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# Binuclear Homoleptic Nickel Carbonyls: Incorporation of Ni−Ni Single, Double, and Triple Bonds, $Ni_2(CO)_x$ ($x = 5, 6, 7$)

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**Abstract:** Despite the fact that $Ni(CO)_4$ was discovered more than a century ago, no neutral $Ni_2(CO)_y$ compound has ever been synthesized in macroscopic amounts. In this study we consider a number of such compounds, including the Ni−Ni single-bonded ($\mu$-CO)$Ni_2(CO)_6$, the Ni═Ni double-bonded ($\mu$-CO)$_2Ni_2(CO)_4$, and the Ni≡Ni triple-bonded ($\mu$-CO)$_3Ni_2(CO)_2$. The predicted central bond distances are 2.73 (Ni−Ni), 2.56 (Ni═Ni), and 2.20 Å (Ni≡Ni). The latter compound is predicted to be bound by 34 kcal/mol with respect to $Ni(CO)_4$ + NiCO. Prospects for the synthesis of related dinickel compounds are discussed in some detail.

## Introduction

Binuclear metal carbonyl compounds comprise an important part of the vast class of transition-metal carbonyl complexes.[1] Thus they are the simplest representatives of transition-metal molecular clusters, which have been studied extensively because of their role in organometallic chemistry and catalysis. Binuclear metal carbonyls are also of interest for the study of the nature of metal−metal and metal−carbonyl bonding and for the elucidation of factors governing the choice of a certain structural type among the numerous types persistent in these compounds. This variety of structural types stems from the fact that carbonyl groups in transition-metal binuclear complexes may be terminal (connected to only one metal), symmetrically bridging (the carbonyl is equidistant from both metal atoms and lies in the plane orthogonal to the metal−metal bond), or semibridging (the metal−carbon bonds in the bridge are not equivalent). Many theoretical studies have been devoted to these complexes[2−13] with the objective of understanding the observed structural types. Quite a number of these studies deal with binuclear complexes of transition metals of odd atomic number, i.e., such compounds as $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ which are well-characterized experimentally. From transition metals of even atomic number, only $Fe_2(CO)_9$ has been well-characterized experimentally.[14]

It is well-known that the simple 18-electron rule is often successful in predicting the gross formulas of the transition-metal complexes. (It should be noted that the 18-electron rule is less successful for complexes with hard donors, the so-called Werner-type complexes.) For the binuclear complexes each metal−carbon bond to a bridging carbonyl group and each metal−metal bond (a single bond is supposed) provide one electron to the metal atoms, while each terminal carbonyl donates two electrons to the metal atom to which it is bonded. According to this rule, the next even electron transition metal, i.e., Ni, should form a binuclear carbonyl with the formula $Ni_2(CO)_7$. There are several communications reporting the experimental characterization of the ionic species $Ni_2(CO)_8^+$, $Ni_2(CO)_7^-$, and $Ni_2(CO)_6^+$, where structures with one and two bridging carbonyls were proposed,[15] on the ternary complex $Ni_2(CO)_3Cl_4$ with three bridging carbonyls,[16] and binuclear carbonyl complexes with small bite bridging bidentate phosphine ligands.[17−19] The Ni−Ni distances in these complexes were found by X-ray diffraction to be in the 2.577−2.694 Å range. In addition, the $Ni_2(CO)_6H^-$ anion has been isolated and characterized by X-ray diffraction.[20] However, the elongated Ni−Ni distance (2.864 Å) and the results of semiempirical theoretical studies[21] indicate that the nickel atoms are joined by a three-center Ni−H−Ni bond. To the best of our knowledge, there have been neither experimental nor theoretical studies of neutral binuclear nickel carbonyl complexes $Ni_2(CO)_y$.

The lack of experimental evidence for the existence of $Ni_2(CO)_y$ compounds appears to be the reason for the limited

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theoretical interest in binuclear nickel carbonyls, in contrast to the abundance of theoretical work on binuclear carbonyls of the other first row transition metals such as Cr, V, Mn, Fe, Co, and Cu. The aim of this work was to predict plausible structures for homoleptic binuclear nickel carbonyl complexes and to understand the factors governing their formation.

