

**TRINUCLEAR NICKEL CLUSTERS,  $[\text{Ni}_3(\mu_3\text{-L})(\mu_3\text{-I})(\mu_2\text{-dppm})_3]^{n+}$  (L = I<sup>-</sup>, CO, CNCH<sub>3</sub>, CN-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, CN-*i*-C<sub>3</sub>H<sub>7</sub>, CN-*t*-C<sub>4</sub>H<sub>9</sub>, CN-*n*-C<sub>4</sub>H<sub>9</sub>, NO<sup>+</sup>) AND THE “DIMER OF TRIMER” HEXANUCLEAR NICKEL CLUSTERS  $\{[\text{Ni}_3(\mu_3\text{-I})(\mu_2\text{-dppm})_3]_2(\mu_3, \mu_3, \eta^1, \eta^1\text{-CN-R-NC})\}^{2+}$ , (R = -(CH<sub>2</sub>)<sub>6</sub>-, *p*-C<sub>6</sub>H<sub>4</sub>): CHARACTERIZATION OF LARGE CLUSTERS BY MASS SPECTROMETRY**

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**Abstract**—The mass spectra of a series of trinuclear nickel clusters of the general formula  $[\text{Ni}_3(\mu_3\text{-L})(\mu_3\text{-I})(\mu_2\text{-dppm})_3]^{n+}$ , where L = I<sup>-</sup> (1), CO (2), CNCH<sub>3</sub> (3), CN-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (4), CN-*i*-C<sub>3</sub>H<sub>7</sub> (5), CN-*t*-C<sub>4</sub>H<sub>9</sub> (6), CN-*n*-C<sub>4</sub>H<sub>9</sub> (7), and NO<sup>+</sup> (8) and *n* = 0, 1, 2 were measured by Plasma Desorption (PD) and Fast Atom Bombardment (FAB) mass spectrometry. Strong molecular ion peaks were observed for all of the trinuclear clusters except 8 by both techniques. Ion fragmentation followed similar pathways in both ionization modes. Dimers of trinuclear clusters,  $\{[\text{Ni}_3(\mu_3\text{-I})(\mu_2\text{-dppm})_3]_2(\mu_3, \mu_3, \eta^1, \eta^1\text{-CN-R-NC})\}^{2+}$ , where R = -(CH<sub>2</sub>)<sub>6</sub>- (9) and 1,4-C<sub>6</sub>H<sub>4</sub> (10) were prepared by the reaction of two equivalents of 1 with one equivalent of the appropriate diisocyanide, CN-R-NC. Clusters 9 and 10 were not distinguishable from simple trimers such as 3–7 by <sup>31</sup>P NMR and optical spectroscopies, but were unambiguously identified by PD and FAB mass spectrometry. The parent ions are different for the two techniques: MI<sup>+</sup> in the former case and M<sup>+</sup> in the latter.

The study of metal cluster compounds has been a particularly active area of inorganic chemistry.<sup>1–3</sup> Attention has been focussed on the structural,<sup>3</sup> catalytic,<sup>4–6</sup> and electrochemical<sup>7</sup> properties of clusters as well as their ability to mimic catalyst metal surfaces.<sup>8,9</sup>

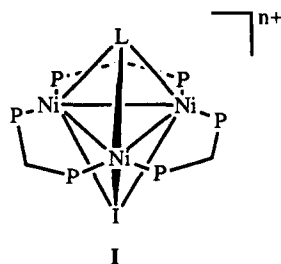
The difficulty of obtaining mass spectrometric analyses on high molecular weight cluster complexes is well documented.<sup>10,11</sup> The use of gentle ionization techniques such as fast atom bombardment (FAB)<sup>11–19</sup> and laser desorption (LD)<sup>20,21</sup> mass spectrometry has enabled the determination of molecular weights of many cluster compounds. Recently, plasma desorption (PD) mass spectrometry has become widely accepted as a viable

technique for the analysis of large biomolecules.<sup>22,23</sup> This technique uses high energy fragments emitted during the spontaneous fission of <sup>252</sup>Cf to desorb large molecules. These molecules are then analyzed by a time-of-flight mass analyzer. While plasma desorption mass spectra of peptides and proteins are routinely reported in the mass range, *m/z* 2000–15,000, very little has been done in the field of inorganic chemistry. PD analyses of ionic coordination compounds,<sup>24</sup> metallocene complexes<sup>25</sup> and large gold<sup>26</sup> and platinum<sup>27</sup> clusters have been reported.

We report the use of PD and FAB mass spectrometry to characterize trinuclear nickel clusters of the structural type I, supported by the ligand dppm (dppm = bis(diphenylphosphino)methane) and by two triply-bridging ligands, one of which is always iodide. The clusters are formulated as

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$[\text{Ni}_3(\mu_3\text{-L})(\mu_3\text{-I})(\mu_2\text{-dppm})_3]^{n+}$ , where L = I<sup>-</sup> (**1**), CO (**2**), CNCH<sub>3</sub> (**3**), CN-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**4**), CN-*i*-C<sub>3</sub>H<sub>7</sub> (**5**), CN-*t*-C<sub>4</sub>H<sub>9</sub> (**6**), CN-*n*-C<sub>4</sub>H<sub>9</sub> (**7**), and NO<sup>+</sup> (**8**) with  $n = 1$  except for **1** ( $n = 0$ ) and **8** ( $n = 2$ ).

