

## Synthesis and Structural Characterization of Bimetallic Iron–Nickel Carbido Cluster Complexes

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In acetonitrile solvent,  $\text{Fe}_5(\text{CO})_{15}(\mu_5\text{-C})$ , **1**, reacts with  $\text{Ni}(\text{COD})_2$  at room temperature to afford the iron–nickel complex  $\text{Fe}_5\text{Ni}(\text{NCMe})(\text{CO})_{15}(\mu_6\text{-C})$ , **3**. The acetonitrile ligand in **3** can be replaced by CO and  $\text{NH}_3$  to yield  $\text{Fe}_5\text{Ni}(\text{CO})_{16}(\mu_6\text{-C})$ , **4**, and  $\text{Fe}_5\text{Ni}(\text{NH}_3)(\text{CO})_{15}(\mu_6\text{-C})$ , **6**, respectively. When refluxed in acetonitrile solvent, compound **3** loses a vertex to form the square pyramidal  $\text{Fe}_4\text{Ni}$  complex  $\text{Fe}_4\text{Ni}(\text{NCMe})_2(\text{CO})_{12}(\mu_5\text{-C})$ , **7**. Compound **7** readily converts to  $\text{Fe}_4\text{Ni}(\text{NCMe})(\text{CO})_{13}(\mu_5\text{-C})$ , **8**, by losing one of its acetonitrile ligands. Addition of acetonitrile to **8** gives compound **7**. When heated to 110 °C under an atmosphere of CO, both compounds **7** and **8** furnish the octahedral  $\text{Fe}_4\text{Ni}_2$  complex  $\text{Fe}_4\text{Ni}_2(\text{CO})_{15}(\mu_6\text{-C})$ , **9**. All six compounds were structurally characterized by single-crystal X-ray diffraction analyses.

### Introduction

A recent and now widely used approach for preparing bimetallic nanoparticle catalysts is from bimetallic molecular cluster complexes.<sup>1</sup> Bimetallic nanoparticle catalysts have been shown to exhibit superior catalytic properties,<sup>2</sup> because of the presence of different metals such that one metal performs a certain role in a catalytic cycle and the other performs another function.<sup>3</sup> Supported bimetallic Fe–Ni particles have also been of interest in heterogeneous catalysis.<sup>4</sup>

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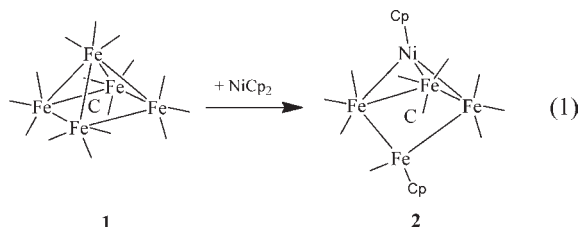
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For example, it has been shown that it is possible to increase the activity of Ni based catalysts by alloying them with Fe for the hydrogenation of CO to methane, an important reaction that is used in several industrial processes.<sup>4a</sup>

Recently, mixed-metal nitride clusters of Fe–Ni were obtained using the nitrido anion  $[\text{Fe}_4(\text{CO})_{12}(\text{N})]^-$ .<sup>5</sup> Iron carbide carbonyl cluster complexes, especially  $\text{Fe}_5(\text{CO})_{15}(\mu_5\text{-C})$ , **1**, have always been of considerable interest to metal cluster researchers,<sup>6</sup> and in a previous study we reported that **1** reacts with  $\text{NiCp}_2$  via metal–metal exchange and metal cluster rearrangement processes, to yield the bimetallic Ni–Fe carbide containing cluster complex,  $\text{NiFe}_4(\text{Cp})_2(\text{CO})_{10}(\mu_5\text{-C})$ , **2**, see eq 1.<sup>7</sup>



Herein we report on the reaction of **1** with bis(1,5-cyclooctadiene)nickel(0),  $\text{Ni}(\text{COD})_2$ , in acetonitrile solvent to afford the nickel–iron complex  $\text{Fe}_5\text{Ni}(\text{NCMe})(\text{CO})_{15}(\mu_6\text{-C})$ ,

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Table 1. Crystallographic Data for Compounds 3, 4, and 6

	3	4	6
empirical formula	NiFe <sub>5</sub> O <sub>15</sub> NC <sub>18</sub> H <sub>3</sub>	NiFe <sub>5</sub> O <sub>16</sub> C <sub>17</sub>	NiFe <sub>5</sub> O <sub>15</sub> NC <sub>16</sub> H <sub>3</sub>
formula weight	811.17	798.13	787.15
crystal system	orthorhombic	triclinic	orthorhombic
lattice parameters			
<i>a</i> (Å)	17.3484(6)	9.0290(5)	20.8118(11)
<i>b</i> (Å)	9.2771(3)	9.5672(5)	10.3605(5)
<i>c</i> (Å)	15.7591(5)	15.5994(8)	10.7284(6)
$\alpha$ (deg)	90	85.381(1)	90
$\beta$ (deg)	90	83.673(1)	90
$\gamma$ (deg)	90	63.223(1)	90
<i>V</i> (Å <sup>3</sup> )	2536.31(14)	1194.96(11)	2313.3(2)
space group	<i>Pna</i> 2 <sub>1</sub> (# 33)	<i>P</i> $\bar{1}$ (# 2)	<i>Pna</i> 2 <sub>1</sub> (# 33)
<i>Z</i> value	4	2	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	2.124	2.218	2.260
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	3.586	3.805	3.927
temperature (K)	296	296	296
2 $\Theta_{\text{max}}$ (deg)	56.00	58.00	51.98
no. obs. ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	5301	4679	4301
no. parameters	363	352	344
goodness of fit	1.066	1.038	1.004
max. shift in cycle	0.001	0.000	0.001
residuals <sup>a</sup> :R1; wR2	0.0304; 0.0670	0.0380; 0.1091	0.0333; 0.0786
absorption correction	multiscan	multiscan	multiscan
max/min	0.7461/0.5169	0.9278/0.4882	0.6948/0.5072
largest peak in final diff. map (e <sup>-</sup> /Å <sup>3</sup> )	0.593	0.617	0.681

$$^a R = [\sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{\text{hkl}} |F_{\text{obs}}|] / [\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}, w = 1/\sigma^2(F_{\text{obs}}); \text{GOF} = [\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}.$$

3. In addition, some chemistry with **3** was also studied which gave new Fe–Ni carbide clusters with varying Fe–Ni ratios.