## Theoretical Methods

Prediction of the structure and thermochemical parameters of transition-metal complexes has become possible with the development of modern Density Functional Theory (DFT) methods.[12] In the present work, the hybrid HF/DFT method known as B3LYP was initially used. This method combines Becke's three-parameter exchange functional[23a] with the Lee−Yang−Parr correlation functional,[24a] as realized in the GAUSSIAN 94 program.[25] Later studies employed the pure DFT method BP86, which incorporates the Becke 1988 exchange functional[23b] with Perdew's 1986 treatment of correlation.[24b]

For C and O, the standard Huzinaga−Dunning double-$\zeta$ basis set[26] with one set of pure spherical harmonic d polarization functions [$\alpha_d$(C) = 0.75 and $\alpha_d$(O) = 0.85], designated (9s5p1d/4s2p1d), was used. For Ni the Wachters basis set[27a] in the contracted and augmented (by two sets of p functions with $\alpha$ = 0.2646, 0.104 and one set of d functions with $\alpha$ = 0.1316) form proposed by Hood and Schaefer[27b] (14s11p6d/10s8p3d) was used. A methodological discussion of the merits of this basis set[13] was given in our previous paper on $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ using analogous basis sets.

The default integration grid (75 radial shells, 302 angular points) and SCF convergence criterion ($10^{-8}$) were used in optimization, but in some cases with optimization problems, specified in the text, a larger grid (99 radial shells, 434 angular points) and tighter SCF convergence criterion ($10^{-10}$) were employed.

## Results and Discussion

There are three plausible structures for the binuclear nickel−carbonyl complex which can be formed in agreement with the 18e$^-$ rule, assuming a single bond between the nickel atoms: $\mu$-carbonylhexacarbonyldinickel with one bridging CO **1**, tri-$\mu$-carbonyltetracarbonyldinickel with three bridging carbonyls **2**, and penta-$\mu$-carbonyl dicarbonyl dinickel with five bridging carbonyls **3**.

The structure of $\mu$-carbonylhexacarbonyldinickel optimized within the $C_{2v}$ point group **1** has one imaginary vibrational frequency (14$i$ cm$^{-1}$). The low value of this imaginary frequency suggests that the downhill motion is associated with some change in the conformations of the $Ni(CO)_3$ groups. Indeed, the repulsion of carbonyl groups is maximal at $C_{2v}$ symmetry. Lowering of symmetry to $C_2$ by rotation of $Ni(CO)_3$ groups provides minimal repulsion between carbonyls, and the energy minimum was found at this symmetry (**4**, Figure 2).

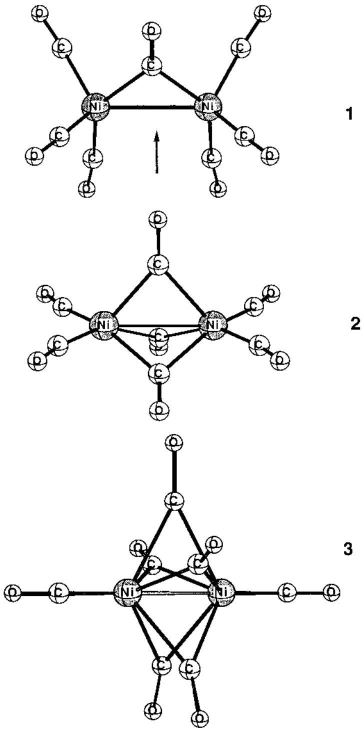

**Figure 1.** Plausible isomers of $Ni_2(CO)_7$ which satisfy the 18-electron rule.

The structure of tri-$\mu$-carbonyltetracarbonyldinickel optimized at the highest possible symmetry ($C_{2v}$, **2**, Figure 1) is a stationary point of Hessian index two (798$i$, 212$i$ cm$^{-1}$). The substantial value of both imaginary vibrational frequencies suggests that the search for the minimum may involve significant structural changes. Indeed, while optimizing without symmetry restrictions two of the bridging carbonyls become terminal, and such optimization results in the $\mu$-carbonylhexacarbonyldinickel structure (**1**, Figure 1). All attempts to optimize the structure of penta-$\mu$-carbonyl dicarbonyl dinickel **3** failed, since under $D_{5h}$ symmetry there are severe SCF convergence problems, and without symmetry restrictions this species dissociates into $Ni_2(CO)_4$ + 3 CO.

Thus, among structures which satisfy the 18e$^-$ rule under assumption of a single Ni−Ni bond, only $\mu$-carbonylhexacarbonyldinickel is found to be a genuine minimum. Its structure may be regarded as two $Ni(CO)_4$ tetrahedra sharing a common vertex. Two other structures may be derived (see Figure 2) from two $Ni(CO)_4$ tetrahedra sharing an edge $Ni_2(CO)_6$, **5**, and or a face $Ni_2(CO)_5$, **6**.