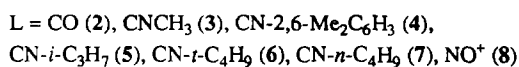
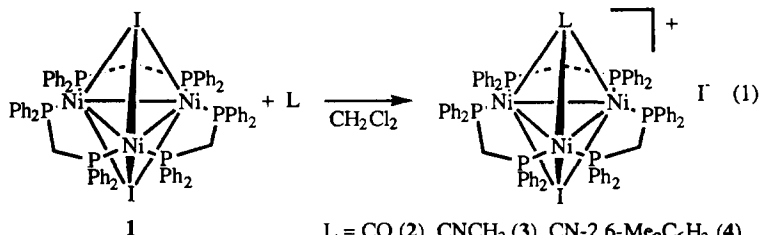


In general, the larger family of  $\pi$ -acceptor ligand capped clusters, **2–8**, are readily prepared from the diiodo derivative  $[\text{Ni}_3(\mu_3\text{-I})_2(\mu_2\text{-dppm})_3]$  (**1**), by substitution of the  $\pi$ -acceptor ligand (L = CO, CNR, NO<sup>+</sup>) for one capping iodide, eq. (1).<sup>28</sup> Clusters **1**,

Schlenk techniques. Solvents were reagent or HPLC grade and dried over the appropriate drying agents. Ni(COD)<sub>2</sub><sup>32,33</sup> and methyl isocyanide<sup>34</sup> were prepared by literature methods. Anhydrous NiI<sub>2</sub> and *i*-propyl isocyanide were purchased from Strem; dppm, *n*-butyl isocyanide, and *t*-butyl isocyanide were purchased from Aldrich; and 2,6-dimethylphenylisocyanide was purchased from Fluka. CO and NO were purchased from Matheson. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were obtained on Varian XL-200 spectrometers. <sup>31</sup>P chemical shifts are reported with respect to 85% H<sub>3</sub>PO<sub>4</sub>. All NMR data were obtained in CD<sub>3</sub>CN unless otherwise noted.

#### Preparation of $[\text{Ni}_3(\mu_3\text{-I})_2(\text{dppm})_3]$ (**1**)

Cluster **1** was prepared by comproportionation of two equivalents of Ni<sup>0</sup> with one equivalent of Ni<sup>II</sup>.<sup>28</sup>



**2**, and **3** were characterized by X-ray diffraction earlier.<sup>28–30</sup> Several of these and related triangular nickel clusters display photochemical<sup>28</sup> or electrocatalytic<sup>31</sup> activity toward the reduction of CO<sub>2</sub>. The PD and FAB mass spectra of the clusters are presented here for the first time. They form molecular ions with  $m/z$  in the range 1484–1587.

We also report the extension of the iodide substitution cluster synthesis method, eq. (1), to prepare larger hexanuclear clusters. In particular, new “dimer of trimer” clusters **9** and **10** have been prepared by reactions of the diisocyanides CN-(CH<sub>2</sub>)<sub>6</sub>-NC, and 1,4-(CN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, eq. (2). These clusters form molecular ions with  $m/z$  in the range 3049–3168. It has not been possible to characterize these clusters crystallographically to date. We demonstrate the utility of PD and FAB mass spectrometry in establishing the identity of the hexanuclear clusters. The interpretation of this data rests on our understanding of the fragmentation of the unlinked trinuclear clusters **1–8**, which we will discuss first.

## EXPERIMENTAL

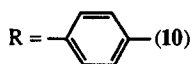
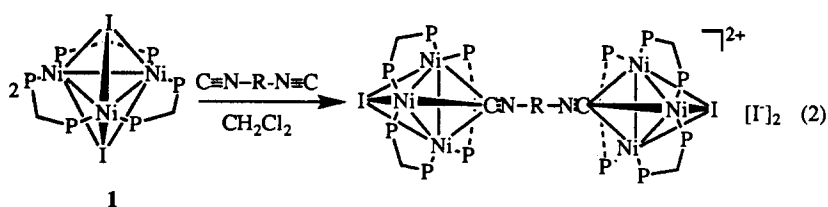
### Materials and physical measurements

All manipulations were performed in an N<sub>2</sub> atmosphere using an inert atmosphere glove box or

Two equivalents of Ni(COD)<sub>2</sub> were dissolved in toluene and 3 equivalents of dppm were added, with stirring, to afford a red intermediate. One equivalent of anhydrous NiI<sub>2</sub> dissolved in hot methanol or 2-methoxyethanol was then added, leading to the immediate formation of **1** as a dark green precipitate. Yields of 90% were obtained by simple filtration and the yield may be increased by concentration of the filtrate. Both cluster **1** and its singly oxidized cluster radical **1**<sup>+</sup> were also characterized by X-ray diffraction.<sup>28</sup> <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.5–6.6 (m, 60 H, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P),  $\delta$  5.1 (M, 6 H, PCH<sub>2</sub>P). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -14.2 (s). UV/vis:  $\lambda_{\text{max}}$  = 651 nm,  $\epsilon$  = 7840 M<sup>-1</sup> cm<sup>-1</sup>.

#### Preparation of $[\text{Ni}_3(\mu_3\text{-CO})(\mu_3\text{-I})(\text{dppm})_3][\text{I}]$ (**2**)

Cluster **1**, 0.39 g (0.25 mmol), was dissolved in 50 cm<sup>3</sup> CH<sub>2</sub>Cl<sub>2</sub>. An excess of CO gas was bubbled through the solution for 3 min and the solution was stirred for 1 h until the color changed to red. The solution was then purged with N<sub>2</sub> and the product precipitated by addition of three volumes of pentane, recovered by filtration and dried *in vacuo*. Cluster **2** was also characterized by X-ray diffraction.<sup>30</sup> Yield: 0.34 g (85%). <sup>1</sup>H NMR:  $\delta$  7.3–6.8



(m, 60 H,  $(C_6H_5)_2P$ ),  $\delta$  4.15, 4.05 (2 d, 6H,  $PCH_2P$ ).  $^{31}P$  NMR:  $\delta$  3.1 (s). IR:  $\nu(CO)$  1724  $cm^{-1}$ . UV/vis:  $\lambda_{max} = 520$  nm,  $\epsilon = 6310$   $M^{-1} cm^{-1}$ .