### Experimental Section

**General Data.** Unless indicated otherwise, all reactions were performed under an atmosphere of Argon. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrophotometer. <sup>1</sup>H NMR were recorded on a Bruker 400 spectrometer operating at 399.993 MHz. Elemental analyses were performed by Columbia Analytical Services (Tucson, AZ). Mass spectrometric measurements performed by direct-exposure probe using electron impact ionization (EI) were made on a VG 70S instrument and electrospray mass spectrometric measurements were obtained on a MicroMass Q-ToF spectrometer at the University of South Carolina, Columbia, SC. Bis(1,5-cyclooctadiene)nickel(0), Ni(COD)<sub>2</sub>, was purchased from Strem Chemicals, used without further purification, and stored and handled in a drybox. NH<sub>3</sub> was purchase form Matheson Tri-Gas as pure ammonia gas. Fe<sub>5</sub>(CO)<sub>15</sub>( $\mu_5$ -C), **1**, was prepared according to the previously published procedure.<sup>6b</sup> Product separations were performed by TLC in air on Analtech silica gel GF 250 or 500  $\mu\text{m}$  glass plates. Silica gel (60–200  $\mu\text{m}$ , 70–230 mesh) used for chromatographic separations was purchased from Silicycle. Florisil (F100–500, 60–100 mesh) used for product purifications was purchased from Fisher Scientific.

**Preparation of Fe<sub>5</sub>Ni(NCMe)(CO)<sub>15</sub>( $\mu_6$ -C), **3**.** A 100 mg (0.14 mmol) amount of **1** and a 58 mg (0.21 mmol) amount of Ni(COD)<sub>2</sub> were dissolved in 20 mL of acetonitrile in a 50 mL 3-neck round-bottom flask. The solution was stirred at room temperature for 10 min at which time IR showed complete consumption of the starting material, **1**. The solvent was removed in vacuo, and the residue was washed with hexane several times to remove any green side product of Fe<sub>3</sub>(CO)<sub>12</sub>. The purple colored residue was dissolved in methylene chloride and filtered through florisil to give 61.8 mg of **3** (54% yield). Spectral data for **3**: IR  $\nu_{\text{CO}}$  (cm<sup>-1</sup> in hexane): 2078(w), 2064 (w),

2032 (s), 2007 (v); <sup>1</sup>H NMR (CDCl<sub>3</sub> in ppm):  $\delta$  = 2.59 (s, 3 H, CH<sub>3</sub>). EI/MS: *m/z* 769 (M<sup>+</sup>), 657(M<sup>+</sup> – 4CO), 601 (M<sup>+</sup> – 2CO), 545 (M<sup>+</sup> – 2CO), 461 (M<sup>+</sup> – 3CO). The isotope distribution pattern is consistent with the presence of one nickel atom and five iron atoms.

**Preparation of Fe<sub>5</sub>Ni(CO)<sub>16</sub>( $\mu_6$ -C), **4**.** A 100 mg (0.12 mmol) amount of **3** was dissolved in 20 mL of toluene in a 50 mL 3-neck round-bottom flask equipped with a reflux condenser. Carbon monoxide gas (1 atm) was bubbled through the solution, and the solution was refluxed at 110 °C with stirring for 1 h. The solvent was removed in vacuo, and the product was separated on a silica gel column to yield a purple band of **4** (60 mg, 61% yield) eluted by pure hexane. The compound was identified by IR in the  $\nu_{\text{CO}}$  region.<sup>6b</sup> Spectral data for **4**: IR  $\nu_{\text{CO}}$  (cm<sup>-1</sup> in hexane): 2100(w), 2064 (m), 2042 (s), 2039 (s), 2015 (m), 1883(vw, br).

**Preparation of Fe<sub>5</sub>Ni(NH<sub>3</sub>)(CO)<sub>15</sub>( $\mu_6$ -C), **6**.** **Conversion of 3 to 6.** A 10.3 mg (0.013 mmol) amount of **3** was dissolved in 8 mL of methylene chloride in a 50 mL 3-neck round-bottom flask. Ammonia gas (1 atm) was bubbled through the solution, and the solution was stirred at 0 °C (maintained in an ice bath) for about 15 min at which time TLC showed complete consumption of the starting material. The solvent was removed in vacuo, and the product was redissolved in methylene chloride and filtered through florisil to give 8.1 mg of **6** (82% yield). Spectral data for **6**: IR  $\nu_{\text{CO}}$  (cm<sup>-1</sup> in hexane): 2074(w), 2050 (w), 2033 (s), 2023 (m, sh), 2006 (w); <sup>1</sup>H NMR (CDCl<sub>3</sub> in ppm):  $\delta$  = 3.30 (s, 3 H, NH<sub>3</sub>). EI/MS: *m/z* 786 (M<sup>+</sup>), 730(M<sup>+</sup> – 2CO), 674 (M<sup>+</sup> – 2CO), 646 (M<sup>+</sup> – CO), 618 (M<sup>+</sup> – CO), 590(M<sup>+</sup> – CO), 562 (M<sup>+</sup> – CO). The isotope distribution pattern is consistent with the presence of one nickel atom and five iron atoms. Elemental Anal. Calcd: C, 24.41; H, 0.38; N, 1.77% Found: C, 24.36; H, 0.64; N, 1.72%.

**Conversion of 4 to 6.** A 15 mg (0.018 mmol) amount of **4** was dissolved in 20 mL of methylene chloride in a 50 mL 3-neck round-bottom flask. Then ammonia gas (1 atm) was bubbled through the solution, and the solution was stirred at 0 °C (maintained in an ice bath) for 10 min at which time IR showed complete consumption of the starting material. The solvent was removed in vacuo, and the product was redissolved in methylene chloride and filtered through florisil to give 11.4 mg of **6** (77% yield).