The edge-sharing structure with the highest symmetry ($D_{2h}$) has an imaginary vibrational frequency of 189$i$ cm$^{-1}$. Lowering the symmetry to $C_{2v}$ also results in a transition state with vibrational frequency 41$i$ cm$^{-1}$, and only in $C_s$ symmetry were we able to locate a minimum with the B3LYP method **5**. However, the energy differences between this minimum and the more symmetric structures are only 0.1 ($C_{2v}$ ) and 1.0 kcal/mol ($D_{2h}$). The BP86 method, however, gives the energy minimum at $C_{2v}$ (**5**, Figure 2). These structures will satisfy the 18e$^-$ rule if a double bond between the nickel atoms is assumed. Indeed, the equilibrium Ni−Ni bond length 2.559 Å in di-$\mu$-carbonyltetracarbonyldinickel **5** is substantially shorter than the 2.728 Å in $\mu$-carbonylhexacarbonyldinickel **4**. Distortions of the equilibrium structure from the $D_{2h}$ geometry may reflect the tendency toward dissociation with $Ni(CO)_4$ elimination.

The face-sharing structure $Ni_2(CO)_5$ (**6**) was found to be a minimum at the highest possible symmetry $D_{3h}$. According to

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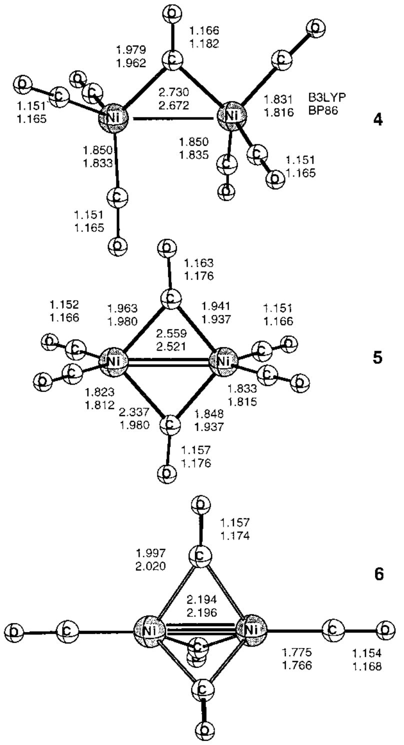

**Figure 2.** The optimized structures of binuclear nickel carbonyls produced by condensation of Ni(CO)$_4$ tetrahedra: vertex-sharing **4**, edge-sharing **5**, and face-sharing **6**. These structures satisfy the 18-electron rule assuming nickel−nickel single **4**, double **5,** and triple **6** bonds.

the 18e$^-$ rule tri-$\mu$-carbonyldicarbonyldinickel should have a triple Ni≡Ni bond. The very short predicted Ni−Ni bond (2.196 Å) provides evidence in favor of this suggestion. Note also the short terminal Ni−C bond (1.775 Å).

Before discussing the thermochemical properties of the predicted binuclear nickel carbonyls it is useful to ascertain the reliability of the method employed for the predictions of mononuclear nickel carbonyl compounds, the dissociation energies of which are known experimentally. The structures of Ni(CO)$_n$ ($n$ = 1−4) were optimized (**7**−**10**, Figure 3) and our predictions of the dissociation energies of the Ni(CO)$_n$ molecules are compared with the best previous quantum chemical estimates and with experiment in Table 1. This comparison shows that the B3LYP/DZP method provides a good reproduction of the experimental dissociation energies.

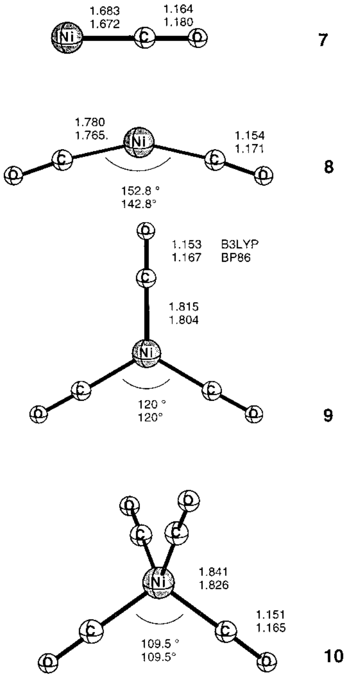

**Figure 3.** The optimized structures of mononuclear nickel carbonyls.

**Table 1.** Comparison of Theoretical and Experimental Ni(CO)$_n$ → Ni($^3$D) + $n$CO Dissociation Energies (kcal/mol)

| molecule | CCSD(T)[a] | B3LYP | exp[b] | exp[c] |
|---|---|---|---|---|
| NiCO | 34.5 | 37.9 | 35 | 40.5 ± 5.8 |
| Ni(CO)$_2$ | 77.1 | 82.9 | 86 | |
| Ni(CO)$_3$ | 111.7 | 114.3 | 115 | |
| Ni(CO)$_4$ | 141.5 | 138.0 | | 137.6 ± 1.2 |

[a] Reference 37. A (14s,11p,6d,3f/5s,4p,3d,1f) basis set was used for Ni and (9s,5p/3s,2p) for C and O. [b] Private communication cited in ref 47. [c] Reference 48.