*Preparation of*  $[Ni_3(\mu_3-CNR)(\mu_3-I)(dppm)_3][I]$ , R =  $CH_3$  (3), 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (4), i-C<sub>3</sub>H<sub>7</sub> (5), t-C<sub>4</sub>H<sub>9</sub> (6), n-C<sub>4</sub>H<sub>9</sub> (7)

The preparation of the isopropyl derivative, 5, exemplifies the synthetic procedure used for 3–7. Cluster 1, 0.25 g (0.16 mmol), was dissolved in 30 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> and one equivalent of i-propylisocyanide (0.011 g, 0.0145 cm<sup>3</sup>) was added with stirring. The solution turned violet within 5 min, signalling the completion of the reaction. 150 cm<sup>3</sup> of pentane was added to induce precipitation of the product which was recovered by filtration, washed with pentane, and dried *in vacuo*. Yield: 0.23 g (88%).

The other isocyanide capped clusters were made by the same procedure. The xylyl derivative (4) had to be stirred overnight in order to achieve complete reaction, but the other isocyanides reacted completely in under 20 min.

3:  $^1H$  NMR:  $\delta$  7.3–6.8 (m, 60H,  $(C_6H_5)_2P$ ),  $\delta$  4.1, 4.0 (2 d, 6H,  $PCH_2P$ ),  $\delta$  4.2 (s, 3H,  $CH_3NC$ ).  $^{31}P$  NMR:  $\delta$  1.1 (s). IR:  $\nu(CN) = 1922, 1862$   $cm^{-1}$ . UV/vis:  $\lambda_{max} = 527$  nm,  $\epsilon = 3800$   $M^{-1} cm^{-1}$ . Cluster 3 was also characterized by X-ray crystallography.<sup>29</sup>

4:  $^1H$  NMR:  $\delta$  7.2–6.7 (m, 63 H,  $(C_6H_5)_2P$ ,  $(CH_3)_2C_6H_3NC$ ),  $\delta$  4.0, 4.2 (2 d, 6H,  $PCH_2P$ ),  $\delta$  2.11 (s, 6H,  $(CH_3)_2C_6H_3NC$ ).  $^{31}P$  NMR:  $\delta$  -1.9 (s). IR:  $\nu(CN) = 1848, 1820$   $cm^{-1}$ . UV/vis:  $\lambda_{max} = 542$  nm,  $\epsilon = 3380$   $M^{-1} cm^{-1}$ .

5:  $^1H$  NMR:  $\delta$  7.3–6.8 (m, 60 H,  $(C_6H_5)_2P$ ),  $\delta$  4.1 (2 d, 6H,  $PCH_2P$ ),  $\delta$  4.75 (m, 1H,  $CNCH(CH_3)_2$ ),  $\delta$  1.8 (d, 6H,  $CNCH(CH_3)_2$ ).  $^{31}P$  NMR:  $\delta$  -0.2 (s). IR:  $\nu(CN) = 1861, 1815$   $cm^{-1}$ . UV/vis:  $\lambda_{max} = 534$  nm,  $\epsilon = 4470$   $M^{-1} cm^{-1}$ .

6:  $^1H$  NMR:  $\delta$  7.2–6.7 (m, 60 H,  $(C_6H_5)_2P$ ),  $\delta$  4.0,

4.2 (2 d, 6H,  $PCH_2P$ ),  $\delta$  1.84 (s, 9H,  $CNC(CH_3)_3$ ).  $^{31}P$  NMR:  $\delta$  -1.4 (s). IR:  $\nu(CN) = 1901, 1870$   $cm^{-1}$ . UV/vis:  $\lambda_{max} = 539$  nm,  $\epsilon = 3780$   $M^{-1} cm^{-1}$ .

7:  $^1H$  NMR:  $\delta$  7.2–6.7 (m, 60 H,  $(C_6H_5)_2P$ ),  $\delta$  4.1 (2 d, 6H,  $PCH_2P$ ),  $\delta$  4.4 (t, 2H,  $CNCH_2CH_2CH_2CH_3$ ),  $\delta$  2.4 (m, 2H,  $CNCH_2CH_2CH_2CH_3$ ),  $\delta$  1.4 (m, 2H,  $CNCH_2CH_2CH_2CH_3$ ),  $\delta$  0.9 (t, 3H,  $CNCH_2CH_2CH_2CH_3$ ).  $^{31}P$  NMR:  $\delta$  -0.7 (s). IR:  $\nu(CN) = 1890, 1846$   $cm^{-1}$ . UV/vis:  $\lambda_{max} = 527$  nm,  $\epsilon = 3800$   $M^{-1} cm^{-1}$ .

*Preparation of*  $[Ni_3(\mu_3-NO)(\mu_3-I)(dppm)_3](BF_4)I$ , (8)

A solution of  $1^{+}$  in THF was prepared from 1 and  $AgBF_4$ .<sup>28</sup> NO was rapidly bubbled through the solution for 4 min during which time the solution turned blue. Stirring was continued for 5 min during which time the blue color intensified; the solution was then purged with N<sub>2</sub> and filtered to remove an insoluble white coproduct. The solution was evaporated to dryness and the product recrystallized from THF/ether. Yield: 0.213 g (30%).  $^1H$  NMR:  $\delta$  7.3–6.8 (m, 60H,  $(C_6H_5)_2P$ ),  $\delta$  4.3 (broad singlet, 6H,  $PCH_2P$ ).  $^{31}P$  NMR:  $\delta$  24.1 (s). IR:  $\nu(NO) = 1754$   $cm^{-1}$ . UV/vis:  $\lambda_{max} = 520$  nm,  $\epsilon = 4850$   $M^{-1} cm^{-1}$ .

