, which is assigned to a formal double bond.

A triplet perpendicular structure **IIIc-t** (Fig. 5 and Table 6) is found for $(C_4H_4)_2Ni_2(CO)$ at 10.5 kcal mol^{-1} (B3LYP) or 16.0 kcal mol^{-1} (BP86) above the global minimum **IIIa-s**. In this triplet structure one of the cyclobutadiene rings (the "top" ring in Fig. 5) is an $\eta^{2,2}$ ring using two carbon atoms to bond to one nickel atom and the other two carbon atoms to bond to the second nickel atom. The other cyclobutadiene ring (the "bottom" ring in Fig. 5) has two of its carbon atoms bonded exclusively to the carbonyl-free nickel atom (the "left" nickel atom in Fig. 5) and the other two carbon atoms in bridging positions between the two nickel atoms. Electron counting is less clear in **IIIc-t**. The predicted Ni=Ni bond length in **IIIc-t** of 2.472 Å (B3LYP) or 2.287 Å (BP86) is longer than that in the singlet **IIIa-s** and thus can correspond to a formal double bond.

The second type of $(C_4H_4)_2Ni_2(CO)$ structure is a cisoid dimetallocene structure with a bridging CO ligand, which is found in the singlet structure **IIIb-s** and the triplet structure **IIId-t** (Fig. 5 and Table 6). These structures are of considerably higher energy than the perpendicular structures, with **IIIb-s** lying 19.5 kcal mol^{-1} (B3LYP) or 13.8 kcal mol^{-1} (BP86) and the triplet structure **IIId-t** lying 20.0 kcal mol^{-1} (B3LYP) or 23.8 kcal mol^{-1} (BP86) above the global minimum **IIIa-s**. The bridging η^2-μ-CO groups in **IIIb-s** and **IIId-t** can be considered to be formal four-electron donors to the pair of metal atoms since they bond to one of the metal atoms as a normal two-electron donor linear CO ligand and to the other metal atom through an electron pair from a C–O π bond. These four-electron donor CO groups are characterized by unusually short Ni–O distances and unusually low ν(CO) frequencies (Table 6). Thus, the Ni–O distances are 2.322 Å (B3LYP) or 2.348 Å (BP86) in **IIIb-s** and 2.095 Å (B3LYP) or 2.110 Å (BP86) in **IIId-t**. Furthermore, the ν(CO) frequencies (BP86) are 1758 cm^{-1} in **IIIb-s** and 1701 cm^{-1} in **IIId-t**, which are ~100 cm^{-1} below any of the ν(CO) frequencies of the two-electron donor carbonyl groups found in this work. In the singlet **IIIb-s** the Ni=Ni distance of 2.336 Å (B3LYP or BP86) is consistent with the formal double bond needed to give both nickel atoms the favored 18-electron configuration with the four-electron donor carbonyl group. In the triplet **IIId-t** the Ni–Ni distance of 2.573 Å (B3LYP) or 2.514 Å (BP86) is ~0.2 Å longer than in the singlet **IIIb-s** consistent with the formal single bond necessary to give both nickel atoms the 17-electron configuration for a binuclear triplet with the four-electron donor η^2-μ-CO group.

3.2 Dissociation energies

Table 7 compares the carbonyl dissociation energies of the $(C_4H_4)_2Ni_2(CO)_n$ derivatives with those of the isoelectronic $(C_5H_5)_2Co_2(CO)_n$ derivatives using the lowest energy structures. In determining these dissociation energies, the fragments were allowed to fully relax. For comparison, the experimental carbonyl dissociation energies[38] are 27 kcal mol^{-1}, 41 kcal mol^{-1}, and 37 kcal mol^{-1} for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively. Thus the carbonyl dissociation energy of $(C_4H_4)_2Ni_2(CO)_3$ is seen to fall in the same range as the homoleptic carbonyls of the first-row transition metals, whereas that of $(C_4H_4)_2Ni_2(CO)_2$ is significantly higher by a factor of nearly two. The significantly higher dissociation energy of $(C_4H_4)_2Ni_2(CO)_2$ relative to $(C_4H_4)_2Ni_2(CO)_3$ may relate at least partially to stronger M–CO $\pi \rightarrow \pi^*$ backbonding in the derivative with fewer carbonyl groups.