**Table 2.** Crystallographic Data for Compounds **7**, **8**, and **9**.

	<b>7</b>	<b>8</b>	<b>9</b>
empirical formula	NiFe <sub>4</sub> O <sub>12</sub> N <sub>2</sub> C <sub>17</sub> H <sub>6</sub>	NiFe <sub>4</sub> O <sub>13</sub> NC <sub>16</sub> H <sub>3</sub>	Ni <sub>2</sub> Fe <sub>4</sub> O <sub>15</sub> C <sub>16</sub>
formula weight	712.35	699.30	772.98
crystal system	monoclinic	monoclinic	monoclinic
lattice parameters			
<i>a</i> (Å)	9.6040(3)	9.5977(5)	10.5011(7)
<i>b</i> (Å)	15.3859(6)	15.5438(8)	10.9743(8)
<i>c</i> (Å)	16.0687(6)	14.7267(8)	20.5591(14)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	106.2706(5)	91.1432(9)	90.551(1)
$\gamma$ (deg)	90	90	90
<i>V</i> (Å <sup>3</sup> )	2279.31(14)	2196.6(2)	2369.2(3)
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (# 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (# 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (# 14)
<i>Z</i> value	4	4	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	2.076	2.115	2.167
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	3.362	3.489	4.013
temperature (K)	100	100	296
2 $\Theta_{\text{max}}$ (deg)	62.00	63.00	52.90
no. obs. ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	6821	5286	3226
no. parameters	327	317	334
goodness of fit	1.107	1.008	1.056
max. shift in cycle	0.004	0.001	0.000
residuals <sup>a</sup> :R1; wR2	0.0197; 0.0485	0.0364; 0.0755	0.0499; 0.1158
absorption correction	multiscan	multiscan	multiscan
max/min	0.8773/ 0.3774	0.9659/0.4417	0.9240/0.5007
largest peak in final diff. map (e <sup>-</sup> /Å <sup>3</sup> )	0.443	0.951	1.563

$$^a R = \frac{\sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|)}{\sum_{\text{hkl}} F_{\text{obs}}}; R_w = \left[ \frac{\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum_{\text{hkl}} w F_{\text{obs}}^2} \right]^{1/2}, w = 1/\sigma^2(F_{\text{obs}}); \text{GOF} = \left[ \frac{\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{(n_{\text{data}} - n_{\text{vari}})} \right]^{1/2}.$$

Note: In both cases the reactions do proceed at room temperature; however, owing to some decomposition, the yields at 0 °C are better.

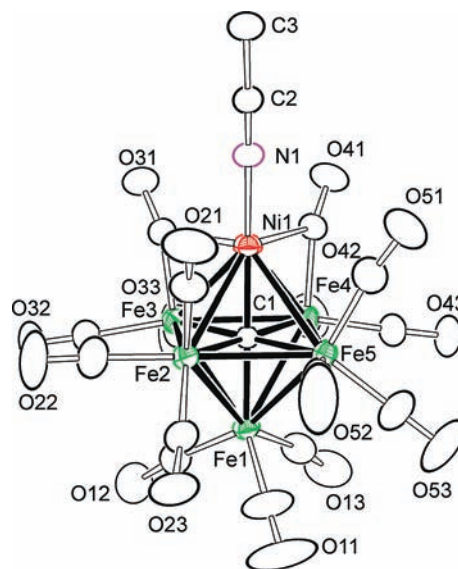
**Preparation of Fe<sub>4</sub>Ni(NCMe)<sub>2</sub>(CO)<sub>12</sub>( $\mu_5$ -C), **7**.** A 21 mg (0.026 mmol) amount of **3** was dissolved in 15 mL of acetonitrile in a 50 mL 3-neck round-bottom flask equipped with a reflux condenser. The solution was then heated to reflux with stirring for 10 min at which time IR showed complete consumption of the starting material. The solvent was removed in vacuo, and the product was dissolved in acetonitrile and filtered through silica gel to give 12.6 mg of **7** (68% yield). Spectral data for **7**: IR  $\nu_{\text{CO}}$  (cm<sup>-1</sup> in methylene chloride): 2087(w), 2066 (w), 2054 (m), 2030 (s), 2016 (vs), 1941 (w,br); <sup>1</sup>H NMR (CDCl<sub>3</sub> in ppm):  $\delta$  = 2.45 (s, 6H, CH<sub>3</sub>). Elemental Anal. Calcd: C, 28.66; H, 0.85; N, 3.93% Found: C, 28.51; H, 0.88; N, 3.93%.

Note: Compound **7** slowly decomposes when dissolved in solvents other than acetonitrile.

**Preparation of Fe<sub>4</sub>Ni(NCMe)(CO)<sub>13</sub>( $\mu_5$ -C), **8**.** **Photolysis of **3** to **8**.** A 15 mg (0.018 mmol) amount of **3** was dissolved in 10 mL of benzene in a 50 mL 3-neck round-bottom flask equipped with a reflux condenser. The solution was irradiated using a high-pressure mercury UV lamp (American Ultraviolet Co.) at the 125 wpi setting for 25 min at which time IR showed complete consumption of the starting material. The solvent was removed in vacuo, and the product was dissolved in methylene chloride and filtered through silica gel to give 8.2 mg of **8** (63% yield). Spectral data for **8**: IR  $\nu_{\text{CO}}$  (cm<sup>-1</sup> in hexane): 2111(w), 2075 (w), 2065 (w), 2054 (m), 2043 (w), 2033 (s), 2017 (m), 2010 (m), 1942 (w); <sup>1</sup>H NMR (CDCl<sub>3</sub> in ppm):  $\delta$  = 2.31 (s, 3H, CH<sub>3</sub>). ES<sup>+</sup>/MS for M<sup>+</sup>, 699. The isotope distribution pattern is consistent with the presence of one nickel atom and four iron atoms.

**Conversion of **7** to **8**.** A 31.9 mg (0.045 mmol) amount of **7** was dissolved in 10 mL of methylene chloride in a 50 mL 3-neck round-bottom flask. Then the solution was stirred at room temperature for 15 min at which time IR showed complete consumption of the starting material. The solvent was removed in vacuo, and the product was redissolved in methylene chloride and filtered through silica gel to give 21.5 mg of **8** (68% yield).

**Conversion of **8** to **7**.** A 21.5 mg (0.031 mmol) amount of **8** was dissolved in 10 mL of acetonitrile in a 50 mL 3-neck

**Figure 1.** ORTEP showing the molecular structure of Fe<sub>5</sub>Ni(NCMe)(CO)<sub>15</sub>( $\mu_6$ -C), **3** at 40% thermal ellipsoid probability.

round-bottom flask. Then the solution was stirred at room temperature for 15 min at which time IR showed complete consumption of the starting material. The reaction solution was filtered through silica gel to give 21.2 mg of **7** (97% yield).

