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Binuclear Nickel Carbonyls with the Small Bite Chelating Diphosphine Ligands Methylaminobis(difluorophosphine) and Methylenebis(dimethylphosphine): Formation of Ni=Ni Double Bonds in Preference to Ligand Cleavage

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Abstract

The structures and thermochemistry of the triads of binuclear nickel carbonyl complexes (bid)Ni₂(CO)_n (*n* = 6, 5, 4) and (bid)₂Ni(CO)_n (*n* = 4, 3, 2) of the small-bite bidentate chelating diphosphines CH₃N(PF₂)₂ and (Me₂P)₂CH₂ have been investigated using density functional theory. The lowest-energy structures of the carbonyl-richest (bid)Ni₂(CO)₆ and (bid)₂Ni₂(CO)₄ structures have long Ni···Ni distances indicating the lack of direct nickel bonds. Similarly, the lowest energy structures of the intermediate (bid)Ni₂(CO)₅ and (bid)₂Ni₂(CO)₃ systems have Ni–Ni distances of ~2.7 Å and intact diphosphine ligands. Furthermore, the lowest energy structures of the carbonyl-poorest (bid)Ni₂(CO)₄ and (bid)₂Ni₂(CO)₂ systems have shorter Ni=Ni distances of ~2.5 Å suggesting formal double bonds and retain the intact diphosphine ligands. This contrasts with the previously studied binuclear iron carbonyls [CH₃N(PF₂)₂]₂Fe₂(CO)₆ and [CH₃N(PF₂)₂]₂Fe₂(CO)₄ for which ligand cleavage to separate CH₃NPF₂ and PF₂ units rather than Fe=Fe double bond formation occurs in the lowest energy structures. The experimental [(Me₂P)₂CH₂]₂Ni₂(CO)₄ structure with the boat form of the NiPCPNiPCP eight-membered lies ~0.5 kcal/mol in energy below the higher energy isomer with the chair form of the NiPCPNiPCP ring at the M06-L/TZP level of theory.

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1. Introduction

Transition metal complexes of small bite bidentate phosphines of the general type $Z(PX_2)_2$ (Z = one atom bridging group; X = alkyl, aryl, or halogen) are of interest in forming four-membered chelate rings with a single metal atom or five-membered chelate rings with an $M-M$ unit (Figure 1). Since five-membered chelate rings are generally more favorable than four-membered chelate rings, such small bite bidentate phosphines are of particular interest in stabilizing metal-metal bonded binuclear complexes. In a search for small bite bidentate phosphines that are also strong back-bonding ligands like carbon monoxide and PF_3 , methylaminobis(difluorophosphine), $MeN(PF_2)_2$, is of particular interest¹ because of its facile synthesis from methylamine, phosphorus trichloride, and antimony trifluoride² and its resemblance to the strong back-bonding ligand PF_3 . Despite the electron releasing properties of the bridging methylamino group, $MeN(PF_2)_2$ is still a sufficiently strong back-bonding ligand to form the white volatile air-stable zerovalent metal derivatives $[MeN(PF_2)_2]_3M$ ($M = Cr, Mo, W$) containing four-membered carbon-free NP_2M chelate rings analogous to the corresponding hexacarbonyls $M(CO)_6$.^{3,4}

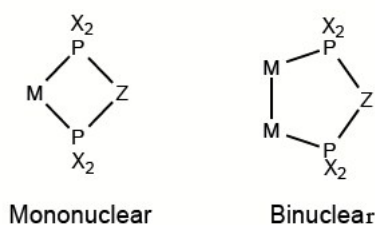


Figure 1. Chelating of small bite bidentate diphosphines to single metals and to binuclear M_2 units. For the chelate small bite bidentate diphosphines discussed in this paper $X = F$ and $Z = MeN$ for $MeN(PF_2)_2$ and $X = Me$ and $Z = CH_2$ for $(Me_2P)_2CH_2$.

In addition to forming the mononuclear $[MeN(PF_2)_2]_3M$ ($M = Cr, Mo, W$) complexes containing four-membered NP_2M chelate rings, the $MeN(PF_2)_2$ ligand also forms binuclear metal carbonyl complexes with five-membered NP_2M_2 chelate rings (Figure 1). For example, reaction of $Fe_3(CO)_{12}$ with excess $CH_3N(PF_2)_2$ in boiling tetrahydrofuran initially gives the yellow diiron hexacarbonyl derivative $[CH_3N(PF_2)_2]_2Fe_2(CO)_6$, shown by X-ray crystallography to have a structure consisting of two square pyramidal $P_2Fe(CO)_3$ units linked by the two ligands without an iron-iron bond (Figure 2).⁵ This structure can be considered as two five-coordinate $L_2Fe(CO)_3$ units related to the well-known $Fe(CO)_5$ and linked by the $MeN(PF_2)_2$ ligand leading to an eight-membered $FePNPFePNP$ ring. This product was relatively unstable evolving carbon monoxide in

solution to give the diiron pentacarbonyl derivative $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$, which could also be obtained directly by reaction of $\text{CH}_3\text{N}(\text{PF}_2)_2$ with $\text{Fe}_3(\text{CO})_{12}$ under more forcing conditions. This product is related to the well-known $\text{Fe}_2(\text{CO})_9$ by replacing four carbonyl groups with two bridging $\text{MeN}(\text{PF}_2)_2$ ligands forming a pair of fused five-membered NP_2Fe_2 chelate rings sharing the Fe–Fe edge.

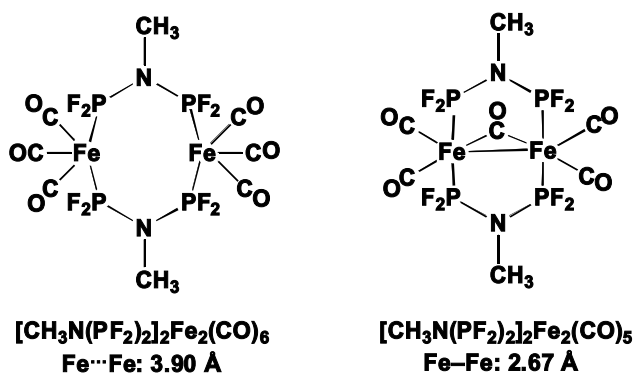


Figure 2. Binuclear $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Fe}_2(\text{CO})_n$ derivatives that have been synthesized and structurally characterized by X-ray crystallography.