The dicarbonyl $(C_4H_4)_2Ni_2(CO)_2$ is found to be thermodynamically stable with respect to disproportionation into $(C_4H_4)_2Ni_2(CO)_3$ **Ia-s** + $(C_4H_4)_2Ni_2(CO)$ **IIIa-s**, as indicated by a predicted energy of 24.1 kcal mol^{-1} (BP86) for this reaction.

Table 7 Dissociation energies (kcal mol^{-1}) for the successive removal of carbonyl groups from $(C_4H_4)_2Ni_2(CO)_n$ and $(C_5H_5)_2Co_2(CO)_n$ derivatives

	B3LYP	BP86
$(C_4H_4)_2Ni_2(CO)_3$ (**Ia-s**) → $(C_4H_4)_2Ni_2(CO)_2$ (**IIa-s**) + CO	26.1	22.3
$(C_4H_4)_2Ni_2(CO)_2$ (**IIa-s**) → $(C_4H_4)_2Ni_2(CO)$ (**IIIb-s**) + CO	48.1	60.2
$(C_5H_5)_2Co_2(CO)_3$ (**Ib**) → $(C_5H_5)_2Co_2(CO)_2$ (**IIa**) + CO	23.3	25.4
$(C_5H_5)_2Co_2(CO)_2$ (**IIa**) → $(C_5H_5)_2Co_2(CO)$ (**IIIa**) + CO	60.0	70.0

4. Discussion

4.1 The perpendicular structures of $(C_4H_4)_2Ni_2(CO)_2$ and $(C_4H_4)_2Ni_2(CO)$

One of the most striking features predicted for the binuclear cyclobutadienenickel carbonyls $(C_4H_4)_2Ni_2(CO)_n$ is the low energy of the perpendicular structures with bridging C_4H_4 rings and terminal carbonyl groups relative to the isomeric coaxial structures with terminal C_4H_4 rings and terminal or bridging carbonyl groups. Thus, for the monocarbonyl $(C_4H_4)_2Ni_2(CO)$ the perpendicular structure **IIIa-s** (Fig. 5 and Table 6) is the global minimum and for the dicarbonyl $(C_4H_4)_2Ni_2(CO)_2$ the perpendicular structure **IIb-s** lies <10 kcal mol^{-1} above the coaxial global minimum **IIa-s** (Fig. 4 and Table 4). The relatively low energies of these perpendicular structures contrast with the isoelectronic cyclopentadienylcobalt system, where the perpendicular $(\mu\text{-}C_5H_5)_2Co_2(CO)_2$ structure lies at the high energy of 36 ± 3 kcal mol^{-1} above the $(C_5H_5)_2Co_2(\mu\text{-}CO)$ global minimum.[14] For the monocarbonyl $(C_5H_5)_2Co_2(CO)$ the perpendicular structure is not the global minimum but lies $\sim$9 kcal mol^{-1} above the $(C_5H_5)_2Co_2(\mu\text{-}CO)$ bent global minimum. Thus cyclobutadiene rings appear to have a greater tendency to bridge a pair of metal atoms than do cyclopentadienyl rings.

The two nickel atoms in the perpendicular dicarbonyl $(\mu\text{-}C_4H_4)_2Ni_2(CO)_2$ (**IIb-s** in Fig. 4) are equivalent. The two bridging C_4H_4 rings lie essentially on top of each other with the Ni═Ni bond inbetween. Their eight carbon atoms thus form an elongated cube of ideal D_{4h} symmetry. The bonding of the C_4H_4 rings to the pair of nickel atoms can essentially be described as $\eta^{2,2}$ in which each C_4H_4 ring has a double bond attached to each nickel atom. Each nickel atom in **IIb-s** receives a total of six electrons from the surrounding ligands. Combining these six electrons with two more electrons from a Ni═Ni bond gives each nickel atom in **IIb-s** the favored 18-electron configuration.