**Preparation of Fe<sub>4</sub>Ni<sub>2</sub>(CO)<sub>15</sub>( $\mu_6$ -C), **9**.** **Conversion of **7** to **9**.** A 21.2 mg (0.029 mmol) amount of **7** was dissolved in 15 mL of toluene in a 50 mL 3-neck round-bottom flask equipped with a reflux condenser. Then carbon monoxide gas (1 atm) was bubbled through the solution and the solution was then heated to reflux with stirring for 30 min at which time IR showed complete consumption of the starting material. The solvent was removed in vacuo, and the product was dissolved in methylene chloride and filtered through silica gel to give 10.4 mg of **9** (45% yield). Spectral data for **9**: IR  $\nu_{\text{CO}}$  (cm<sup>-1</sup> in hexane): 2111(w),

**Table 3.** Selected Intramolecular Distances and Angles for Compounds **3** and **6**<sup>a</sup>

atom	atom	distance (Å)		atom	atom	distance (Å)	
		<b>3</b>	<b>6</b>			<b>3</b>	<b>6</b>
Ni(1)	Fe(2)	2.7149(7)	2.7666(9)	Fe(1)	Fe(4)	2.6880(7)	2.7055(9)
Ni(1)	Fe(3)	2.5653(7)	2.5361(8)	Fe(1)	Fe(5)	2.6875(7)	2.6847(8)
Ni(1)	Fe(4)	2.5424(7)	2.5365(8)	Fe(2)	Fe(3)	2.7214(7)	2.6655(8)
Ni(1)	Fe(5)	2.7233(7)	2.6911(8)	Fe(2)	Fe(5)	2.6671(7)	2.6717(8)
Fe(1)	Fe(2)	2.7009(7)	2.6450(8)	Fe(3)	Fe(4)	2.7163(7)	2.7440(8)
Fe(1)	Fe(3)	2.6804(7)	2.7511(9)	Fe(4)	Fe(5)	2.6817(7)	2.7070(9)

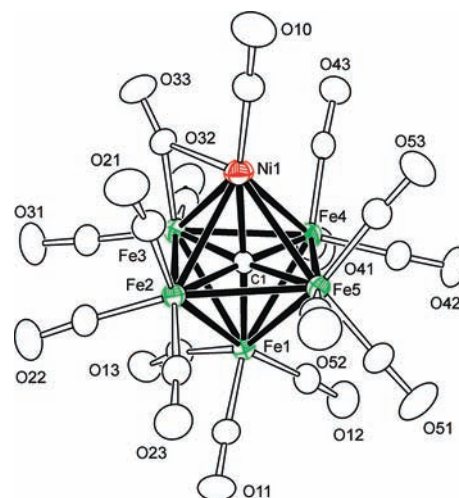
atom	atom	atom	angle (deg)	
			<b>3</b>	<b>6</b>
Fe(4)	Ni(1)	Fe(3)	64.25(2)	65.50(2)
Fe(4)	Ni(1)	Fe(2)	92.79(2)	91.84(3)
Fe(3)	Ni(1)	Fe(2)	61.972(19)	60.17(2)
Fe(4)	Ni(1)	Fe(5)	61.117(19)	62.29(2)
Fe(3)	Ni(1)	Fe(5)	92.38(2)	93.63(3)
Fe(2)	Ni(1)	Fe(5)	58.739(19)	58.60(2)
Ni(1)	Fe(2)	Fe(3)	56.314(18)	55.63(2)
Ni(1)	Fe(3)	Fe(4)	57.464(18)	57.26(2)
Ni(1)	Fe(3)	Fe(2)	61.714(19)	64.21(2)
Fe(4)	Fe(3)	Fe(2)	88.92(2)	89.63(2)
Ni(1)	Fe(4)	Fe(5)	62.771(19)	61.66(2)
Ni(1)	Fe(4)	Fe(3)	58.28(2)	57.24(2)
Fe(2)	Fe(5)	Ni(1)	60.473(19)	62.11(2)
Fe(4)	Fe(5)	Ni(1)	56.112(18)	56.05(2)

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

2076 (m), 2065 (m), 2054 (w), 2043 (s), 2033 (m), 2028 (m), 2022 (m), 1963 (w). EI/MS:  $m/z$  772 ( $M^+$ ), 744 ( $M^+ - CO$ ), 716 ( $M^+ - CO$ ). The isotope distribution pattern is consistent with the presence of two nickel atoms and four iron atoms.

**Conversion of **8** to **9**.** A 21.5 mg (0.031 mmol) amount of **8** was dissolved in 15 mL of toluene in a 50 mL 3-neck round-bottom flask equipped with a reflux condenser. Then carbon monoxide gas (1 atm) was bubbled through the solution, and the solution was then heated to reflux with stirring for 30 min at which time IR showed complete consumption of the starting material. The solvent was removed in vacuo, and the product was dissolved in methylene chloride and filtered through silica gel to give 10.4 mg of **9** (44% yield).

**Crystallographic Analysis.** Single crystals of **3**, **4**, **6**, **8**, and **9** suitable for diffraction analysis were all grown by slow evaporation of solvent from solutions in hexane/methylene chloride solvent mixture at  $-20$  °C. Single crystals of **7** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution of hexane/methylene chloride/acetonitrile solvent mixture at  $-20$  °C. The data crystals for **3**, **4**, **6**, and **9** were glued onto the end of a thin glass fiber. Data crystals for **7** and **8** were mounted onto the end of a thin glass fiber using Paratone-N. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å).<sup>8</sup> The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.<sup>8</sup> Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on  $F^2$ , by using the SHELXTL software package.<sup>9</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically



**Figure 2.** ORTEP showing the molecular structure of  $Fe_5Ni(CO)_{16}$  ( $\mu_6-C$ ), **4** at 40% thermal ellipsoid probability.

idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Tables 1 and 2.

Compounds **3** and **6** crystallized in the orthorhombic crystal system. The systematic absences in the intensity data were consistent with either of the space groups  $Pnma$  or  $Pna2_1$ . The structure could only be solved in the latter space group. Compound **4** crystallized in the triclinic crystal system. The space group  $P\bar{1}$  was assumed and confirmed by the successful solution and refinement of the structure. Compounds **7**, **8**, and **9** crystallized in the monoclinic crystal system. For compounds **7** and **9** the systematic absences in the intensity data were consistent with the unique space group  $P2_1/c$  and for compound **8** the systematic absences in the intensity data were consistent with the unique space group  $P2_1/n$ .

(8) Apex2 Version 2.2-0 and SAINT+ Version 7.46A; Bruker Analytical X-ray System, Inc.: Madison, WI, 2007.

(9) Sheldrick, G. M. SHELXTL, Version 6.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.