A limitation in the ability to synthesize $\text{MeN}(\text{PF}_2)_2$ complexes is the susceptibility one of its P–N bonds to undergo cleavage to give separate PF_2 and MeNPF_2 units that each can bridge the pair of central metal atoms. This process occurs particularly when reactions of $\text{MeN}(\text{PF}_2)_2$ with metal carbonyls are carried out under forcing conditions in an attempt to replace all or almost all of the carbonyl groups with $\text{MeN}(\text{PF}_2)_2$ ligands. Thus the product $\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}_2(\text{CO})$ obtained by photolysis of $\text{Fe}_3(\text{CO})_{12}$ with excess $\text{MeN}(\text{PF}_2)_2$ is not a maximally substituted $\text{Fe}_2(\text{CO})_9$ derivative but instead $(\text{CH}_3\text{N}=\text{PF}_2)[\mu\text{-CH}_3\text{N}(\text{PF}_2)_2]_3\text{Fe}_2(\mu\text{-PF}_2)(\text{CO})$ in which one of the $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands has undergone phosphorus-nitrogen bond cleavage to form separate CH_3NPF_2 and PF_2 units (Figure 3).⁶ Similarly, the photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ with excess $\text{CH}_3\text{N}(\text{PF}_2)_2$ leads to complete substitution of the four carbonyl groups with two $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands, similar to the $\text{Cr}(\text{CO})_6/\text{CH}_3\text{N}(\text{PF}_2)_2$ photolysis noted above. However, the product is shown by X-ray crystallography to be $[\mu\text{-CH}_3\text{N}(\text{PF}_2)_2](\mu\text{-CH}_3\text{NPF}_2)(\mu\text{-PF}_2)\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2$ in which the two $\eta^5\text{-C}_5\text{H}_5\text{Fe}$ units are bridged by three different groups, namely an intact $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand, a CH_3NPF_2 unit, and a PF_2 unit (Figure 3).⁷ The bridging $\text{CH}_3\text{NPF}_2 + \text{PF}_2$ combination donates a total of six electrons to the dimetal system rather than only four electrons from an intact $\text{CH}_3\text{N}(\text{PF}_2)_2$ unit and is thus likely to arise in unsaturated metal complexes. Theoretical work on $[\text{MeN}(\text{PF}_2)_2]_2\text{Fe}_2(\text{CO})_n$ derivatives ($n = 6, 5, 4$) predicts the experimental

structures (Figure 2) for $n = 6$ and 5 but an $\text{Fe}_2(\text{CO})_4(\mu\text{-CH}_3\text{NPF}_2)_2(\mu\text{-PF}_2)_2$ structure with separate bridging PF_2 and $\text{CH}_3\text{N}(\text{PF}_2)_2$ units.⁸

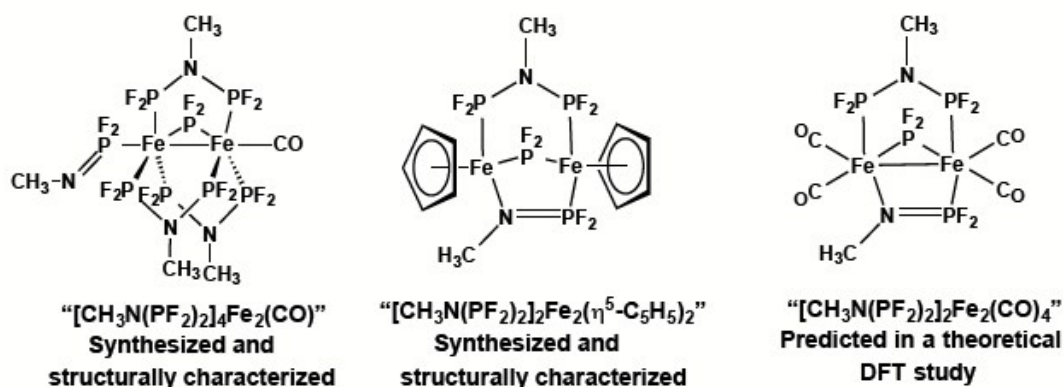


Figure 3. Examples of metal complexes in which an $\text{MeN}(\text{PF}_2)_2$ ligand has split into separate MeNPF_2 and PF_2 units.

The other small bite chelating bidentate diphosphine of interest is methylenebis(dimethylphosphine) $(\text{Me}_2\text{P})_2\text{CH}_2$, in which each phosphorus atom is bonded only to carbon atoms. This small bite bidentate diphosphine is the opposite of $\text{MeN}(\text{PF}_2)_2$ in being a strongly basic ligand with limited back-bonding ability. The small size and high basicity of $(\text{Me}_2\text{P})_2\text{CH}_2$ lead to metal carbonyl complexes having a relatively electron-rich and sterically unencumbered central metal atom. This is most obviously reflected in an increased air sensitivity of metal carbonyl complexes of $(\text{Me}_2\text{P})_2\text{CH}_2$.⁹

Homoleptic binuclear nickel carbonyls $\text{Ni}_2(\text{CO})_n$ has never been synthesised, although they have been studied by density functional theory.¹⁰ However, small bite bidentate diphosphine ligands are able to stabilize binuclear nickel carbonyls.¹¹ Thus the reaction of $\text{Ni}(\text{CO})_4$ with the small bite biphosphine $(\text{Me}_2\text{P})_2\text{CH}_2$ has been reported to yield $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ with two $(\text{Me}_2\text{P})_2\text{CH}_2$ molecules serving as bridging $\text{Ni}(\text{CO})_2$ groups forming an eight-membered $\text{Ni}_2\text{P}_4\text{C}_2$ ring¹² (Figure 4) related to the $[\text{MeN}(\text{PF}_2)_2]_2\text{Fe}_2(\text{CO})_6$ structure in Figure 2. The reaction of $[\text{C}_5\text{H}_5\text{NiCO}]_2$ with $(\text{Me}_2\text{P})_2\text{CH}_2$ in boiling tetrahydrofuran results in displacement of the cyclopentadienyl rather than carbonyl groups to give yellow $[(\text{Me}_2\text{P})_2\text{CH}_2]_3\text{Ni}_2(\text{CO})_2$.⁹ A related $[\text{MeN}(\text{PF}_2)_2]_3\text{Ni}_2(\text{CO})_2$ complex of methylaminobis(difluorophosphine) has also been synthesized.⁴

The present paper explores the chemistry of binuclear nickel carbonyl complexes of $\text{MeN}(\text{PF}_2)_2$ and $(\text{Me}_2\text{P})_2\text{CH}_2$ using density functional theory (DFT). This research has included the metal complex triads $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$), $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), and

$[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$). The stoichiometries of these triads were chosen to cover possible structures without a nickel-nickel bond and with nickel-nickel bonds if the ligands remain intact and the nickel atoms have the favored 18-electron configuration.^{13,14,15,16,17} In contrast to the previous study⁸ on binuclear $\text{CH}_3\text{N}(\text{PF}_2)_2$ iron carbonyl complexes, nickel-nickel bonds in all the low-energy structures were found in preference to phosphorus-nitrogen or phosphorus-carbon bond cleavage of the ligands.

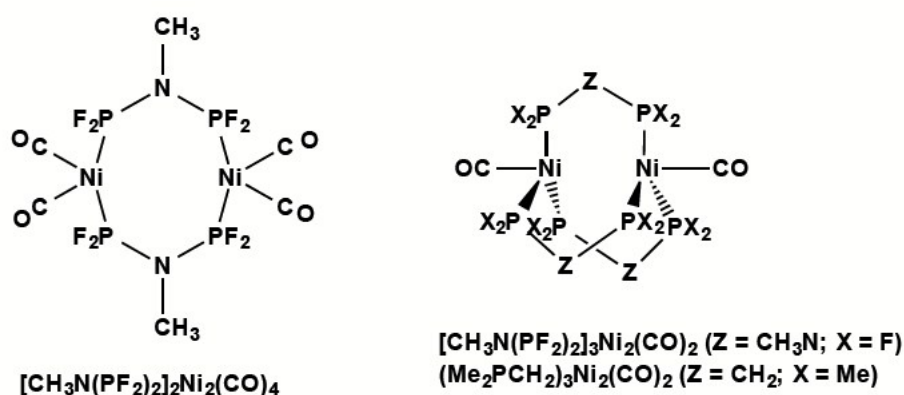


Figure 4. Experimentally known binuclear nickel carbonyl complexes of the small bite chelating diphosphines $\text{MeN}(\text{PF}_2)_2$ and $(\text{Me}_2\text{P})_2\text{CH}_2$.