**Table 2.** Dissociation Energies (kcal/mol) for the Minima of Several Dinickel Carbonyl Complexes Predicted with the B3LYP/DZP Method[a]

| | | | $D_e$ | | |
|---|---|---|---|---|---|
| structure | design. | sym. | diss. to Ni(CO)$_4$ + Ni(CO)$_n$. | diss. to Ni$_2$ + $n$CO | $N_{\mathrm{imag}}$[b] |
| ($\mu$-CO)Ni$_2$(CO)$_6$ | **1** | $C_{2v}$ | | | 1 |
| ($\mu$-CO)Ni$_2$(CO)$_6$ | **4** | C$_2$ | 1 | 210 | 0 |
| ($\mu$-CO)$_3$Ni$_2$(CO)$_4$ | **2** | $C_{2v}$ | | | 2 |
| ($\mu$-CO)$_2$Ni$_2$(CO)$_4$ | | $D_{2h}$ | | | 1 |
| ($\mu$-CO)$_2$Ni$_2$(CO)$_4$ | | $C_{2v}$ | | | 1 |
| ($\mu$-CO)$_2$Ni$_2$(CO)$_4$ | **5** | $C_s$ | 14 | 192 | 0 |
| ($\mu$-CO)$_3$Ni$_2$(CO)$_2$ | **6** | $D_{3h}$ | 34 | 167 | 0 |

[a] The symmetries and designations of several other stationary points studied in this work are also reported. [b] Number of imaginary vibrational frequencies.

The thermochemical characteristics of the binuclear nickel carbonyls are collected in Table 2. As expected, all three molecules are stable with respect to dissociation to Ni$_2$ + $n$CO. This measure of stability decreases in going from $\mu$-carbonylhexacarbonyldinickel **4** to tri-$\mu$-carbonyldicarbonyldinickel **6**. However, the more important measure of dissociation is to Ni(CO)$_4$ + Ni(CO)$_n$. Dissociation with the elimination of Ni(CO)$_4$ appears to be the lowest energy channel in all cases. Di-$\mu$-carbonyltetracarbonyldinickel **5** and especially $\mu$-carbonylhexacarbonyldinickel **4** have marginal energies with respect to this dissociation. Only tri-$\mu$-carbonyldicarbonyldinickel has a substantial dissociation energy, namely 34 kcal/mol. Since among DFT methods the BP86 method often gives the most reliable thermochemical predictions we reoptimized the structures **4**−**6** and Ni(CO)$_n$ by this method. The general tendency in the geometrical changes in going from B3LYP to BP86 is the decrease of the Ni−Ni bond lengths and the lengthening of CO. This tendency can be traced to the nickel dimer and free CO (Figure 4). However, for the tri-$\mu$-carbonyldicarbonyldinickel the geometrical parameters of the central cage change very little, while the terminal NiC bonds become shorter and the CO bonds longer (Figure 2). The dissociation energy for the Ni(CO)$_4$ elimination from tri-$\mu$-carbonyldicarbonyldinickel at the BP86/DZP level is 50 kcal/mol, compared to 34 kcal/mol with B3LYP. Thus this molecule appears to be substantially stable. This property and the high symmetry of **6** would appear to make it a plausible candidate to be synthesized. Since vibrational spectroscopy is a widespread tool for the identification of transition-metal carbonyls, we report the predicted vibrational spectrum of this molecule (Table 3). The predicted infrared spectrum contains only three strong bands, and two of them

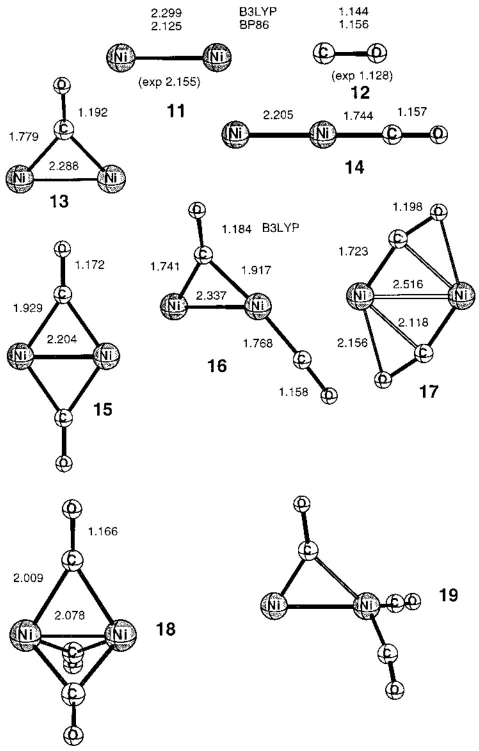

**Figure 4.** The optimized structures of model binuclear nickel carbonyls demonstrating the strengthening of the nickel−nickel bond with increasing number of bridging carbonyls (**13**, **15**−**18**).