**Table 4.** Selected Intramolecular Distances and Angles for Compound 4<sup>a</sup>

atom	atom	distance (Å)	atom	atom	distance (Å)
Ni(1)	Fe(2)	2.6613(7)	Fe(1)	Fe(4)	2.6415(7)
Ni(1)	Fe(3)	2.5095(7)	Fe(1)	Fe(5)	2.7354(7)
Ni(1)	Fe(4)	2.6957(8)	Fe(2)	Fe(3)	2.7237(7)
Ni(1)	Fe(5)	2.6705(7)	Fe(2)	Fe(5)	2.6910(7)
Fe(1)	Fe(2)	2.6615(7)	Fe(3)	Fe(4)	2.6957(7)
Fe(1)	Fe(3)	2.7194(7)	Fe(4)	Fe(5)	2.6588(7)

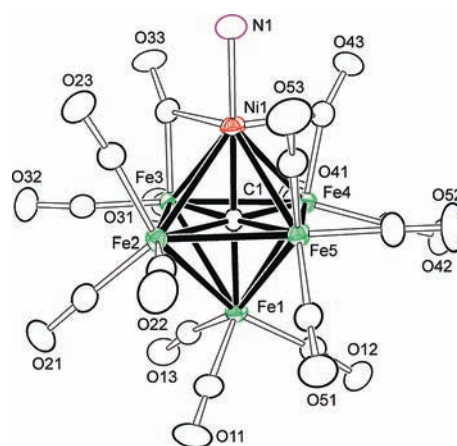
atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Fe(3)	Ni(1)	Fe(2)	63.49(2)	Ni(1)	Fe(3)	Fe(4)	62.26(2)
Fe(3)	Ni(1)	Fe(5)	94.17(2)	Ni(1)	Fe(3)	Fe(2)	60.97(2)
Fe(2)	Ni(1)	Fe(5)	60.623(19)	Fe(4)	Fe(3)	Fe(2)	89.41(2)
Fe(3)	Ni(1)	Fe(4)	62.26(2)	Fe(5)	Fe(4)	Fe(3)	90.27(2)
Fe(2)	Ni(1)	Fe(4)	90.74(2)	Fe(5)	Fe(4)	Ni(1)	59.827(19)
Fe(5)	Ni(1)	Fe(4)	59.400(19)	Fe(3)	Fe(4)	Ni(1)	55.480(19)
Ni(1)	Fe(2)	Fe(5)	59.857(19)	Fe(4)	Fe(5)	Ni(1)	60.77(2)
Ni(1)	Fe(2)	Fe(3)	55.538(19)	Fe(4)	Fe(5)	Fe(2)	90.89(2)
Fe(5)	Fe(2)	Fe(3)	89.00(2)	Ni(1)	Fe(5)	Fe(2)	59.521(19)

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

## Results and Discussion

The reaction of  $\text{Fe}_5(\text{CO})_{15}(\mu_5\text{-C})$ , **1**, with  $\text{Ni}(\text{COD})_2$  in acetonitrile solvent at room temperature afforded the new bimetallic Fe–Ni cluster complex  $\text{Fe}_5\text{Ni}(\text{NCMe})(\text{CO})_{15}(\mu_6\text{-C})$ , **3**, in 54% yield. Compound **3** was characterized by a combination of IR,  $^1\text{H}$  NMR, mass spectrometry, and single crystal X-ray diffraction analyses. An Oak Ridge thermal ellipsoid plot (ORTEP) showing the molecular structure of **3** is shown in Figure 1. Selected bond distances and angles are listed in Table 3. Compound **3** consists of an octahedral cluster of five iron atoms and one nickel atom with the carbide ligand encapsulated in the center of the  $\text{Fe}_5\text{Ni}$  octahedron. The Ni–Carbide distance of 1.831(3) Å, is not significantly different from the Fe–Carbide distances, range 1.888(3)–1.916(3) Å. Also the Fe–Carbide distances are similar to the Fe–Carbide distances in **1**, range 1.87(3)–1.96(3) Å, and in the hexanuclear iron carbide anionic cluster complex  $[\text{PPN}]_2[\text{Fe}_6(\text{CO})_{15}(\text{SO}_2)(\mu_6\text{-C})]$ ,<sup>10</sup> range 1.870(10)–1.915(7) Å. There is a terminal acetonitrile ligand from the reaction solvent that is coordinated to the Ni atom. There are two bridging CO ligands, and these bridge the Ni(1)–Fe(3) bond (2.5653(7) Å), and the Ni(1)–Fe(4) bond (2.5424(7) Å) and these two metal–metal bonds are shorter than all the other metal–metal bonds in the octahedral framework, range 2.6671(7)–2.7214(7) Å. Compound **3** contains 86 cluster valence electrons which is in accord to conventional electron counting theories if all six transition metal atoms formally have an 18-electron configuration.<sup>11</sup>

When solutions of **3** were exposed to carbon monoxide gas, compound **3** reacts with CO at 110 °C to furnish the binary carbonyl cluster complex  $\text{Fe}_5\text{Ni}(\text{CO})_{16}(\mu_6\text{-C})$ , **4**, in 61% yield. Compound **4** was prepared a number of years ago by Muetterties et al.,<sup>6b</sup> and its structure was formulated accurately based on IR, mass spectrometry, and elemental analyses. We have now obtained a crystal structure for compound **4** which is shown in Figure 2. Selected bond distances and angles are listed in Table 4. As can be seen in



**Figure 3.** ORTEP showing the molecular structure of  $\text{Fe}_5\text{Ni}(\text{NH}_3)(\text{CO})_{15}(\mu_6\text{-C})$ , **6** at 40% thermal ellipsoid probability.

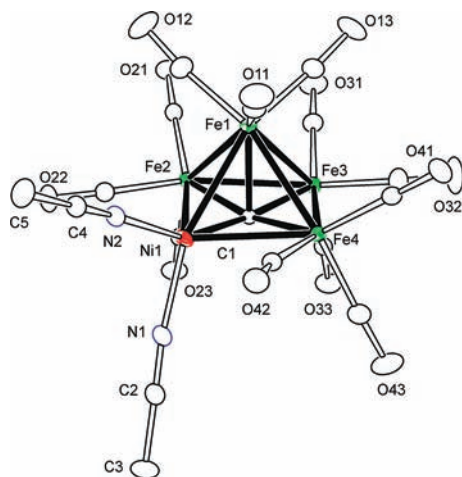
Figure 2 the structure is very similar to compound **3** where the acetonitrile ligand on the Ni atom has been replaced by a carbonyl group. Compound **4** is isostructural to the known platinum–ruthenium mixed-metal cluster complex  $\text{PtRu}_5(\text{CO})_{16}(\mu_6\text{-C})$ , **5**,<sup>12</sup> that was prepared previously by Adams and Wu. Just like in compound **5**, one of the metal–metal bonds has a bridging carbonyl group, Ni(1)–Fe(3) = 2.5095(7) Å, which is considerably shorter than all the other metal–metal bonds in **4**. Compound **4** can be prepared by the reaction of the dianion  $[\text{NET}_4]_2\text{-}[\text{Fe}_5(\text{CO})_{14}(\mu_5\text{-C})]$  with  $\text{Ni}(\text{COD})_2$  to yield  $[\text{Fe}_5\text{Ni}(\text{CO})_{14}(\text{COD})(\mu_5\text{-C})]^{2-}$ . Substitution of the COD group with CO followed by oxidation with  $\text{Fe}^{3+}$  then gives the desired compound **4**.<sup>6b</sup> The yield of this reaction is not reported, and in our hands we were able to obtain a maximum yield of 15% following this previously reported procedure. Our preparation is a more convenient and perhaps “better” yielding procedure for the synthesis of compound **4**.