2. Theoretical Methods

Electron correlation effects were considered by using density functional theory (DFT) methods, which have been suggested as a practical and effective computational tool, especially for organometallic compounds.^{18,19,20,21,22,23,24,25} Thus, in the present study, the computations were carried out by two selected DFT methods implemented in the Gaussian 09 program package²⁶, namely B3LYP, BP86, and M06-L. The B3LYP method is the hybrid HF-DFT method using a combination of the three-parameter Becke functional (B3) with the Lee-Yang-Parr (LYP) generalized gradient correlation functional.^{27,28} The BP86 method combines Becke's 1988 exchange functional (B)²⁹ with Perdew's 1986 gradient corrected correlation functional (P86).³⁰ The local density functional, M06-L^{31,32}, is designed to capture the main dependence of the exchange-correlation energy on local spin density, spin density gradient, and spin kinetic energy density. It is parametrized to satisfy the uniform-electron-gas limit and to have good performance for both main-group chemistry and transition metal chemistry.

The calculations were performed using the double- ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon, nitrogen, oxygen, fluorine, and phosphorus atoms add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{N}) = 0.80$, $\alpha_d(\text{O}) = 0.85$, $\alpha_d(\text{F}) = 1.0$, and $\alpha_d(\text{P}) = 0.6$ to the standard Huzinaga-

Dunning contracted DZ sets^{33,34} and are designated (9s5p1d/4s2p1d) for the carbon, nitrogen, oxygen and fluorine atoms and (11s7p1d/6s4p1d) for the phosphorus atom. For hydrogen, a set of p polarization functions $\alpha_p(\text{H}) = 0.75$ is added to the Huzinaga-Dunning DZ set. The loosely contracted DZP basis set for nickel is the Wachter's primitive set³⁵ augmented by two sets of p functions and a set of d functions contracted according to Hood, Pitzer, and Schaefer designated (14s11p6d/10s8p3d).³⁶

The geometries of all structures were fully optimized using the DZP B3LYP and DZP BP86 methods. The fine grid (75 radial shells, 302 angular points)³⁷ was the default for evaluating integrals numerically, and the tight (10^{-8} hartree) designation was the default for the self-consistent field (SCF) energy convergence. The finer (120, 974) integration grid³⁷ was used only to re-examining the small imaginary vibrational frequencies.

In order to test the computational accuracy of the above two DFT methods, we initially optimized the experimentally known compound¹² $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ at the B3LYP/DZP and BP86/DZP levels of theory. The lowest-energy optimized structure was different from the experimental structure. In order to resolve this discrepancy, we reoptimized the low-energy singlet structures in the present paper employing a new local density functional of M06-L with triple- ζ valence quality plus polarization³⁸ (TZP) basis sets using the empirical dispersion correction by Grimme's DFT-D3 method.³⁹ The most stable singlet structure of $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ predicted by M06-L/TZP is similar to the experimental structure. In addition, the results predicted by the three functionals are generally in agreement. Therefore, only the M06-L/TZP results for the structure geometries and relative energies are discussed in the text. However, the BP86/DZP method appears to be more reliable for the prediction of $\nu(\text{CO})$ frequencies, probably coincidentally.^{40,41} The results of the B3LYP/DZP and BP86/DZP methods are presented in the Supporting Information. In addition, the energies of all of the triplet structures were found to be higher than those of the isomeric singlet structures. Therefore the triplet structures are not discussed in this paper but are presented in the Supporting Information.

Each structure in this paper is designated as **PF-XY-EN** or **PMe-XY-EN**, where PF and PMe refer to the ligands $\text{MeN}(\text{PF}_2)_2$ and $(\text{Me}_2\text{P})_2\text{CH}_2$, respectively; **X** refers to the number of ligands; **Y** refers to the number of carbonyl groups; **E** refers to the order of relative energies, and **N** indicates the spin state multiplicity (**S** = singlet and **T** = triplet) for the triads $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$), $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), and $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$). Thus, the global minimum of $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$ is designated as **PF-16-1S** and that of $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ as **PMe-24-1S**.

3. Results and Discussion

3.1 Structures with one $\text{MeN}(\text{PF}_2)_2$ ligand

3.1.1 $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$. The structure **PF-16-1S** is predicted to be the lowest energy $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$ structure (Figure 5). In **PF-16-1S** the two $\text{Ni}(\text{CO})_3$ groups are arranged in *syn* positions relative to the central $\text{MeN}(\text{PF}_2)_2$ ligand. A slightly higher energy singlet $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$ structure **PF-16-2S**, lying 0.8 kcal/mol in energy above **PF-16-1S**, is similar to **PF-16-1S** except for a *anti* rather than *syn* arrangement of the two $\text{Ni}(\text{CO})_3$ groups relative to the central $\text{MeN}(\text{PF}_2)_2$ ligand. The singlet $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$ structure **PF-16-3S**, lying 2.3 kcal/mol above **PF-16-1S**, is similar to **PF-16-1S** and **PF-16-2S** but with a still different arrangement of the $\text{Ni}(\text{CO})_3$ groups relative to the $\text{MeN}(\text{PF}_2)_2$ ligand. All three $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$ structures have long $\text{Ni}\cdots\text{Ni}$ distances indicating the lack of direct nickel-nickel bonds. Nevertheless, each nickel atom in each of the three $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$ structures has the favored 18-electron configuration. The predicted $\nu(\text{CO})$ frequencies from 2163 to 2085 cm^{-1} in the three $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$ structures by the M06-L/TZP method are higher than the experimentally observed range of 2090 to 1985 cm^{-1} and indicate exclusively terminal CO groups in these structures.^{5,9} The $\nu(\text{CO})$ frequencies from 2069 to 2006 cm^{-1} predicted by the BP86/DZP method for the $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$ structures are closer to the experimental values in accord with expectation.

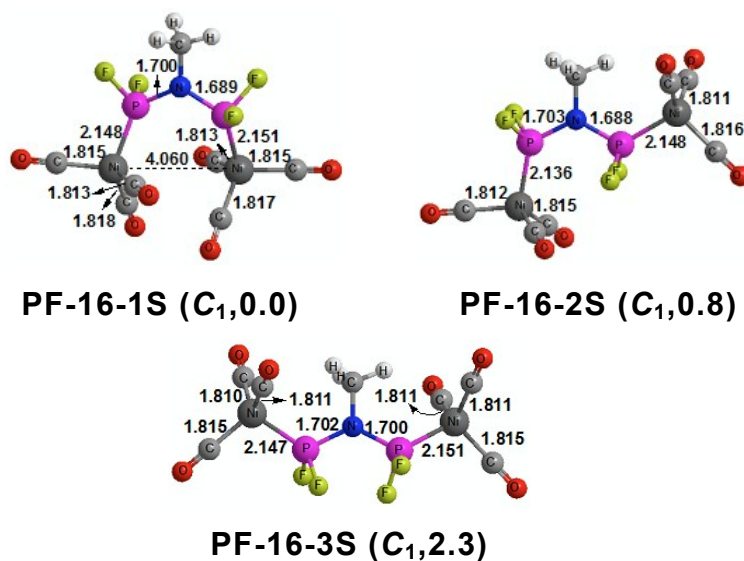


Figure 5. The three singlet $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_6$ structures. The numbers for bond distances (Å) and the relative energies are shown in parentheses were obtained by the M06-L method. The data in all of the other figures in the present paper have the same arrangement.