belong to stretching vibrations of the terminal and bridging carbonyls. Note that the frequency difference between these two CO stretches (67 cm$^{-1}$) is not large. One may expect additional observable bands in the Raman spectrum of this molecule, where some bands, e.g. the breathing vibration of the nickel−carbonyl cage, which also could be interpreted as an Ni−Ni stretch (260 cm$^{-1}$), may be of substantial intensity.

To rationalize the change in the Ni−Ni bonding with the increase of number of carbonyls we attempted to analyze the structure of the molecular orbitals (MO) in the diatomic nickel molecule and in some simple carbonyl complexes. The structures of the $Ni_2$ molecule and the closed shell ground states of $Ni_2$-CO, $Ni_2(CO)_2$, and $Ni_2(CO)_3$ were accordingly optimized with the B3LYP method.

For $Ni_2CO$, only one minimum was found on the potential energy surface (PES) corresponding to the structure with the CO molecule in the bridging position between the two nickel atoms (**13**, Figure 4). The structure with the linear arrangement of atoms **14** lies 23.6 kcal/mol higher than **13** and has one imaginary vibrational frequency (13$i$ cm$^{-1}$) of symmetry. Among the five frequencies corresponding to molecular rotations and translations (which should have zero frequencies), there is one of magnitude comparable to the imaginary mode. Therefore, we reoptimized the structure and evaluated vibrational frequencies with a larger grid for the numerical integration. The rotational frequency decreased almost by the order of magnitude, while the genuine imaginary vibrational frequency grew slightly to 16$i$. Thus structure **14** appears to be a true transition state.

The structure of the $Ni_2(CO)_2$ molecule with two bridging carbonyls and $D_{2h}$ symmetry appears to be a stationary point **15** with three imaginary vibrational frequencies. Lowering the symmetry to $C_{2v}$ results in a transition state with one imaginary frequency, and the structure of $C_s$ symmetry appears to be the global minimum **16**. The local minimum of $C_{2h}$ symmetry **17** was predicted to lie 14.1 kcal/mol above **16**.

**Table 3.** Predicted Harmonic Vibrational Frequencies (cm$^{-1}$) and IR Intensities (km/mol) for Tri-$\mu$-carbonyldicarbonyldinickel, ($\mu$-CO)$_3$Ni$_2$(CO)$_2$, Structure **6**

| $\omega$ | intens. | sym. | assign. |
|---|---|---|---|
| 2147 | | $A'_1$ | $\nu_s$ CO t |
| 2108 | 2400 | $A''_2$ | $\nu_{as}$ CO t |
| 2060 | | $A'_1$ | $\nu_s$ CO b |
| 2041 | 1053 | $E'$ | $\nu_d$ CO b |
| 524 | | $A'_1$ | $\nu_s$_Ni −C t |
| 490 | 85 | $A''_2$ | $\nu_{as}$ Ni−C t |
| 461 | | $E''$ | $\delta$_NiCO t |
| 451 | 8 | $E'$ | $\delta$ NiCO t |
| 421 | 1 | $E'$ | $\nu'_d$ NiCNi |
| 350 | | $A'_1$ | $\nu'_s$ NiCNi |
| 301 | 18 | $E'$ | $\delta_d$ NiCNi |
| 260 | | $A'_1$ | $\nu$ NiCNi |
| 244 | | $A'_2$ | $\delta_s$ NiCNi |
| 236 | | $E''$ | $\nu''_d$ NiCNi |
| 139 | | $A''_2$ | $\nu''_{as}$ NiCNi |
| 122 | | $A''_2$ | CO b wag |
| 87 | | $E''$ | CO b wag |
| 69 | 1 | $E'$ | CO b wag |
| 64 | | $E''$ | CO b wag |
| 55 | 0 | $E'$ | CO b wag |

The $Ni_2(CO)_3$ molecule of $D_{3h}$ symmetry **18** with the carbonyl cage analogous to the $Ni_2(CO)_5$ (**6**) has an imaginary vibrational frequency of 80$i$ cm$^{-1}$. The removal of symmetry restrictions in the optimization procedure results in **19**, a structure analogous to **16** but with two terminal carbonyls attached to Ni instead of the one in **16**.