Both compounds **3** and **4** react with ammonia gas at 0 °C to give the compound  $\text{Fe}_5\text{Ni}(\text{NH}_3)(\text{CO})_{15}(\mu_6\text{-C})$ , **6**, in 82% and 77% yields, respectively. The solid state structure of **6** is shown in Figure 3, and selected bond distances and angles are listed in Table 3. The structure of compound **6** is similar to

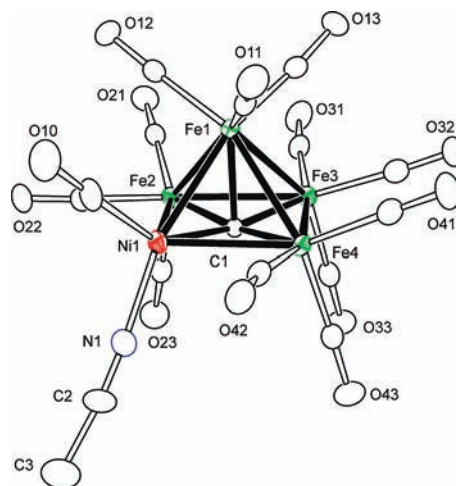
(10) Bogdan, P. L.; Sabat, M.; Sunshine, S. A.; Woodcock, C.; Shriver, D. F. *Inorg. Chem.* **1988**, *27*, 1904–1910.

(11) (a) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311–319. (b) Mingos, D. M. P. *Introduction to Cluster Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1990; Chapter 2.

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**Figure 4.** ORTEP showing the molecular structure of  $\text{Fe}_4\text{Ni}(\text{NCMe})_2(\text{CO})_{12}(\mu_5\text{-C})$ , **7** at 50% thermal ellipsoid probability.



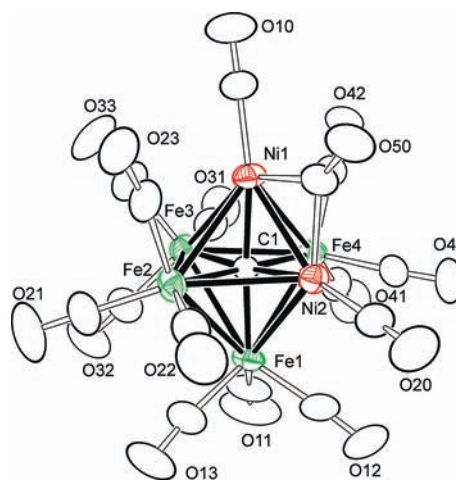
**Figure 5.** ORTEP showing the molecular structure of  $\text{Fe}_4\text{Ni}(\text{NCMe})_2(\text{CO})_{13}(\mu_5\text{-C})$ , **8** at 50% thermal ellipsoid probability.

**Table 5.** Selected Intramolecular Distances and Angles for Compounds **7** and **8**<sup>a</sup>

		distance (Å)		
atom	atom	<b>7</b>	<b>8</b>	
Ni(1)	Fe(1)	2.5612(2)	2.5129(5)	
Ni(1)	Fe(2)	2.6696(2)	2.6467(5)	
Ni(1)	Fe(4)	2.5913(2)	2.6077(5)	
Fe(1)	Fe(2)	2.5802(2)	2.5948(5)	
Fe(1)	Fe(3)	2.6346(2)	2.6144(5)	
Fe(1)	Fe(4)	2.5527(2)	2.5879(5)	
Fe(2)	Fe(3)	2.6265(2)	2.6399(5)	
Fe(3)	Fe(4)	2.6253(2)	2.6323(5)	
		angle (deg)		
atom	atom	atom	<b>7</b>	<b>8</b>
Fe(1)	Ni(1)	Fe(4)	59.394(6)	60.681(14)
Fe(1)	Ni(1)	Fe(2)	59.068(6)	60.319(14)
Fe(4)	Ni(1)	Fe(2)	91.320(7)	90.295(16)
Fe(4)	Fe(1)	Ni(1)	60.890(7)	61.471(14)
Ni(1)	Fe(1)	Fe(2)	62.562(7)	62.395(15)
Fe(4)	Fe(1)	Fe(2)	94.295(8)	91.903(17)
Ni(1)	Fe(1)	Fe(3)	89.704(8)	92.924(17)
Fe(4)	Fe(1)	Fe(3)	60.783(7)	60.790(14)
Fe(2)	Fe(1)	Fe(3)	60.473(7)	60.896(14)
Fe(1)	Fe(2)	Fe(3)	60.789(7)	59.919(14)
Fe(1)	Fe(2)	Ni(1)	58.370(6)	57.286(14)
Fe(3)	Fe(2)	Ni(1)	87.572(8)	89.370(16)
Fe(4)	Fe(3)	Fe(1)	58.067(6)	59.107(14)
Fe(2)	Fe(3)	Fe(1)	58.737(6)	59.184(14)
Fe(4)	Fe(3)	Fe(2)	91.538(8)	89.911(16)
Fe(1)	Fe(4)	Ni(1)	59.716(6)	57.848(13)
Ni(1)	Fe(4)	Fe(3)	89.260(8)	90.381(16)

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

both compounds **3** and **4**; however, there now is an ammonia ligand on the Ni atom. It is interesting to note here that the replacement of the acetonitrile ligand in **3** by an ammonia group and replacement of a carbonyl ligand by an ammonia group is very facile. This is surprising since both CO and NCMe are better coordinating ligands than ammonia as both CO and NCMe are good  $\sigma$  donors as well as good



**Figure 6.** ORTEP showing the molecular structure of  $\text{Fe}_4\text{Ni}_2(\text{CO})_{15}(\mu_6\text{-C})$ , **9** at 40% thermal ellipsoid probability.