3.1.2 $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_5$. Two singlet energetically low-lying $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_5$ structures were found (Figure 6). The lowest lying $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_5$ structure is the singlet **PF-15-1S**, having an Ni–Ni distance of 2.632 Å, corresponding to a formal single bond thereby giving each nickel atom the favored 18-electron configuration. This Ni–Ni bond in **PF-15-1S** is bridged by a single CO group, predicted by the M06-L/TZP method to exhibit a $\nu(\text{CO})$ frequency of 1971 cm^{-1} . This bridging $\nu(\text{CO})$ frequency in **PF-15-1S** is significantly lower than the terminal $\nu(\text{CO})$ frequencies in **PF-15-1S**, ranging from 2148 to 2093 cm^{-1} . The other singlet $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_5$ structure **PF-15-2S** lies 1.1 kcal/mol in energy above **PF-15-1S**. Structure **PF-15-2S** is similar to **PF-15-1S** except for the approximate right angle rather than a straight angle between the bridging CO group and the face formed by the Ni–Ni bond and the bridging $\text{MeN}(\text{PF}_2)_2$ ligand.

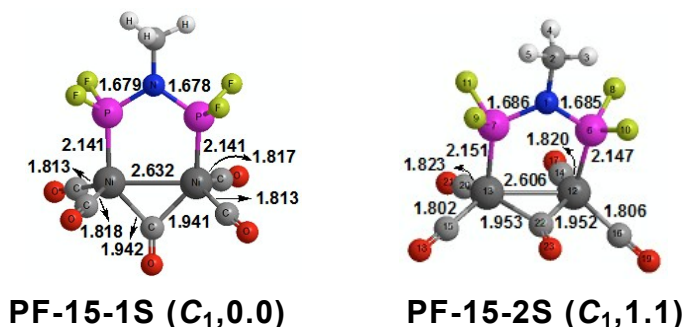


Figure 6. The two singlet $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_5$ structures.

3.1.3 $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_4$. Two singlet structures were optimized for $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_4$ (Figure 7). The lowest energy $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_4$ structure, **PF-14-1S**, has an intact bridging $\text{MeN}(\text{PF}_2)_2$ ligand and a Ni=Ni distance of 2.361 Å. The Ni=Ni distance in **PF-14-1S** is $\sim 0.27\text{ Å}$ shorter than the Ni–Ni single bond distance in the $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_5$ structures discussed above and thus suggests a formal double bond in **PF-14-1S**. Such a Ni=Ni double bond gives each nickel atom in **PF-14-1S** the favored 18-electron configuration. Two of the CO groups in **PF-14-1S** are bridging CO groups exhibiting a relatively low $\nu(\text{CO})$ frequency of 2002 cm^{-1} (M06-L/TZP) or 1884 cm^{-1} (BP86/DZP).

The singlet $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_4$ structure **PF-14-2S** lies at the relatively high energy of 14.2 kcal/mol above **PF-14-1S**. The $\text{MeN}(\text{PF}_2)_2$ ligand in **PF-14-1S** has broken into separate PF_2 and MeNPF_2 units by P–N bond rupture. The Ni–Ni distance of 2.602 Å in **PF-14-2S** is similar to that in the $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_5$ structures **PF-15-1S** and **PF-15-2S** (Figure 6) and thus suggests the formal single bond required to give each nickel atom the favored 18-electron configuration in a $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_4$ structure in which the $\text{MeN}(\text{PF}_2)_2$ ligand has ruptured into separate MeNPF_2 and PF_2 units.

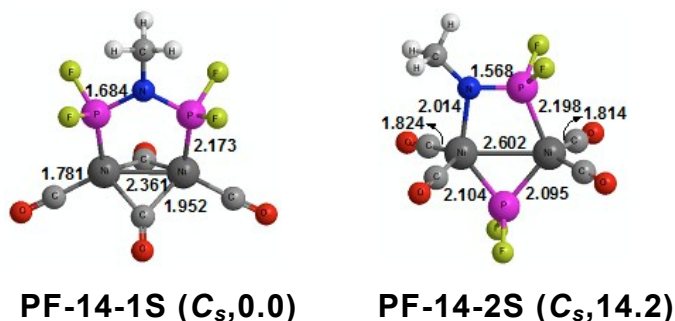


Figure 7. The two singlet $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_4$ structures.

3.2 Structures with two $\text{MeN}(\text{PF}_2)_2$ ligands

3.2.1 $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_4$. Two singlet $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_4$ structures were found (Figure 8). The lowest energy structure **PF-24-1S** has C_{2v} symmetry with two intact $\text{MeN}(\text{PF}_2)_2$ ligands bridging the pair of nickel atoms. The long $\text{Ni}\cdots\text{Ni}$ distance of 4.046 Å in **PF-24-1S** clearly indicates the absence of a direct nickel-nickel bond thereby giving each nickel atom the favored 18-electron configuration. The predicted $\nu(\text{CO})$ frequencies from 2141 to 2084 cm^{-1} indicate exclusively terminal CO groups in **PF-24-1S**. One of the two terminal CO groups on each nickel atom in **PF-24-1S** is oriented towards the same side of the eight-membered NiPNPNiPNP ring corresponding to a *syn* stereoisomer. A slightly higher energy singlet $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_4$ structure **PF-24-2S**, lying 1.5 kcal/mol above **PF-24-1S**, is the *anti* stereoisomer of **PF-24-1S** with terminal CO groups on opposite sides of the eight-membered ring.

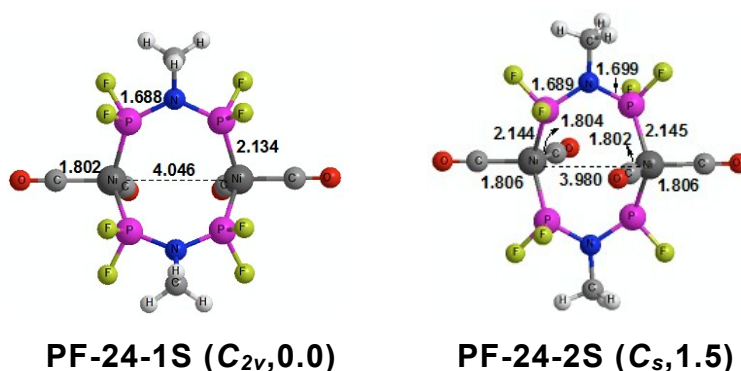


Figure 8. The two singlet $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_4$ structures.

3.2.2 $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_3$. Two singlet $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_3$ structures were found (Figure 9). In the lowest energy structure **PF-23-1S** the nickel atoms form an isosceles triangle with the bridging carbonyl carbon. The predicted $\text{Ni}\text{--}\text{Ni}$ distance in **PF-23-1S** of 2.574 Å can be interpreted as a formal single bond thereby giving each nickel atom the

avored 18-electron configuration. The bridging carbonyl group in **PF-23-1S** has a predicted infrared $\nu(\text{CO})$ frequency of 1958 cm^{-1} (M06-L/TZP) or 1882 cm^{-1} (BP86/DZP).