These results indicate that only structure **13** (with one bridging carbonyl) is a genuine minimum of the highest possible symmetry among the $Ni_2(CO)_n$ ($n = 1-3$) structures. Nevertheless, we shall discuss the occupation of the valence orbitals in these structures to see how the geometry and number of CO molecules attached to an $Ni_2$ unit affect the strength of the Ni−Ni bond.

The $Ni_2$ molecule was first identified in the vapor phase over liquid nickel by Kant,[28] who reported the dissociation energy to be 54.5 kcal/mol. Subsequently $Ni_2$ was observed in argon matrices by DeVore et al.[29] and by Moskovits and Hulse.[30] In the seemingly definitive recent gas-phase spectral study of this molecule by Morse and co-workers,[31] values of $D_0 = 2.042$ eV (47.1 kcal/mol) and $r_0 = 2.1545$ Å were reported.

The assignment of the ground state of the $Ni_2$ molecule is still the subject of discussion.[32−42] The $^3\Sigma_u{}^+$, $^3\Sigma_g{}^-$, $^1\Sigma_g{}^+$, $^1\Sigma_u{}^-$,

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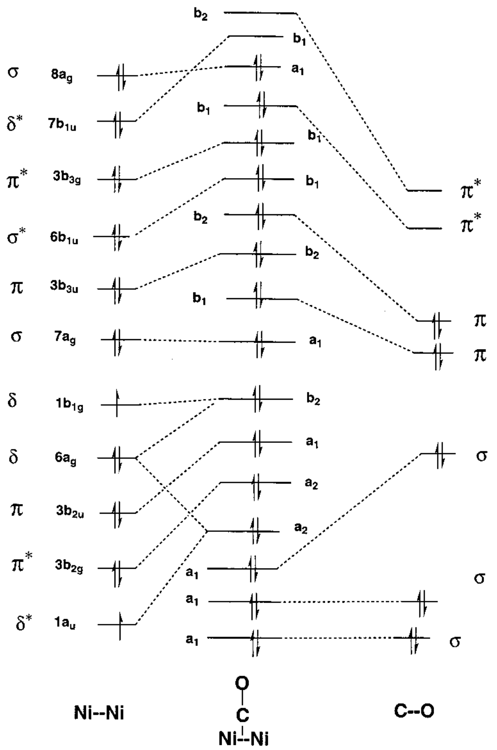

**Figure 5.** The scheme of the valence molecular orbitals of the nickel dimer, nickel dimer with a bridging carbonyl, and the isolated CO molecule.

$^3\Gamma_u$, and $^2\Gamma_g$ states have been estimated to be nearly degenerate. Nevertheless, it is commonly recognized that when Ni atoms in their $3d^94s$ configuration form the diatomic $Ni_2$ molecule, the two 4s electrons constitute a $\sigma$ bonding orbital and there are two holes in the $\delta$ shell. We adopt the $^3\Sigma_u^+$ as a ground state, since in the B3LYP method used in the present work it is 0.5 kcal/mol lower than the $^1\Sigma_g^+$ state.

Reduced to the $D_{2h}$ point group, the highest $D_{\infty h}$ subgroup that can be fully exploited by most quantum chemical codes, this triplet state $Ni_2$ will be of $^3B_{1u}$ symmetry with the electron configuration

$$...1b^1_{1g}\,6a^2_g\,1a^1_u\,6b^2_{1u}\,3b^2_{2u}\,3b^2_{3u}\,3b^2_{2g}\,3b^2_{3g}\,7a^2_g\,7b^2_{1u}\,8a^2_g$$

With the exclusion of the $8a_g$ orbital, which is the 4s Ni$-$4s Ni bonding orbital, the 10 other valence shell orbitals listed above are symmetric and antisymmetric combinations of the 3d orbitals of the two nickel atoms. The $a_g$ combination of 3d orbitals is $\sigma$ (bonding) and the $b_{1u}$ combination is $\sigma^*$ (antibonding). Combinations of the four other orbitals of each nickel produce four bonding and four antibonding orbitals (Figure 5). Thus, only the $\sigma$ (4s$-$4s) orbital ($8a_g$) provides bonding in the $Ni_2$ molecule, since the number of the occupied bonding orbitals is equal to that of the antibonding orbitals. This $\sigma$ bond makes the nickel dimer bound; otherwise it would be a weakly bound van der Waals molecule analogous in some way to the noble gas diatomics.