*Preparation of*  $\{[Ni_3(\mu_3-I)(dppm)_3]_2(\mu_3, \mu_3, \eta^1, \eta^1-CN(CH_2)_6NC)\}_2 I_2$  (9).

Cluster 1, 0.828 g (0.523 mmol), was dissolved in 150 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>. To this 0.36 mg (0.040 cm<sup>3</sup>, 0.5 equivalents) of 1,6-diisocyanohexane was added by syringe. The solution turned from green to violet within 2 min. The solution volume was reduced to 40 cm<sup>3</sup> by evaporation after which the flask was cooled to -20°C and allowed to sit for 2 days. A microcrystalline violet solid precipitated and was recovered by filtration, washed with pentane, and dried *in vacuo*. Yield: 0.434 g (53%).  $^1H$  NMR:  $\delta$  7.4–6.8 (m, 120 H,  $(C_6H_5)_2P$ ),  $\delta$  4.65 (t, 4 H,

$\text{C}\equiv\text{NCH}_2\text{CH}_2\text{CH}_2$ );  $\delta$  4.3 (m, 12 H,  $\text{PCH}_2\text{P}$ );  $\delta$  2.7 (m, 4 H,  $\text{C}\equiv\text{NCH}_2\text{CH}_2\text{CH}_2$ );  $\delta$  1.8 (m (approximate triplet), 4 H,  $\text{C}\equiv\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}\equiv\text{C}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $-0.16$  (s). IR:  $\nu(\text{CN})$  1889, 1814, 1722  $\text{cm}^{-1}$ . UV/vis:  $\lambda_{\text{max}} = 565$  nm,  $\epsilon = 13,700$   $\text{M}^{-1} \text{cm}^{-1}$ .

*Preparation of*  $\{[\text{Ni}_3(\mu_3\text{-I})(\text{dppm})_3]_2(\mu_3, \mu_3, \eta^1, \eta^1\text{-CNC}_6\text{H}_4\text{NC})\}_2$  (**10**)

Cluster **1**, 0.710 g of (0.45 mmol), was dissolved in 50  $\text{cm}^3$  of  $\text{CH}_2\text{Cl}_2$  and 0.0287 g (0.50 equivalents) of 1,4 phenylene diisocyanide was added to the solution. The reaction mixture turned violet within 3 min. It was then evaporated to dryness. The solid was redissolved in hot methanol and the flask cooled to  $-20^\circ\text{C}$  and allowed to sit overnight. The product was recovered by filtration, washed with pentane, and dried *in vacuo*. Yield: 0.54 g (76%).  $^1\text{H}$  NMR:  $\delta$  7.7 (s, 4H,  $\text{C}\equiv\text{NC}_6\text{H}_4\text{N}\equiv\text{C}$ );  $\delta$  7.4–6.8 (m, 120 H,  $(\text{C}_6\text{H}_5)_2\text{P}$ );  $\delta$  4.3 (m, 12 H,  $\text{PCH}_2\text{P}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $+1.76$  (s). IR:  $\nu(\text{CN})$  1798, 1717  $\text{cm}^{-1}$ . UV/vis:  $\lambda_{\text{max}} = 562$  nm,  $\epsilon = 12,200$   $\text{M}^{-1} \text{cm}^{-1}$ .

*Plasma desorption mass spectrometry*

$^{252}\text{Cf}$  plasma desorption mass spectra were obtained using a Bioion 20R (Bioion KB, Uppsala) PD mass spectrometer. A solution of the analyte was electrosprayed onto a nitrocellulose-coated Mylar target which was immediately inserted into the mass spectrometer. Data were collected for 30 min at an acceleration potential of 17,000 V.

*Fast atom bombardment mass spectrometry*

FAB spectra were obtained using a 50/50 mixture of dithioerythritol and dithiothreitol or 50/50 glycerol and thioglycerol as the matrix. A Kratos MS-50 mass spectrometer (Kratos Analytical Inc., Ramsey, New Jersey) equipped with a Kratos FAB ion source was used in this study. The atom gun used xenon and produced a neutral atom beam at 7–8 keV with an ion current of approximately 1 mA. The mass spectrometer was calibrated over the range  $m/z$ : 400–3000 using the peaks of  $\text{Cs}_{n+1}\text{I}_n^+$ .

## RESULTS AND DISCUSSION

The PD and FAB mass spectra of clusters **1–8** are presented in Tables 1 and 2. Representative spectra for **4** are depicted in Figs 1 and 2. Except for **8** (where  $\text{L} = \text{NO}^+$ ), the molecular ion signal is strong for all the compounds in both PD and FAB mass spectra, thereby enabling molecular weight

determinations for these clusters. Since there are five isotopes of nickel and the clusters contain at least 75 carbon atoms, the molecular ion is composed of a relatively large number of isotopomers. Generally good agreement was found between the calculated average molecular mass of a fragment and the most intense ion of the isotopic distribution, as determined by mass spectrometry (see Tables 1 and 2). The fragmentation pathways for the compounds in both PD and FAB modes are qualitatively similar and are summarized in Scheme 1. Dahl and coworkers observed oligomerization of clusters in the PD mass spectrum of platinum carbonyl clusters,<sup>27</sup> but the nickel trimers **1–8** do not oligomerize, which greatly aids identification of the parent peak.