The next singlet $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_3$ structure **PF-23-2S**, lying 8.0 kcal/mol in energy above **PF-23-1S**, can be derived from **PF-24-1S** by removal of one of the terminal CO groups (Figure 9). The Ni→Ni distance of 2.590 Å in **PF-23-2S** can be interpreted as a formal dative single bond from the nickel atom bearing two CO groups to the nickel atom bearing only a single CO group. This gives each nickel atom the favored 18-electron configuration. The predicted $\nu(\text{CO})$ frequencies from 2094 to 2132 cm^{-1} (M06-L/TZP) in **PF-23-2S** indicate exclusively terminal CO groups.

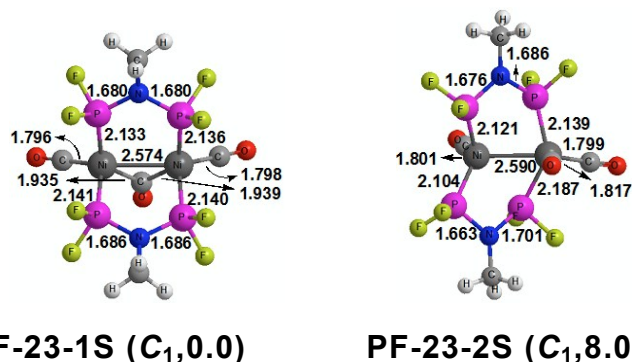


Figure 9. The two singlet $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_3$ structures.

3.2.3 $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_2$. Two singlet $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_2$ structures were found (Figure 10). The predicted Ni=Ni distance of 2.393 Å in the lowest energy structure **PF-22-1S** is ~ 0.2 Å shorter than the Ni-Ni single bond distances in the $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_5$ (Figure 6) and $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_3$ (Figure 9) structures thereby suggesting a formal double bond in **PF-22-1S**. One of the two CO groups in **PF-22-1S** is a bridging CO group exhibiting a relatively low $\nu(\text{CO})$ frequency of 1959 cm^{-1} (M06-L/TZP). The combination of two intact bridging $\text{MeN}(\text{PF}_2)_2$ ligands and a Ni=Ni double bond gives each nickel atom in **PF-22-1S** the favored 18-electron configuration.

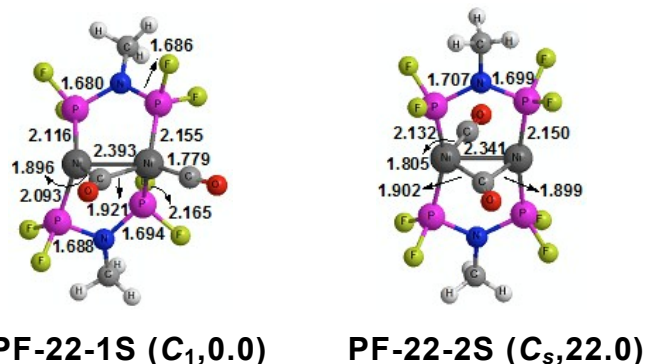


Figure 10. The two singlet $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_2$ structures.

The relatively high energy $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_2$ structure **PF-22-2S**, lying 22.0 kcal/mol above **PF-22-1S**, is similar to **PF-22-1S** except for a different angle of the terminal CO group relative to the Ni=Ni double bond.

3.3 Structures with one $(\text{Me}_2\text{P})_2\text{CH}_2$ ligand

3.3.1 $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_6$. Three singlet $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_6$ structures were found within ~ 5 kcal/mol of energy indicating a fluxional system. The lowest energy $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_6$ structure **PMe-16-1S** has the two $\text{Ni}(\text{CO})_3$ groups in *anti* positions relative to the central $(\text{Me}_2\text{P})_2\text{CH}_2$ ligand (Figure 11). A slightly higher energy singlet $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_6$ structure **PMe-16-2S**, lying 0.7 kcal/mol above **PMe-16-1S**, is similar to **PMe-16-1S** except for a *syn* rather than an *anti* arrangement of the two $\text{Ni}(\text{CO})_3$ groups relative to the central $(\text{Me}_2\text{P})_2\text{CH}_2$ ligand. This leads to a shorter, but still long non-bonding Ni $\cdots$ Ni distance of 4.599 Å in **PMe-16-2S**, clearly indicating the lack of a direct nickel-nickel bond. The remaining low-energy $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_6$ structure **PMe-16-3S**, lying 4.3 kcal/mol above **PMe-16-1S**, is also a *syn* stereoisomer similar to **PMe-16-2S** but with a different orientation of the $(\text{Me}_2\text{P})_2\text{CH}_2$ ligand relative to the $\text{Ni}(\text{CO})_3$ units. The predicted $\nu(\text{CO})$ frequencies in the three $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_6$ structures range from 2052 cm^{-1} to 2130 cm^{-1} (M06-L/TZP) indicating exclusively terminal CO groups. Each nickel atom in each of the three $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_6$ structures has the favored 18-electron configuration.

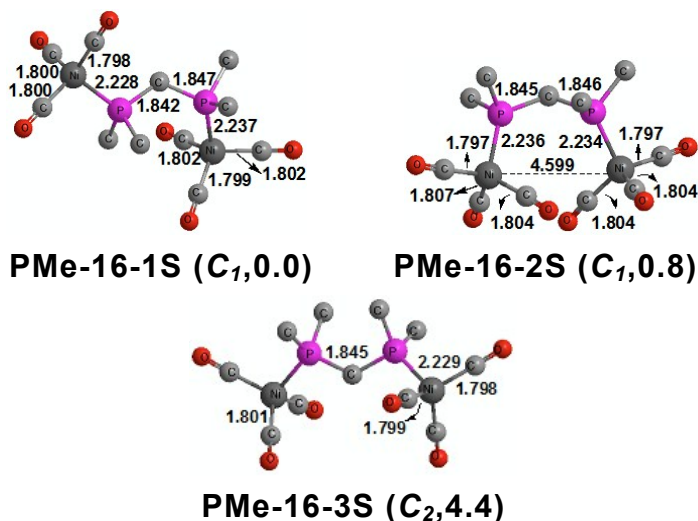


Figure 11. The three singlet $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_6$ structures. Hydrogen atoms are omitted for clarity in the structures of the $(\text{Me}_2\text{P})_2\text{CH}_2$ nickel carbonyl complexes.

3.3.2 $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_5$. Two singlet $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_5$ structures were optimized (Figure 12). The lowest energy $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_5$ structure is the singlet

PMe-15-1S, having a Ni–Ni distance of 2.607 Å, corresponding to a formal single bond thereby giving each nickel atom the favored 18-electron configuration. This Ni–Ni bond is bridged by both a single CO group and the (Me₂P)₂CH₂ ligand. The bridging $\nu(\text{CO})$ frequencies in **PMe-15-1S** of 1883 cm⁻¹ (M06-L/TZP) are significantly lower than the terminal $\nu(\text{CO})$ frequencies, which range from 2034 cm⁻¹ to 2112 cm⁻¹ (M06-L/TZP) in **PMe-15-1S** in accord with expectation.