The two nickel atoms in the perpendicular monocarbonyl $(\mu\text{-}C_4H_4)_2Ni_2(CO)$ (**IIIa-s** in Fig. 5) are non-equivalent, since only one of the nickel atoms has a terminal carbonyl group bonded to it. In order to balance the electronic configurations of the two nickel atoms, one of the C_4H_4 rings is twisted, so that three of its carbons are within bonding distance of the carbonyl-free nickel, leaving only the fourth carbon within bonding distance of the carbonyl-bearing nickel. This ring is thus an $\eta^{3,1}$ bonded ring rather than an $\eta^{2,2}$ bonded ring. The twist of the $\eta^{3,1}\text{-}C_4H_4$ ring relative to the $\eta^{2,2}\text{-}C_4H_4$ ring in $(\mu\text{-}C_4H_4)_2Ni_2(CO)$ (**IIIa-s** in Fig. 5) leads to an approximate elongated square antiprismatic arrangement of the two C_4H_4 rings. Each nickel in $(\mu\text{-}C_4H_4)_2Ni_2(CO)$ (**IIIa-s**) receives five electrons from the surrounding ligands because of the twist of one C_4H_4 ring relative to the other. For the carbonyl-free nickel, three of these five electrons come from three carbons of the $\eta^{3,1}\text{-}C_4H_4$ ring and the other two electrons from two carbons of the $\eta^{2,2}\text{-}C_4H_4$ ring. For the carbonyl-bearing nickel, two electrons come from the carbonyl group, two from the $\eta^{2,2}\text{-}C_4H_4$ ring, and the fifth electron from one carbon of the $\eta^{3,1}\text{-}C_4H_4$ ring. A formal Ni≡Ni triple bond in **IIIa-s** gives both nickel atoms the favored 18-electron configuration. This triple bond is consistent with the $\sim$2.25 Å Ni≡Ni bond distance in **IIIa-s** (Fig. 5), which is significantly shorter than the $\sim$2.32 Å Ni═Ni double bond distance in $(\mu\text{-}C_4H_4)_2Ni_2(CO)_2$ (**IIb-s** in Fig. 4).

4.2 Other comparisons between $(C_4H_4)_2Ni_2(CO)_n$ and $(C_5H_5)_2Co_2(CO)_n$ structures

A previous theoretical study[14] of $(C_5H_5)_2Co_2(CO)_n$ structures included only singlet structures. However, since some triplet structures are found in the chemistry of cyclopentadienylmetal carbonyls, notably $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$,[36,39,40] we also investigated triplet structures of the $(C_4H_4)_2Ni_2(CO)_n$ (n = 3, 2, 1) derivatives. In all cases the triplet structures were found to be of higher energy than the singlet structures. For $(C_4H_4)_2Ni_2(CO)_3$ the difference between the energies of the singlet and triplet structures was particularly large, with the lowest lying triplet structures at $\sim$22 kcal mol^{-1} above the global minimum **Ia-s**.

The tricarbonyl $(C_5H_5)_2Co_2(CO)_3$ is known but has not yet been characterized structurally by X-ray diffraction.[4] However, its ν(CO) infrared spectrum clearly indicates a structure with one bridging carbonyl group and two terminal carbonyl groups. This $(C_5H_5)_2Co_2(CO)_2(\mu\text{-}CO)$ structure is found to be the lowest energy structure in the previous theoretical study[14] when the B3LYP functional was used. However, use of the BP86 functional predicted a triply bridged $(C_5H_5)_2Co_2(\mu\text{-}CO)_3$ structure. Our current results clearly predict an analogous $(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ structure to be the lowest energy structure with both *cis* and *trans* isomers, namely **Ia-s** and **Ib-s**, respectively (Fig. 2), being within $\sim$2 kcal mol^{-1} in energy, thereby suggesting a fluxional system. The triply bridged structure $(C_4H_4)_2Ni_2(\mu\text{-}CO)_3$ was found not to be a genuine minimum but a transition state with a relatively large imaginary vibrational frequency. Following the corresponding normal mode leads to the singly bridged structure $(C_4H_4)_2Ni_2(CO)_2(\mu\text{-}CO)$ (**Ib-s**).