$\pi$ -acceptor ligands, whereas an  $\text{NH}_3$  ligand is only capable of  $\sigma$  donation.<sup>13,14</sup>

Thermolysis of compound **3** up to temperatures of 110 °C in solvents other than acetonitrile (benzene and toluene solvent at reflux) decomposed compound **3** to give insoluble, probably metallic particles. However, when compound **3** was refluxed in acetonitrile solvent, the new  $\text{Fe}_4\text{Ni}$  carbido cluster complex  $\text{Fe}_4\text{Ni}(\text{NCMe})_2(\text{CO})_{12}(\mu_5\text{-C})$ , **7**, was obtained in 68% yield. An ORTEP showing the molecular structure of **7** is shown in Figure 4, and selected bond distances and angles are listed in Table 5. The complex consists of a square pyramidal cluster of four iron atoms and one nickel atom with a peripheral or exposed carbido ligand in the center of the base of the square pyramid. The nickel atom in **7** is not in the apical position but occupies one of the basal positions of the square pyramid. The two acetonitrile ligands are terminally coordinated to the nickel atom. The <sup>1</sup>H NMR spectrum for **7** should show two resonances for the methyl groups on

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**Table 6.** Selected Intramolecular Distances and Angles for Compound **9**<sup>a</sup>

atom	atom	distance (Å)	atom	atom	distance (Å)
Ni(1)	Ni(2)	2.4642(11)	Ni(2)	Fe(4)	2.6685(11)
Ni(1)	Fe(2)	2.6686(12)	Fe(1)	Fe(2)	2.6707(12)
Ni(1)	Fe(3)	2.6798(11)	Fe(1)	Fe(3)	2.7188(12)
Ni(1)	Fe(4)	2.6857(11)	Fe(1)	Fe(4)	2.6535(11)
Ni(2)	Fe(1)	2.6874(11)	Fe(2)	Fe(3)	2.6530(12)
Ni(2)	Fe(2)	2.6994(12)	Fe(3)	Fe(4)	2.6505(12)

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
Ni(2)	Ni(1)	Fe(2)	63.31(3)	Fe(4)	Fe(3)	Fe(2)	91.95(4)
Ni(2)	Ni(1)	Fe(3)	92.74(3)	Fe(4)	Fe(3)	Ni(1)	60.51(3)
Fe(2)	Ni(1)	Fe(3)	59.48(3)	Fe(2)	Fe(3)	Ni(1)	60.05(3)
Ni(2)	Ni(1)	Fe(4)	62.24(3)	Fe(3)	Fe(2)	Ni(1)	60.47(3)
Fe(2)	Ni(1)	Fe(4)	90.83(3)	Fe(3)	Fe(2)	Ni(2)	88.24(3)
Fe(3)	Ni(1)	Fe(4)	59.21(3)	Ni(1)	Fe(2)	Ni(2)	54.65(3)
Ni(1)	Ni(2)	Fe(4)	62.95(3)	Fe(4)	Fe(3)	Fe(2)	91.95(4)
Ni(1)	Ni(2)	Fe(2)	62.04(3)	Fe(4)	Fe(3)	Ni(1)	60.51(3)
Fe(4)	Ni(2)	Fe(2)	90.54(4)	Fe(2)	Fe(3)	Ni(1)	60.05(3)
Fe(3)	Fe(2)	Ni(1)	60.47(3)	Fe(3)	Fe(4)	Ni(2)	88.94(3)
Fe(3)	Fe(2)	Ni(2)	88.24(3)	Fe(3)	Fe(4)	Ni(1)	60.29(3)
Ni(1)	Fe(2)	Ni(2)	54.65(3)	Ni(2)	Fe(4)	Ni(1)	54.80(3)

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

each of the NCMe ligands, as the two NCMe ligands are inequivalent. Atom N(1) on one of the NCMe groups has approximate trans coordination to the Ni(1)–Fe(1) bond, N(1)–Ni(1)–Fe(1) = 159.67(3)°, whereas atom N(2) on the other NCMe group is coordinated approximately cis to the same bond, N(2)–Ni(1)–Fe(1) = 103.73(3)°. However, <sup>1</sup>H NMR at room temperature showed a single resonance indicating that the two NCMe groups are rapidly exchanging on the NMR time scale, via most probably a mechanism involving a polytopal rearrangement process on the nickel atom. It is well-known that CO, CNR, NCR, and phosphine ligands undergo rapid exchange process.<sup>15</sup>

Photolysis of compound **3** at room temperature in benzene solvent, however, afforded another Fe<sub>4</sub>Ni carbido cluster complex Fe<sub>4</sub>Ni(NCMe)(CO)<sub>13</sub>(μ<sub>5</sub>-C), **8**, in 63% yield. The molecular structure of **8** is shown in Figure 5, and selected bond distances and angles are listed in Table 5. The structure of **8** is very similar to that of **7**, where in place of one of the NCMe ligands on the nickel atom in **7**, there is a terminal carbonyl ligand. All the bond lengths in **8** are very similar to those found in **7**, see Table 5. When compound **8** is dissolved in acetonitrile solvent at room temperature, substitution of a CO ligand with acetonitrile occurs to give compound **7** in 97% yield. Interestingly when CO was added at room temperature to **7** to obtain **8**, the new compound Fe<sub>4</sub>Ni<sub>2</sub>(CO)<sub>15</sub>(μ<sub>6</sub>-C), **9**, was obtained. Compound **7** when dissolved in solvents other than acetonitrile, such as methylene chloride, slowly “decomposes” to **8** in 68% yield. Compound **9** as shown in Figure 6 (selected bond distances and angles are listed in Table 6) contains an octahedral cluster composed of four iron atoms and two nickel atoms. The two nickel atoms