The [(Me₂P)₂CH₂]₂Ni₂(CO)₅ structure **PMe-15-1S** lies a very large 38.5 kcal/mol below the next lowest energy isomer **PMe-15-2S** and thus appears to be a very favorable structure. The [(Me₂P)₂CH₂]₂Ni₂(CO)₅ structure **PMe-15-2S** has one of the P–C bonds in (Me₂P)₂CH₂ cleaved to form separate Me₂P and Me₂PCH₂ units. Each of these units bridges the pair of nickel atoms thereby donating a total of three electrons each to the central Ni₂ unit. Thus the combined Me₂P + Me₂PCH₂ units obtained from cleaving a P–C bond in a (Me₂P)₂CH₂ ligand donate a total of six electrons to the Ni₂ unit. The long Ni···Ni distance of 3.889 Å in **PMe-15-2S** clearly indicates the lack of a direct nickel–nickel interaction. However, in **PMe-15-2S** both nickel atoms have the favored 18-electron configuration.

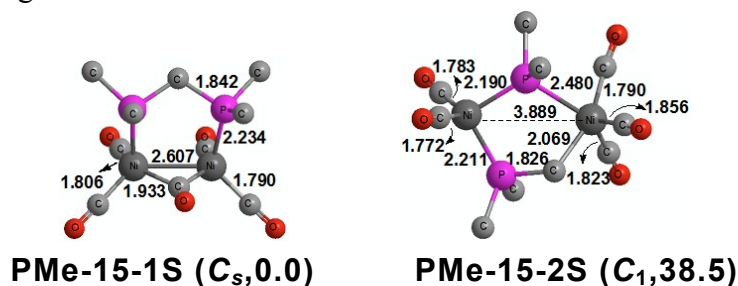


Figure 12. The two singlet [(Me₂P)₂CH₂]₂Ni₂(CO)₅ structures.

3.3.3 [(Me₂P)₂CH₂]₂Ni₂(CO)₄. Two singlet [(Me₂P)₂CH₂]₂Ni₂(CO)₄ structures were found (Figure 13). The lowest energy structure **PMe-14-1S** has two symmetrical bridging CO groups and a short Ni=Ni distance of 2.375 Å similar to the Ni=Ni distances in the corresponding [MeN(PF₂)₂]₂Ni₂(CO)₄ structures interpreted as formal double bonds. This gives each nickel atom in **PMe-14-1S** the favored 18-electron configuration.

The [(Me₂P)₂CH₂]₂Ni₂(CO)₄ structure **PMe-14-1S** lies 21.9 kcal/mol below the next lowest energy [(Me₂P)₂CH₂]₂Ni₂(CO)₄ structure **PMe-14-2S** and thus appears to be a highly favorable structure. Structure **PMe-14-2S** has separate bridging Me₂P and Me₂PCH₂ groups derived from the (Me₂P)₂CH₂ ligand and can be derived from the [(Me₂P)₂CH₂]₂Ni₂(CO)₄ structure **PMe-15-2S** (Figure 12) by simple removal of a terminal CO group (Figure 13). The Ni–Ni distance of 2.684 Å in **PMe-14-2S** suggests the formal single bond required to give each nickel atom the favored 18-electron configuration.

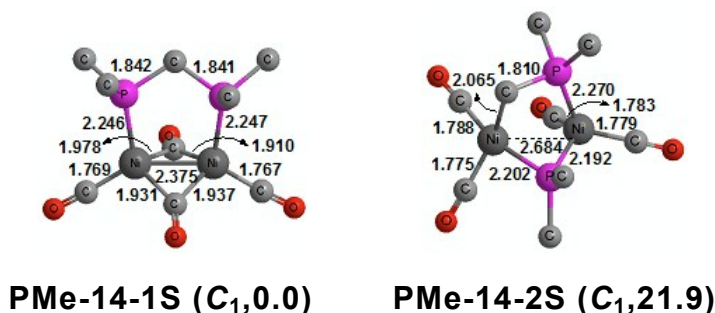


Figure 13. The two singlet $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_4$ structures.

3.4 Structures with two $(\text{Me}_2\text{P})_2\text{CH}_2$ ligands

3.4.1 $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$. Two low-energy $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ structures were found (Figure 14). In the lowest-energy structure **PMe-24-1S** each $(\text{Me}_2\text{P})_2\text{CH}_2$ ligand remains intact and bridges the central Ni_2 unit to form an eight-membered NiPCPNiPCP ring adopting the boat conformation leading to a structure exhibiting C_2 symmetry. The long $\text{Ni}\cdots\text{Ni}$ distance in **PMe-24-1S** of 4.386 Å indicates the absence of a direct nickel-nickel bond thereby giving each nickel atom the favored 18-electron configuration. The experimental $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ structure¹² is similar to **PMe-24-1S** with an essentially identical $\text{Ni}\cdots\text{Ni}$ non-bonding distance of 4.39 Å.

The second $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ structure **PMe-24-2S**, lying only 0.5 kcal/mol in energy above **PMe-24-1S**, is similar to **PMe-24-1S** except for a chair rather than a boat conformation of the eight-membered NiPCPNiPCP ring. This leads to a structure with C_{2h} rather than C_2 symmetry (Figure 14). The nickel coordination geometry in **PMe-24-2S** is approximately tetrahedral with P-Ni-P angles of 108.1°. The $\text{Ni}\cdots\text{Ni}$ non-bonding distance of 4.654 Å in **PMe-24-2S** is a significantly longer than that in **PMe-24-1S**.

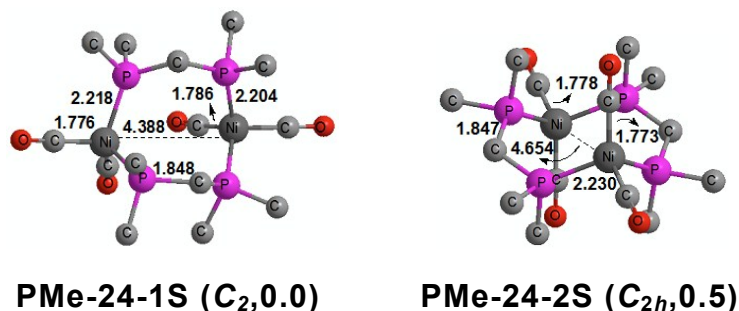
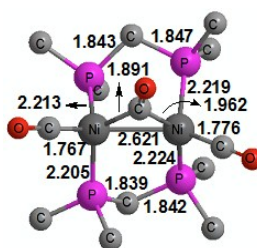


Figure 14. The two singlet $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ structures.