For $(C_4H_4)_2Ni(CO)_2$ and $(C_5H_5)_2Co_2(CO)_2$ the lowest energy structures are very similar, namely doubly bridged structures with sufficiently short M═M distances to correspond to the formal double bonds to give each metal atom the favored 18-electron configuration. The main point of difference between the dicarbonyls is the smaller energy difference between this doubly carbonyl-bridged global minimum and the higher energy perpendicular structures with bridging rings and terminal carbonyl groups.

The global minimum for the monocarbonyl $(C_4H_4)_2Ni_2(CO)$ is the perpendicular structure **IIIa-s** (Fig. 5), as noted above. However, a higher energy $(C_4H_4)_2Ni_2(CO)$ structure **IIIb-s** at $\sim$17 kcal mol^{-1} above **IIIa-s** has a four-electron bridging $\eta^2\text{-}\mu\text{-}CO$ carbonyl group, as indicated by a relatively short Ni–O distance of $\sim$2.34 Å. This means that a formal Ni═Ni double bond is sufficient to give both nickel atoms in **IIIb-s** the favored 18-electron configuration. Similar four-electron bridging carbonyl groups were not found in the previous theoretical study[14] for $(C_5H_5)_2Co_2(CO)$. Instead the global minimum for $(C_5H_5)_2Co_2(CO)$ was found to have a normal two-electron donor carbonyl group with a relatively long Co···O distance, thereby requiring a formal Co≡Co triple bond to give both cobalt atoms the favored 18-electron configuration.[14] This difference in the formal metal–metal bond orders in the isoelectronic compounds is apparent in the metal–metal bond distances. Thus in the $(C_4H_4)_2Ni_2(\eta^2\text{-}\mu\text{-CO})$ (**IIIb-s** in Fig. 5 and Table 6) the predicted formal Ni═Ni double bond length is ~2.34 Å whereas in $(C_5H_5)_2Co_2(\mu\text{-CO})$ the predicted formal Co≡Co triple bond length is much shorter at ~2.04 Å.

4.3 A comment on the synthetic prospects

The prospects for synthesizing at least some of the permethylated analogues of the structures predicted in this paper appear to be good, since a potential precursor $[(\eta^4\text{-}Me_4C_4)_2NiCl_2]_2$ is available in good yield from 3,4-dichloro-1,2,3,4-tetramethylcyclobutene ($Me_4C_4Cl_2$) and excess $Ni(CO)_4$.[1] This reaction is interesting since the $Ni(CO)_4$ serves as a nickel source to dechlorinate the dichlorocyclobutene. However, $Ni(CO)_4$ is not a powerful enough reducing agent to lead to a carbonylated nickel(0) product but instead only to the nickel(II) derivative $[(\eta^4\text{-}Me_4C_4)_2NiCl_2]_2$. It thus appears that in order to obtain tetramethylcyclobutadiene nickel carbonyl derivatives, such as the mononuclear $(\eta^4\text{-}Me_4C_4)Ni(CO)_2$, a stronger reducing agent needs to be added to the $Me_4C_4Cl_2$/$Ni(CO)_4$ reaction mixture. A relatively electropositive metal such as an alkali or alkaline earth metal might serve this purpose, possibly intercalated on graphite. The mononuclear nickel carbonyl derivative $(\eta^4\text{-}Me_4C_4)Ni(CO)_2$, synthesized by the reductive carbonylation of $[(\eta^4\text{-}Me_4C_4)_2NiCl_2]_2$ in this manner, is a potential source of the binuclear $(\eta^4\text{-}Me_4C_4)_2Ni_2(CO)_n$ derivatives discussed in this paper through photolysis reactions related to the reported photolysis[4,5] of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ to give $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_n$ (n = 3, 2) and the reported photolysis[8,9] of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ to give $(\eta^4\text{-}C_4H_4)_2Fe_2(\mu\text{-CO})_3$.

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