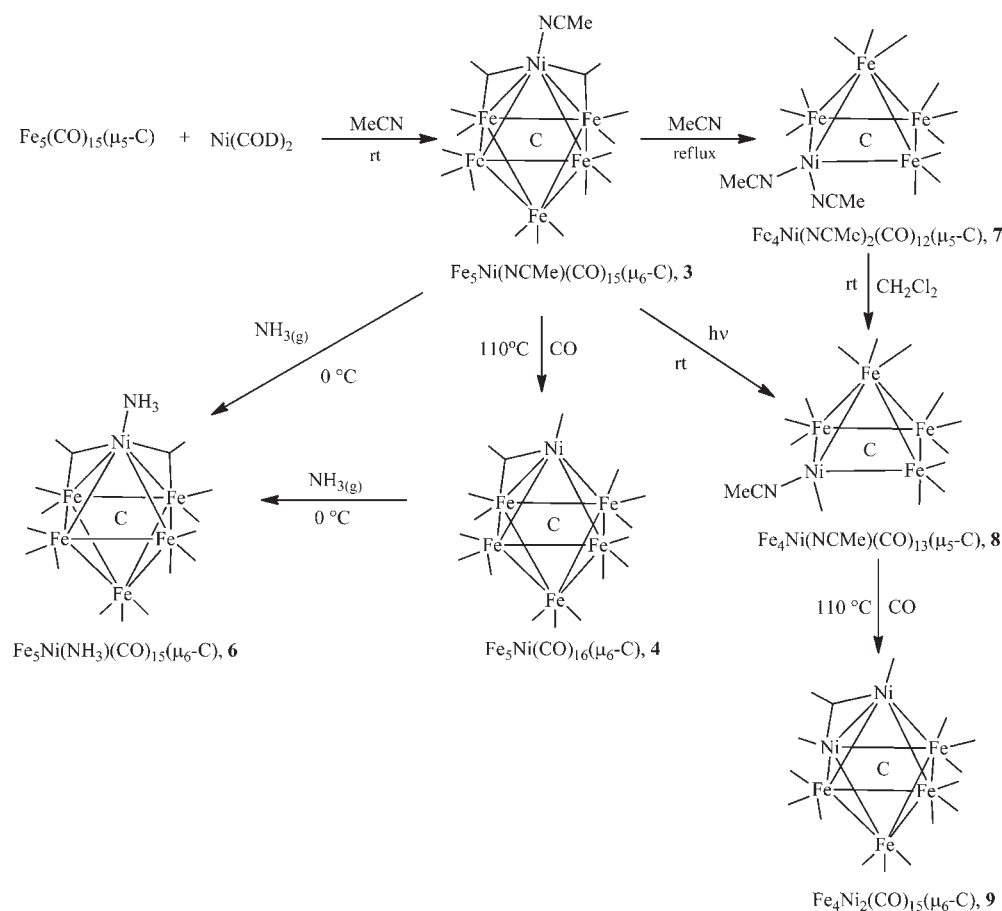
are bonded to each other, with one nickel atom occupying an apical position and the other, one of the positions on the square plane of the octahedron. Just as in compounds **3**, **4**, and **6**, there is a carbon ligand that is encapsulated in the center of the Fe<sub>4</sub>Ni<sub>2</sub> octahedron; Metal–Carbide distances range is 1.861(5)–1.908(5) Å. The Ni(1)–Ni(2) bond distance of 2.4642(11) Å is significantly shorter than that found in the nitrido dianionic cluster complex, [HNi<sub>2</sub>Fe<sub>4</sub>(CO)<sub>13</sub>(μ<sub>6</sub>-C)]<sup>2-</sup>, **10**, (2.724(1) Å),<sup>5</sup> and can be attributed to the carbonyl ligand that bridges the Ni(1)–Ni(2) edge of the octahedron. The other metal–metal bond distances are similar to those found in **10**. With 15 CO ligands the cluster valence count is 86 which is consistent for a *closo* octahedron structure as seen in the solid state for **10**.<sup>11</sup>

Bimetallic Fe–Ni cluster complexes from the reaction of **1** with Ni(COD)<sub>2</sub> were only obtained when the solvent acetonitrile was used. In the other common solvents and/or at elevated temperatures, the reaction of **1** with Ni(COD)<sub>2</sub> does proceed, however, mainly with decomposition of the starting materials, and we were unable to isolate and characterize any Ni–Fe bimetallic complexes. As possible control experiments, there was no reaction of Ni(COD)<sub>2</sub> with acetonitrile. In fact Ni(COD)<sub>2</sub> is not soluble in acetonitrile solvent at room temperature. When **1** was dissolved in acetonitrile solvent at room temperature, compound **1** slowly degraded to the trinuclear cluster Fe<sub>3</sub>(CO)<sub>12</sub>. However, when both **1** and Ni(COD)<sub>2</sub> were dissolved in acetonitrile solvent at room temperature as mentioned above, complex **3** formed in 54% yield. It is known and has been shown that the Ru analogue of **1**, Ru<sub>5</sub>(CO)<sub>15</sub>(μ<sub>5</sub>-C) **11**, in acetonitrile solvent forms the open metal framework structure, **12**,<sup>16</sup> as shown in eq 2 via bond homolysis of the square pyramidal geometry of **11** that can provide vacant coordination sites without cluster fragmentation. However, we were not able to detect the presence of such a species when **1** was dissolved in acetonitrile but believe that such a process followed by migration of the

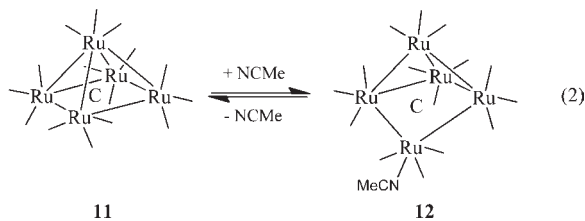
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Scheme 1



acetonitrile ligand to nickel perhaps facilitates the facile formation of **3**.



A summary of the products that were obtained in this study is shown in Scheme 1. The pentairon carbide carbonyl cluster **1** reacts with Ni(COD)<sub>2</sub> in acetonitrile solvent at room temperature to yield the NiFe<sub>5</sub> octahedral cluster, **3**, which has an acetonitrile ligand from the reaction solvent on the nickel atom. The acetonitrile ligand in **3** can be displaced by CO to yield the binary carbonyl cluster complex **4**. Ammonia gas can also replace the acetonitrile ligand in **3** to yield complex **6**. Appropriately compound **4** can be converted to

**6** by reacting with ammonia gas. Compound **3** when dissolved in acetonitrile solvent and heated to reflux results in removal of a vertex occupied by an iron atom in **3** along with substitution of a CO ligand with acetonitrile to give a *nido* octahedral (square pyramidal) cluster **7**. Compound **7** is stable in the solid state and in acetonitrile solvent, but loses one of its acetonitrile ligands in methylene chloride solvent to yield complex **8**. Compound **8** can be converted to **7** by dissolving **8** in acetonitrile solvent. Compound **7** reacts with CO to form the Fe<sub>4</sub>Ni<sub>2</sub> octahedral cluster **9** via first forming compound **8**. Studies of some of these compounds to serve as molecular precursors to new nickel–iron nanoparticle catalysts for applications in heterogeneous catalysis<sup>1</sup> are in progress.

**Acknowledgment.** This research was supported by Start-up Funds provided by the University of Miami.

**Supporting Information Available:** CIF files for each of the structural analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.