The addition to $Ni_2$ of the CO molecule in the bridging position (structure **13**) lowers the symmetry of the system to $C_{2v}$. Under this symmetry, the irreducible representations of the $Ni_2$ orbitals transform according to $11a_1 + 4a_2 + 10b_1 + 4b_2$. Addition of the $a_1$, $b_1$, and $b_2$ valence orbitals of CO gives $12a_1 + 4a_2 + 11b_1 + 5b_2$. However, the distribution of electrons in the $^1A_1$ state of the $Ni_2CO$ molecule is $11a_1 + 4a_2 + 11b_1 + 5b_2$, and one $a_1$ orbital is missing (presumably from the $6a_g$ orbital). Obviously, electrons from this orbital go to singly occupied orbitals originating from the $Ni_2$ $1b_{1g}$ and $1a_u$ orbitals (Figure 5). Since the missing $a_1$ orbital is bonding, we again have a balance of bonding and antibonding Ni$-$Ni orbitals. However, the analysis of the second HOMO ($b_1$) shows that it has $\pi^*$ CO character, and the first LUMO looks like the $7b_{1u}$ Ni$-$Ni antibonding orbital. Thus, the $\pi^*$ CO orbital forces the $\delta^*$ Ni$-$Ni orbital into the space of unoccupied orbitals and again (as in $Ni_2$) we have an excess of one Ni$-$Ni bonding orbital. Formally, the Ni$-$Ni bond in the bridging $Ni_2CO$ may be described as a single bond. The equilibrium Ni$-$Ni bond lengths in the ground state of $Ni_2$ **11** and in $Ni_2CO$ with a bridging carbonyl **13** agree with the above statement. Note that the lengthening of the CO bond in **13** compared to a free CO molecule **12** may be rationalized taking into account the population of the antibonding $\pi^*$ CO orbital in the $Ni_2CO$ molecule. This is well-known in the chemistry of metal carbonyl complexes as back-donation from the metal orbitals to the 2 $\pi$ antibonding orbital of CO.

In the axial approach of CO to $Ni_2$, the $C_{\infty v}$ symmetry is retained, and in the linear molecule $Ni_2CO$ with the terminal carbonyl **14**, the two $\pi^*$ CO become degenerate and both of them appear to be lower in energy than two antibonding Ni$-$Ni orbitals. Now two antibonding Ni$-$Ni orbitals become unoccupied and the Ni$-$Ni bond strengthens. This agrees with the predicted changes in the equilibrium geometry. The Ni$-$Ni bond is significantly shorter in **14** than in **13**.

Our structure **15** with two bridging carbonyls has nearly the same Ni$-$Ni bond length as **14** (Figure 4). The analysis of the MOs of **15** shows that two orbitals with pronounced $\pi^*$ CO character ($b_{1g}$ and $b_{2u}$) are the highest among occupied orbitals, and that the two Ni$-$Ni antibonding orbitals are the lowest among unoccupied orbitals. Note that from the four CO $\pi^*$ orbitals, those that are symmetric with respect to the plane bisecting the Ni$-$Ni bond are occupied. There are three such combinations of $\pi^*$ CO orbitals and we may expect that in the structure with three bridging carbonyls **18** all three low-lying antibonding orbitals of CO become occupied, forcing three Ni$-$Ni antibonding orbitals to be unoccupied. Indeed, in structure **18** we observe the shortest Ni$-$Ni bond, namely 2.078 Å. The reason for the instability of structures **15** and **18** may be rationalized by taking into account the fact that in these structures the HOMOs are $\pi^*$ CO and these systems tend to stabilize themselves by donating electron density from these orbitals to the nickel atoms. These model structures are also too far from the tetrahedral coordination of nickel found in $Ni(CO)_4$.

These very simple considerations help to rationalize the tendency for the strengthening of the Ni$-$Ni bond as the number of bridging carbonyls in the theoretical geometries for the dinickel carbonyl complexes is increased. This scheme also allows us to understand the surprisingly high stability of the tri-$\mu$-carbonyldicarbonyldinickel molecule **6**, which thus arises from three factors: (1) it satisfies the 18-electron rule counting the Ni$-$Ni interaction as a triple bond; (2) it retains the tetrahedral coordination favored by nickel carbonyls; and (3) it has three bridging and two terminal carbonyls which, as shown above, strengthen the Ni$-$Ni bond.

## Synthetic Prospects

Nickel tetracarbonyl, $Ni(CO)_4$, was the first metal carbonyl to be discovered, having been known for more than 100 years[43] despite the fact that $Ni(CO)_4$ readily decomposes to elemental

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[43] Mond, L.; Langer, C.; Quincke, F. *J. Chem. Soc.* **1890**, *57*, 749.