Both ionization modes show fragmentation by pathway (i) (Scheme 1) in which dppm is lost directly from the molecular ion, followed by the loss of a capping ligand, L, to give  $[\text{Ni}_3\text{I}(\text{dppm})_2]^+$  ( $m/z$  1070). However, in **1**, where  $\text{L} = \text{I}^-$ , it is observed that I is not lost from  $[\text{Ni}_3\text{I}_2(\text{dppm})_2]^+$  in either the PD or FAB mass spectra. Instead, loss of NiI is favored, leading to the peaks at  $m/z$  1014,  $\{[\text{Ni}_2\text{I}(\text{dppm})_2]^+\}$  and at  $m/z$  829,  $\{[\text{Ni}(\text{dppm})_2]^+\}$ .

The main difference between the two ionization modes is that direct loss of the ligand L from the molecular ion to yield  $[\text{Ni}_3\text{I}(\text{dppm})_3]^+$  ( $m/z$  1456) [pathway (ii) in Scheme 1] is observed only in the FAB mass spectra of the compounds, and then only weakly. This observation is surprising since CO or CNR might be viewed as the weakest ligands in the clusters (donating two electrons rather than four for dppm or as many as six for the iodide). The  $\{[\text{cluster}] - \text{L}\}^+$  fragment is evidently unstable with respect to further fragmentation. This is especially pertinent for the NO-capped cluster, **8**.

The mass spectrum of **8**, where  $\text{L} = \text{NO}^+$ , is the least informative of those obtained for **2–8**, as no ion containing NO is observed. The identity of **8** and assignment of structure **I** is based on the  $^{31}\text{P}$  and  $^1\text{H}$  NMR data and the observation of a bridging  $\nu(\text{NO})$  band in the IR.<sup>30</sup> The nitrosyl cluster **8** is also a dication. We have successfully observed mass spectra of only the monocations within the series of compounds **2–8**. A monocation would be most easily generated from **8** by loss of  $\text{NO}^+$  to give  $[\text{Ni}_3\text{I}(\text{dppm})_3]^+$  ( $m/z$  1456), and as observed in the fragmentation patterns for **2–7**, this fragment is not particularly stable. It is expected to lose dppm to form  $[\text{Ni}_3(\text{dppm})_2\text{I}]^+$  ( $m/z$  1070), which is observed. The next two fragments expected, based on the mass spectra of **2–7**, are  $[\text{Ni}_2(\text{dppm})_2\text{I}]^+$  ( $m/z$  1014) and  $[\text{Ni}_2(\text{dppm})_2]^+$  ( $m/z$  886). These appear in both the FAB and PD mass spectra of **8**. No peak corresponding to  $\{[\text{Ni}_3(\text{NO})\text{I}(\text{dppm})_3]\text{I}\}^+$  was

Table 1. PD mass spectra of  $[\text{Ni}_3(\mu_3\text{-L})(\mu_3\text{-I})(\text{dppm})_3]^{n+}$ , ( $n = 0, 1, 2$ )<sup>a</sup>

L	M <sup>+</sup>	M <sup>+</sup> - dppm	$[\text{Ni}_3\text{I}(\text{dppm})_2]^+$	$[\text{Ni}_2(\text{dppm})_2]^+$	Others <sup>b</sup>
(1) I <sup>-</sup>					
calc 1583	1583 (100)	1199 (68)	—	—	1013 (71)
(2) CO					
calc 1484	1484 (100)	—	1073 (59)	887 (56)	
(3) CNCH <sub>3</sub>					
calc 1497	1497 (100)	1115 (3)	1072 (66)	888 (52)	1014 (12)
(4) CN-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>					
calc 1587	1587 (98)	1203 (100)	1073 (59)	888 (77)	1014 (70)
(5) CN-i-C <sub>3</sub> H <sub>7</sub>					
calc 1525	1526 (81)	1142 (33)	1073 (56)	890 (100)	955 (25)
(6) CN-t-C <sub>4</sub> H <sub>9</sub>					
calc 1539	1540 (78)	1156 (33)	1073 (24)	890 (100)	
(7) CN-n-C <sub>4</sub> H <sub>9</sub>					
calc 1539	1540 (100)	1156 (40)	1073 (60)	888 (62)	
(8) NO <sup>+</sup>					
calc 1486	1486 (<1%)	—	1073 (43)	890 (100)	1043 (23) 1013 (36)

<sup>a</sup> Mass and intensity (in parentheses) as a percentage of the base peak of ions observed in the PD mass spectra of the clusters 1–8. Only masses above  $m/z$  850 are included.

<sup>b</sup> (>10%, > $m/z$  850).

Table 2. FAB mass spectra of  $[\text{Ni}_3(\mu_3\text{-L})(\mu_3\text{-I})(\text{dppm})_3]^{n+}$ , ( $n = 0, 1, 2$ )<sup>a</sup>

L	M <sup>+</sup>	M <sup>+</sup> - L	M <sup>+</sup> - dppm	$[\text{Ni}_3\text{I}(\text{dppm})_2]^+$	$[\text{Ni}_2(\text{dppm})_2]^+$	Others <sup>b</sup>
(1) I <sup>-</sup>						
calc 1583	1582 (83)	—	1198 (100)	—	—	1013 (74)
(2) CO						
calc 1484	1483 (100)	1456 (6)	1103 (6)	1073 (22)	886 (5)	
(3) CNCH <sub>3</sub>						
calc 1497	1496 (100)	1456 (3)	1113 (8)	1071 (52)	886 (26)	
(4) CN-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>						
calc 1587	1586 (100)	1456 (17)	1202 (98)	1071 (36)	886 (42)	1013 (32)
(5) CN-i-C <sub>3</sub> H <sub>7</sub>						
calc 1525	1524 (100)	1455 (7)	1139 (13)	1070 (22)	885 (17)	
(6) CN-t-C <sub>4</sub> H <sub>9</sub>						
calc 1539	1539 (100)	1456 (10)	1154 (23)	1071 (24)	886 (27)	
(7) CN-n-C <sub>4</sub> H <sub>9</sub>						
calc 1539	1538 (100)	1456 (6)	1154 (14)	1071 (30)	886 (20)	
(8) NO <sup>+</sup>						
calc 1486	—	—	—	1071 (22)	889 (100)	1014 (43)