3.4.2 $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_3$. Only one low-energy singlet structure was found for $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_3$ (Figure 15) at the M06-L/TZP level. This structure **PMe-23-1S**

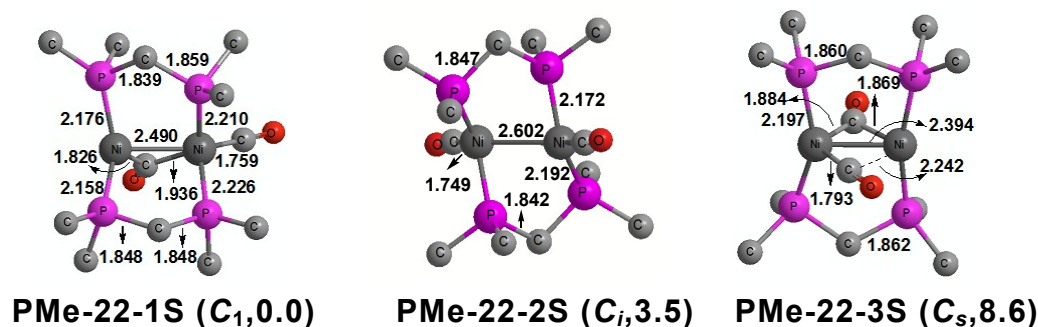
has a Ni–Ni distance of 2.621 Å, corresponding to a formal single bond. This Ni–Ni bond is bridged by a single CO group, predicted by the M06-L method to exhibit a $\nu(\text{CO})$ frequency of 1877 cm^{-1} . This bridging $\nu(\text{CO})$ frequency is significantly lower than the terminal $\nu(\text{CO})$ frequencies of 2027 and 2041 cm^{-1} .



PMe-23-1S ($C_1, 0.0$)

Figure 15. The single $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_3$ structure.

3.4.3 $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_2$. Three singlet $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_2$ structures were found (Figure 16). The lowest energy $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_2$ structure **PMe-22-1S** may be derived from the $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_3$ structure **PMe-23-1S** by removal of a terminal CO group. The Ni=Ni distance of 2.490 Å in **PMe-22-1S** is ~ 0.131 Å shorter than the formal Ni–Ni single bond in **PMe-23-1S** and thus can be interpreted as the formal double bond required to give each nickel atom the favored 18-electron configuration. The bridging CO group in **PMe-22-1S** exhibits the expected low $\nu(\text{CO})$ frequency of 1862 cm^{-1} (M06-L/TZP) whereas the terminal CO group exhibits a significantly higher $\nu(\text{CO})$ frequency of 2026 cm^{-1} in accord with expectation. The $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_2$ structure **PMe-22-3S**, lying 8.6 kcal/mol in energy above **PMe-22-1S** is similar to **PMe-22-1S** except that the terminal CO group in **PMe-22-1S** becomes a semibridging CO group.



PMe-22-1S ($C_1, 0.0$)

PMe-22-2S ($C_i, 3.5$)

PMe-22-3S ($C_s, 8.6$)

Figure 16. The three $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_2$ structures.

A higher energy singlet $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_2$ structure **PMe-22-2S**, lying 3.5 kcal/mol above **PMe-22-1S**, has exclusively terminal CO groups (Figure 16). The

Ni–Ni distance of 2.602 Å in **PMe-22-2S** suggests a formal single bond giving one nickel atom an 18-electron configuration and the other nickel atom a 16-electron configuration.

3.5 Thermochemistry

The reaction energies listed in Tables 1 and 2 are based on the lowest energy singlet state structures. The dissociation energies for the loss of one CO group from the carbonyl richest complexes of the triads, namely **PF-16-1S**, **PF-24-1S**, **PMe-16-1S**, and **PMe-24-1S**, range from 13.5 kcal/mol to 25.5 kcal/mol. This process of dissociation converts one of the remaining terminal CO groups to a bridging CO group and introduces a formal Ni–Ni single bond of length ~2.7 Å. Thus the formation of the Ni–Ni single bond compensates for the two electrons lost upon removal of the CO group.

Table 1. Dissociation energies (in kcal/mol) for the successive removal of carbonyl groups from binuclear nickel carbonyl derivatives [MeN(PF₂)₂]₂Ni₂(CO)_n (*n* = 6, 5), [MeN(PF₂)₂]₂Ni₂(CO)_n (*n* = 4, 3), [(Me₂P)₂CH₂]₂Ni₂(CO)_n (*n* = 6, 5) and [(Me₂P)₂CH₂]₂Ni₂(CO)_n (*n* = 4, 3) at the M06-L/TZP level.

Process	M06-L
MeN(PF ₂) ₂ Ni ₂ (CO) ₆ (PF-16-1S) → MeN(PF ₂) ₂ Ni ₂ (CO) ₅ (PF-15-1S) + CO	18.5
MeN(PF ₂) ₂ Ni ₂ (CO) ₅ (PF-15-1S) → MeN(PF ₂) ₂ Ni ₂ (CO) ₄ (PF-14-1S) + CO	28.5
[MeN(PF ₂) ₂] ₂ Ni ₂ (CO) ₄ (PF-24-1S) → [MeN(PF ₂) ₂] ₂ Ni ₂ (CO) ₃ (PF-23-1S) + CO	13.5
[MeN(PF ₂) ₂] ₂ Ni ₂ (CO) ₃ (PF-23-1S) → [MeN(PF ₂) ₂] ₂ Ni ₂ (CO) ₂ (PF-22-1S) + CO	35.4
[(Me ₂ P) ₂ CH ₂] ₂ Ni ₂ (CO) ₆ (PMe-16-1S) → [(Me ₂ P) ₂ CH ₂] ₂ Ni ₂ (CO) ₅ (PMe-15-1S) + CO	22.1
[(Me ₂ P) ₂ CH ₂] ₂ Ni ₂ (CO) ₅ (PMe-15-1S) → [(Me ₂ P) ₂ CH ₂] ₂ Ni ₂ (CO) ₄ (PMe-14-1S) + CO	25.4
[(Me ₂ P) ₂ CH ₂] ₂ Ni ₂ (CO) ₄ (PMe-24-1S) → [(Me ₂ P) ₂ CH ₂] ₂ Ni ₂ (CO) ₃ (PMe-23-1S) + CO	25.5
[(Me ₂ P) ₂ CH ₂] ₂ Ni ₂ (CO) ₃ (PMe-23-1S) → [(Me ₂ P) ₂ CH ₂] ₂ Ni ₂ (CO) ₂ (PMe-22-1S) + CO	38.9

The corresponding successive dissociation energies for the loss of one terminal CO group from the intermediate complexes of each triad, namely **PF-15-1S**, **PF-23-1S**, **PMe-15-1S**, and **PMe-23-1S**, range from 25.4 kcal/mol to 38.9 kcal/mol. The CO dissociation energies of **PF-23-1S** and **PMe-23-1S** are very high (35.4 kcal/mol and 38.9 kcal/mol). For comparison, the reported CO dissociation energies are 37 ± 2, 41 ± 2, and 25 ± 2 kcal/mol for Cr(CO)₆, Fe(CO)₅ and Ni(CO)₄, respectively.⁴² The high dissociation energies reflect the strength of the metal-carbonyl bonds. During this process of CO dissociation a Ni=Ni double bond is formed with intact ligands bridging the pair of

nickel atoms. This is different from the iron carbonyl complexes $[\text{CH}_3\text{N}(\text{PF}_2)_2]\text{Fe}_2(\text{CO})_n$ ($n = 7, 6$) $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Fe}_2(\text{CO})_n$ ($n = 5, 4$) where P–N bond rupture of one of the bridging $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands is energetically preferred over shortening of the iron-iron distances to give formal Fe=Fe double bonds.⁸ The bridging CO groups become more asymmetrical in all the complexes except for **PMe-14-1S**.