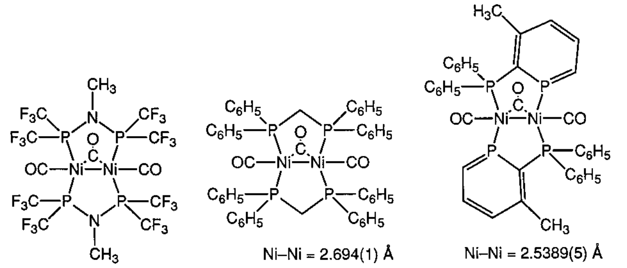

**Figure 6.** Some stable binuclear nickel carbonyl derivatives which have been isolated.

nickel only slightly above room temperature. Attempts to make a nickel carbonyl with a lower CO/Ni ratio isolable under normal laboratory conditions, such as the $Ni_2(CO)_n$ species discussed in this paper, by thermolysis or photolysis of $Ni(CO)_4$, have never succeeded. Thus the only observed anaerobic decomposition product of $Ni(CO)_4$ has been nickel metal.

This chemistry of nickel carbonyls can be contrasted with the corresponding chemistry of $Fe(CO)_5$, where photolysis of $Fe(CO)_5$ readily results in loss of 10% of the carbonyl ligands to give $Fe_2(CO)_9$ by the reaction[44]

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO \tag{1}$$

Isolation of $Fe_2(CO)_9$ from this reaction mixture is facilitated by its insolubility, which means that it can precipitate as it is formed so that it is protected from further reaction. This is actually rather important since $Fe_2(CO)_9$, which has been known for approximately 100 years, decomposes only slightly above room temperature to regenerate $Fe(CO)_5$, as well as a coordinately unsaturated $Fe(CO)_4$ fragment by the reaction

$$Fe_2(CO)_9 \rightarrow Fe(CO)_5 + Fe(CO)_4 \tag{2}$$

In the absence of a substrate to trap the $Fe(CO)_4$ fragment such as a Lewis base ligand to form an $LFe(CO)_4$ complex,[45] the $Fe(CO)_4$ will trimerize to $Fe_3(CO)_{12}$, which is the first procedure that was used to prepare this trinuclear carbonyl.[46]

The decomposition temperature of $Fe(CO)_5$ under a given set of anaerobic reaction conditions appears to be about 100 °C higher than that of $Ni(CO)_4$. Extrapolation of this ~100 °C decomposition temperature difference from the mononuclear metal carbonyls $M(CO)_n$ (M = Fe, Ni) to the corresponding dinuclear metal carbonyls $M_2(CO)_m$ predicts a decomposition temperature well below room temperature (possibly around −60 °C) for at least $Ni_2(CO)_7$ if not the other binuclear nickel carbonyls discussed in this paper. The comparison of nickel and iron carbonyl chemistry suggests that the best chance for synthesizing any of the binuclear nickel carbonyls would be a low-temperature photolysis (e.g., at −100 °C) of $Ni(CO)_4$ in a suitable inert solvent, but use of low-temperature experimental techniques would be essential for isolating $Ni_2(CO)_y$ without decomposition. This predicted very low decomposition temperature of binary binuclear nickel carbonyls probably accounts for the fact that they have never been isolated.

Despite this pessimism about the prospects of isolating and handling any binary binuclear nickel carbonyls under ambient laboratory conditions, experimental work during the last 30 years has demonstrated the ability of stabilizing binuclear nickel carbonyl units by the replacement of four carbonyl groups in $\mu$-carbonylhexacarbonyldinickel ($Ni_2(CO)_7$) with small bite bidentate ditertiary phosphine ligands to give $(diphos)_2Ni_2(CO)_2(\mu\text{-}CO)$ derivatives. Some binuclear nickel carbonyls of this type which have been isolated and structurally characterized[18,49,50] are given in Figure 6. In general, the Ni−Ni bond distances in the structurally characterized $(diphos)_2Ni_2(CO)_2(\mu\text{-}CO)$ derivatives fall in a rather wide range, 2.53−2.69 Å, which in general is lower than the 2.73 Å Ni−Ni bond distance calculated for the parent $\mu$-carbonylhexacarbonyldinickel. The stabilization of $Ni_2(CO)_7$ by such phosphine substitution of carbonyl ligands is typical in metal carbonyl chemistry and arises from an increase in the electron density on the nickel atoms by replacement of CO groups with the weaker acceptor phosphine ligands. The apparent shortening of the Ni−Ni single bond distance calculated for $Ni_2(CO)_7$ by replacement of CO groups with phosphine ligands may also be a consequence of strengthening the Ni−Ni bond through this, resulting increase in the metal electron density.

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**Supporting Information Available:** Table of total energies for stationary points and dissociation energies for the minima of several dinickel carbonyl complexes predicted with the B3LYP/DZP method (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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