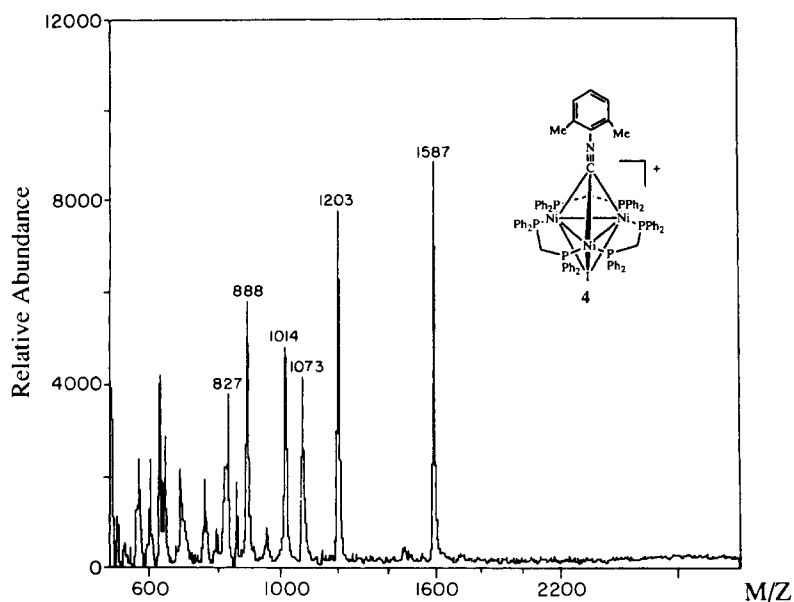
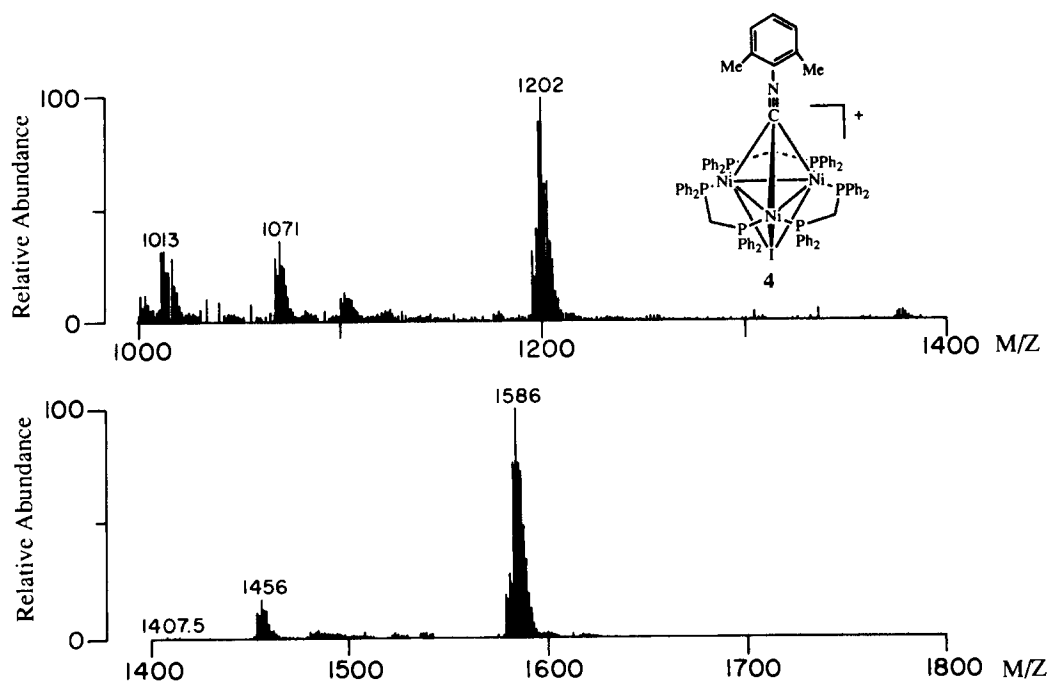
<sup>a</sup> Mass and intensity (in parentheses) as a percentage of the base peak of ions observed in the FAB mass spectra of the clusters 1–8. Only masses above  $m/z$  850 are included.

<sup>b</sup> (>10%, > $m/z$  850).

observed; and no peak corresponding to residual starting material, **1**, ( $M^+ = 1583.1$ ) was observed. We can only conclude that the observed fragments formed by **8** are consistent with those expected for a cluster of structural type **I**.

Overall, the results of PD and FAB mass spectrometric studies of clusters 1–8 provide meaningful mass and fragmentation pattern information. To-

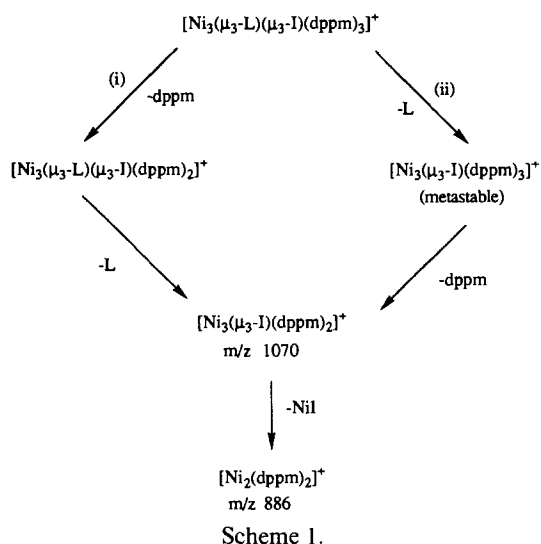
gether with NMR and IR data, the mass spectral data can be used to characterize these cluster compounds at a level of confidence superior to that possible based on conventional elemental microanalytical data. This is important since these clusters, with their high per cent compositions in nickel and carbon, give systematically low per cent carbon microanalytical results, even for crystalline

Fig. 1. PD mass spectrum of **4**.Fig. 2. FAB mass spectrum of **4**.

samples. It is possible that  $\text{Ni}(\text{CO})_4$ , formed during combustion of the clusters, interferes with the complete determination of carbon.