5. Conclusion

The nickel carbonyl complexes of the strong back-bonding fluorophosphine ligand $\text{CH}_3\text{N}(\text{PF}_2)_2$ can be grouped into the two triads $[\text{CH}_3\text{N}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$) and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$) depending on the $\text{CH}_3\text{N}(\text{PF}_2)_2/\text{Ni}$ ratio. In the lowest energy structures in both of these triads, all of the $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands bridge the Ni_2 unit rather than chelate to a single nickel atom to form a four-membered NiPNP chelate ring. The lowest energy carbonyl-richest structure of each triad has a long $\text{Ni}\cdots\text{Ni}$ distance indicating the lack of a direct nickel-nickel bond. The lowest energy structure of the intermediate member of each triad has a Ni–Ni distance of ~ 2.7 Å suggestive of a formal single bond. The lowest energy structure of the carbonyl-poorest member of each triad has a shorter Ni=Ni distance of ~ 2.5 Å suggestive of a formal double bond. All of the lowest energy structures have intact $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands and the favored 18-electron configuration for each nickel atom.

These two triads of $\text{CH}_3\text{N}(\text{PF}_2)_2$ nickel carbonyl complexes can be compared with analogous triads of $\text{CH}_3\text{N}(\text{PF}_2)_2$ iron carbonyl complexes having one more CO group per metal atom in order to retain the favored 18-electron configuration of the metal atoms. In this way the $[\text{CH}_3\text{N}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$) and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$) triads are the analogues of the $[\text{CH}_3\text{N}(\text{PF}_2)_2]\text{Fe}_2(\text{CO})_n$ ($n = 8, 7, 6$) and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Fe}_2(\text{CO})_n$ ($n = 6, 5, 4$) triads. The lowest energy structures for the carbonyl-richest and intermediate members of the $\text{CH}_3\text{N}(\text{PF}_2)_2$ iron carbonyl triads have the same patterns as those for the corresponding nickel carbonyl derivatives, i. e., non-bonding $\text{Fe}\cdots\text{Fe}$ distances for the carbonyl-richest system and formal Fe–Fe single bonds of length ~ 2.7 Å for the intermediate members. However, in the lowest energy structures of the carbonyl-poorest members of the $\text{CH}_3\text{N}(\text{PF}_2)_2$ iron carbonyl triads, phosphorus-nitrogen bond cleavage occurs to give separate CH_3NPF_2 and PF_2 bridging groups which donate a total of six electrons to the central Fe_2 unit. Such structures retain the ~ 2.7 Å Fe–Fe single bond distances of the intermediate members of each $\text{CH}_3\text{N}(\text{PF}_2)_2$ triad, which is sufficient to give each iron atom the favored 18-electron configuration.

The highly basic small bite bidentate ligand $(\text{Me}_2\text{P})_2\text{CH}_2$ was also included in this theoretical study of binuclear nickel carbonyl complexes for comparison with the strong

back-bonding $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand. The preferred types of $(\text{bid})\text{Ni}_2(\text{CO})_n$ structures were found to be similar for both ligands despite the major differences in their basicity and back-bonding. Thus $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_n$ and $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_n$ structures in which cleavage of a ligand P–C bond occurs to form separate bridging Me_2PCH_2 and Me_2P are high-energy structures relative to isomeric structures with intact $(\text{Me}_2\text{P})_2\text{CH}_2$ ligands.

The single experimentally realized compound discussed in this paper is $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$, first reported⁹ as the monomer “ $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}(\text{CO})_2$ ” but shown by Pörschke and co-workers¹² by X-ray crystallography to be the dimer. The experimental structure for $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ is very similar to **PMe-24-1S** with a boat conformation for the NiPCPNiPCP eight-membered ring. This structure lies less than ~ 0.6 kcal/mol in energy below the similar higher energy structure **PMe-24-2S** $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_4$ with a chair conformation for the eight-membered ring.

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Supporting Information Available. Tables S1 to S4: The $\nu(\text{CO})$ vibrational frequencies (cm^{-1}) for the $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$), $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), and $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$) singlet structures at the M06-L/TZP level. Tables S5 to S8: Infrared active $\nu(\text{CO})$ vibrational frequencies (cm^{-1}) predicted for the singlet and triplet structures of $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$), $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), and $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$) singlet and triplet structures at BP86/DZP and B3LYP/DZP levels. Tables S9 to S20: Total energies (E , in hartree), relative energies (ΔE , in kcal/mol), numbers of imaginary vibrational frequencies (N_{img}) at the M06-L/TZP level for the singlet structures of $[\text{MeN}(\text{PF}_2)_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), $[\text{MeN}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$), $[(\text{Me}_2\text{P})_2\text{CH}_2]\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$), and $[(\text{Me}_2\text{P})_2\text{CH}_2]_2\text{Ni}_2(\text{CO})_n$ ($n = 4, 3, 2$). Tables S21 to S33: Total energies (E , in hartree), relative energies (ΔE , in kcal/mol), spin square values $\langle S^2 \rangle$, number of imaginary vibrational frequencies (N_{img}) at the B3LYP/DZP and BP86/DZP levels of the theory for the singlet and triplet structures of

[MeN(PF₂)₂]₂Ni₂(CO)_n (*n* = 6, 5, 4), [MeN(PF₂)₂]₂Ni₂(CO)_n (*n* = 4, 3, 2), [(Me₂P)₂CH₂]₂Ni₂(CO)_n (*n* = 6, 5, 4), and [(Me₂P)₂CH₂]₂Ni₂(CO)_n (*n* = 4, 3, 2). Figure S1: The one triplet structure found for [(Me₂P)₂CH₂]₂Ni₂(CO)₄ at the M06-L/TZP level of theory. Figures S2 to S13: Optimized singlet and triplet structures for [MeN(PF₂)₂]₂Ni₂(CO)_n (*n* = 6, 5, 4), [MeN(PF₂)₂]₂Ni₂(CO)_n (*n* = 4, 3, 2), [(Me₂P)₂CH₂]₂Ni₂(CO)_n (*n* = 6, 5, 4), and [(Me₂P)₂CH₂]₂Ni₂(CO)_n (*n* = 4, 3, 2) by the B3LYP and BP86 methods. Table S34: Theoretical Cartesian coordinates (in Å) for the singlet structures at the M06-L/TZP level. Table S35: Theoretical cartesian coordinates (in Å) for the singlet and triplet structures at BP86/DZP level; Complete Gaussian 09 reference (Reference 26)

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Graphical Abstract

**Binuclear Nickel Carbonyls with
the Small Bite Chelating
Diphosphine Ligands
Methylaminobis(difluorophosphine)
and
Methylenebis(dimethylphosphine):
Formation of Ni=Ni Double Bonds
in Preference to Ligand Cleavage**

The structures and thermochemistry of $(\text{bid})\text{Ni}_2(\text{CO})_n$ ($n = 6, 5, 4$) and $(\text{bid})_2\text{Ni}(\text{CO})_n$ ($n = 4, 3, 2$) ($\text{bid} = \text{CH}_3\text{N}(\text{PF}_2)_2$ and $(\text{Me}_2\text{P})_2\text{CH}_2$) have been investigated using density functional theory. Species with formal Ni=Ni double bonds are energetically favored over isomeric species with cleaved ligands in contrast to related iron carbonyl complexes.

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