The PD and FAB studies have proven particularly useful in the characterization of the "dimers of trimers" clusters, **9** and **10**. These compounds were prepared by reaction of two equivalents of **1** with diisocyanide ligands in which the two isocyanido groups are separated by an aliphatic  $\text{C}_6$  spacer or a 1,4-disubstituted phenyl spacer, as

shown in eq. (2). Although optical and NMR spectroscopies provide data on these systems that are consistent with the "dimer of trimers" structural assignment, they fall short of conclusively establishing it. Evidence for the assigned structure includes the observation of triply-bridging  $\nu(\text{CN})$  bands in the IR spectra, and in particular, the absence of uncoordinated  $\nu(\text{CN})$  bands above  $2100\text{ cm}^{-1}$  for both **9** and **10**. The  $^{31}\text{P}$  NMR and UV/vis spectroscopic data for **9** and **10** are markedly similar



to those of 3–7. The  $^1\text{H}$  NMR may also be assigned on the basis of the presumed “dimer of trimers” structure (see Experimental section). The  $^1\text{H}$  NMR of **9** is similar to that of the *n*-butyl analog **7**, particularly with regard to the chemical shifts of the methylene protons of the isocyanide ligands.<sup>35</sup> We have been unable to obtain X-ray quality crystals of either “dimer of trimers”. It has proven, however, to be relatively straightforward to obtain high quality PD and FAB mass spectra of **9** and **10**. Dahl and coworkers recently reported that they were able to observe the parent ions for the trinuclear nickel clusters  $[\text{Ni}_3\text{Cp}_3(\mu_3\text{-CO})_2]$ ,  $[\text{Ni}_3\text{Cp}_3(\mu_3\text{-CO})(\mu_3\text{-CS})]$ , and  $[\text{Ni}_3\text{Cp}_3(\mu_3\text{-CS})_2]$  and their Cp’ analogs (Cp’ =  $\eta^5\text{-C}_5\text{H}_4\text{Me}$ ) by laser desorption/Fourier transform mass spectroscopy.<sup>36</sup> However, the molecular ion was not observed for the related “dimer of trimers”,  $[\text{Ni}_3\text{Cp}'_3]_2(\text{C}_2\text{S}_6)$ ;<sup>37</sup> the highest mass seen was ( $\text{M}^+ - \text{Cp}'$ ). Other workers have also reported dimers of trinuclear cobalt clusters, but no mass spectra were reported.<sup>38–41</sup> Recently, related diisocyanide linked dimers of triangular palladium and platinum clusters have been reported by Puddephatt.<sup>42,43</sup> Significant differences between the diisocyanide linked “dimers of trimers” of the nickel triad are emerging. The similarity of  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, and IR spectroscopic data for the isocyanide capped clusters **2–7** and the “dimers of trimers”, **9** and **10**, indicate that these “dimers of trimers” are based on two 48-electron  $\text{Ni}_3$  clusters linked by  $\mu_3, \mu_3, \eta^1, \eta^1$ -diisocyanide ligands. The palladium “dimer of trimers”,  $[\{\text{Pd}_3(\text{dppm})_3\}]_2(\text{CNC}_6\text{Me}_4\text{NC})[\text{PF}_6]_2$ , is believed to be based on two 42-electron clusters linked by a  $\mu_3, \mu_3, \eta^1, \eta^1$ -diisocyanide ligand.<sup>42</sup> The platinum system,  $[\{\text{Pt}_3(\mu_3\text{-CO})(\text{dppm})_3\}]_2(\text{CNC}_6\text{H}_4\text{NC})[\text{PF}_6]_2$ , is based on two 44-electron clusters connected by a

linking, but non-bridging,  $\mu_1, \mu_1, \eta^1, \eta^1$ -diisocyanide ligand.<sup>43</sup>

The PD and FAB mass spectra of **9** are presented in Figs 3 and 4. The calculated average molecular weight for **9** is 3049, and the highest peak seen in the FAB spectrum is  $m/z$  3049. In the PD mass spectrum, the highest mass observed is  $m/z$  3177. This is consistent with  $\text{MI}^+$  in which an iodide counterion is desorbed with the dication to form a monocationic species. No peak at  $m/z$  3049 is observed in the PD mass spectrum. The peak at  $m/z$  1589 is assigned to  $[\text{Ni}_3\text{I}(\text{CN}(\text{CH}_2)_6\text{NC})(\text{dppm})_3]^+$  (calc: 1589, found: 1590) and further fragmentation proceeds as summarized in Scheme 1.

The PD and FAB mass spectra for **10** are similar to those of **9**. The parent peak in the PD mass spectrum is weak and occurs at  $m/z$  3170, again consistent with  $\text{MI}^+$  (calc:  $m/z$  3168). The FAB spectrum again shows a parent mass corresponding to  $\text{M}^+$  at  $m/z$  3042 (calc:  $m/z$  = 3041). Both the PD and FAB mass spectra of **10** give a base peak at  $m/z$  1582 which is consistent with  $[\text{Ni}_3\text{I}(\text{CN}-\text{C}_6\text{H}_4\text{-NC})(\text{dppm})_3]^+$  or residual **1** since the average molecular weight is calculated to be 1583 in both cases.

These spectra reveal a contrast between the desorption mechanisms for PD and FAB for the clusters **9** and **10**. We do not observe dications in either the PD or FAB spectra. The observation of only singly-charged parent ions must involve either a single-electron reduction accompanying desorption to generate the monocation in the gas phase or association of the dication with an uncoordinated iodide. The former mechanism predominates in the FAB mass spectra, the latter in the PDMS spectra. Since charge transfer, presumably from the matrix, is crucial to the desorption of **9** and **10**, it is not surprising that strong matrix effects have been observed. For example, the FAB spectrum of **9** in glycerol shown in Fig. 4 is easily assigned, but a FAB spectrum of the same sample in a 50/50 mixture of dithiothreitol and dithioerythritol (DTT/DTE) showed no peaks above 1500.

## CONCLUSIONS

Neutral (**1**) and monocationic (**2–7**) trinuclear nickel clusters generally gave very good mass spectral data in both PD and FAB ionization modes. Intense molecular ions with similar fragmentation pathways were observed in both ionization modes. Although the dicationic cluster **8** did not give a molecular ion, the fragment ions observed were consistent with Scheme 1.

For the dicationic “dimers of trimers”, **9** and **10**, peaks corresponding to  $\text{M}^+$  in the FAB and  $\text{MI}^+$

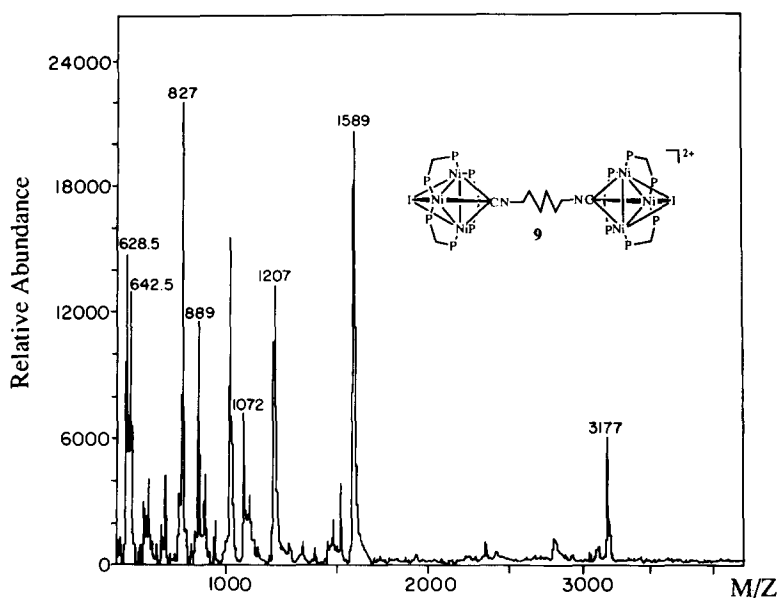


Fig. 3. PD mass spectrum of 9.

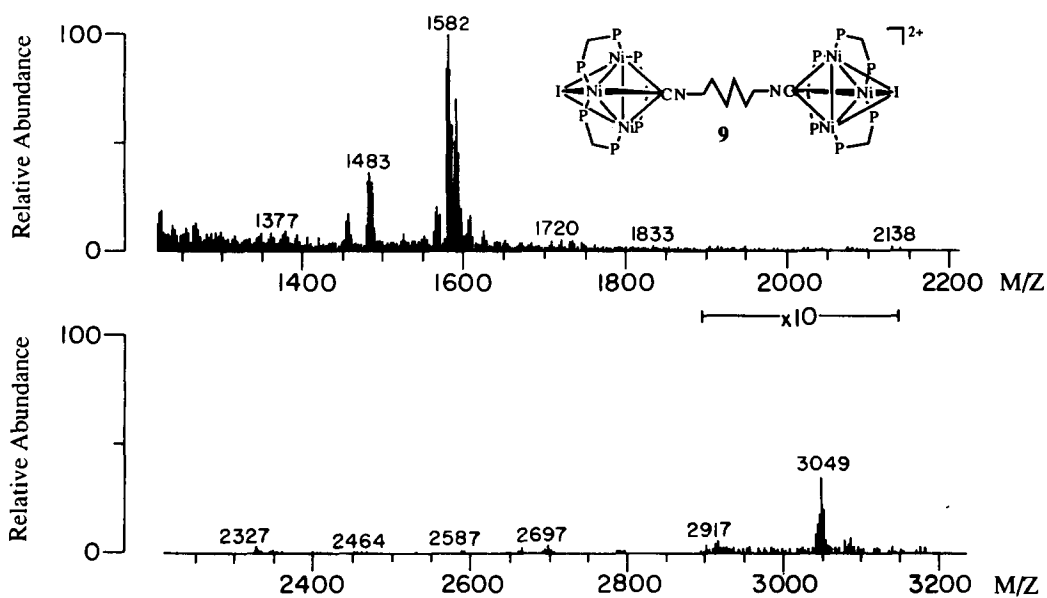


Fig. 4. FAB mass spectrum of 9.

in the PD mass spectra allowed molecular weight determinations. In this way, the hexanuclear nickel clusters were identified and distinguished from the trinickel clusters.

Although FAB has been used in the analysis of metal clusters on a number of occasions, there are few examples of cluster analysis by PD mass spectrometry. In this instance, PD mass spectrometry has been shown to be as useful as FAB in the mass spectrometric analysis of nickel clusters.

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