

# Mixed Fe-Ru Clusters and Ligand-Linked Double and Triple Clusters Derived from the Unsaturated Cluster $\text{Fe}_4(\text{CO})_{11}(\mu_4\text{-PPh})_2$

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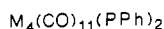
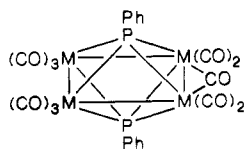
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The basic metal cluster chemistry of the unsaturated cluster  $\text{Fe}_4(\text{CO})_{11}(\text{PPh})_2$  was developed in two directions. Following an improved synthesis of the parent compound the whole series of clusters  $\text{M}_4(\text{CO})_{11}(\text{PPh})_2$  including the  $\text{Fe}_4$ ,  $\text{Fe}_3\text{Ru}$ ,  $\text{Fe}_2\text{Ru}_2$ ,  $\text{FeRu}_3$ , and  $\text{Ru}_4$  members has been obtained and separated. In their unsaturated behavior all members of the series except the  $\text{Fe}_4$  compound resemble the  $\text{Ru}_4$  compound; i.e., they add 2 equiv of CO with cluster unfolding. Further addition and substitution derivatives of the  $\text{Fe}_4$  cluster were obtained with isonitrile and phosphine ligands. Using the *p*-phenylene bidentate ligands  $(\text{MeO})_2\text{P-C}_6\text{H}_4\text{-P(OMe)}_2$  and  $\text{CN-C}_6\text{H}_4\text{-NC}$  the two cluster units  $\text{Fe}_4(\text{CO})_{10}(\text{PPh})_2$  and  $\text{Fe}_4(\text{CO})_9(\text{PPh})_2\text{P(OMe)}_3$  could be linked forming  $\text{Fe}_4\text{-LL-Fe}_4$  double clusters. Analogously the triple cluster  $\text{Fe}_4(\text{CO})_{10}(\text{PPh})_2\text{-(MeO)}_2\text{PC}_6\text{H}_4\text{P(OMe)}_2\text{-Fe}_4(\text{CO})_9(\text{PPh})_2\text{-(MeO)}_2\text{PC}_6\text{H}_4\text{P(OMe)}_2\text{-Fe}_4(\text{CO})_{10}(\text{PPh})_2$  was obtained. The crystal structure of the double cluster  $\text{Fe}_4(\text{CO})_{10}(\text{PPh})_2\text{-(MeO)}_2\text{PC}_6\text{H}_4\text{P(OMe)}_2\text{-Fe}_4(\text{CO})_{10}(\text{PPh})_2$  was determined: triclinic,  $P\bar{1}$ ,  $a = 1135.5$  (6) pm,  $b = 1005.8$  (6) pm,  $c = 1615.2$  (7) pm,  $\alpha = 103.78$  (7)°,  $\beta = 91.38$  (6)°,  $\gamma = 68.34$  (6)°,  $V = 1.660$  (1) nm<sup>3</sup>,  $Z = 1$ .

## Introduction

Although a number of unsaturated organometallic clusters exist,<sup>1</sup> only two of them, namely,  $\text{Fe}_4(\text{CO})_{11}(\text{PPh})_2$  (1)<sup>2-4</sup> and, with more detail,  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ ,<sup>1,5</sup> have been looked at more than superficially with respect to their unsaturation. The observed lability of the  $\text{Fe}_4(\text{CO})_{11}(\text{PR})_2$  systems in the metal as well as in the ligand sphere<sup>2-4</sup> has now prompted us to extend their investigation and to search for similarities and differences between 1 and corresponding ruthenium-containing clusters of which  $\text{Ru}_4(\text{CO})_{11}(\text{PPh})_2$  (5) has been investigated by Haines et al.<sup>6-8</sup>



- 1:  $\text{M}_4 = \text{Fe}_4$
- 2:  $\text{M}_4 = \text{Fe}_3\text{Ru}$
- 3:  $\text{M}_4 = \text{Fe}_2\text{Ru}_2$
- 4:  $\text{M}_4 = \text{FeRu}_3$
- 5:  $\text{M}_4 = \text{Ru}_4$

The objectives of this study were twofold. First, it was intended to improve the preparative yields of 1 and its  $\text{Ru}_4$  analogue 5 and to use the synthetic method as a rational procedure to obtain the  $\text{Fe}_2\text{Ru}_2$  cluster 3. Second, a com-

parative reactivity study of these unsaturated clusters as well as a more sophisticated synthetic utilization of their ligand addition chemistry was planned. The novel redox chemistry of these systems<sup>9</sup> and their framework rearrangements upon reactions with alkynes<sup>10</sup> are reported separately. This paper provides further arguments for the statement<sup>11</sup> that the synthesis of mixed-metal clusters is still more a matter of experience than of systematic planning in that the seemingly straightforward synthesis of 3 from  $\text{Fe}_2(\text{CO})_6(\text{PPh})_2$  and  $\text{Ru}(\text{CO})_n$  fragments has yielded all five compounds 1-5, thereby establishing a complete series of mixed-metal clusters. The exploitation of the facile addition/elimination chemistry of all these clusters has provided a clear distinction between the  $\text{Fe}_4$  compound on one side and all Ru-containing compounds on the other side. In addition it has laid the basis for the extension of the  $\text{Fe}_4\text{P}_2$  cluster chemistry toward ligand-linked multiple clusters. Double clusters of the type  $\text{M}_n\text{-LL-M}_n$  have been reported before.<sup>12,13</sup> Their use, however, was so far limited due to low yields or low stabilities. The high reactivity of 1 has now made such systems available in quantities sufficient for further studies.<sup>9</sup>

## Experimental Section

All experiments were done under prepurified nitrogen in  $\text{N}_2$ -saturated solvents by using Schlenk-type vessels. Normal pressure chromatographic separations were done by using silica gel (0.063-0.2 mm) which had been dried under vacuum for 6 h at 180 °C. Medium-pressure chromatography was done in a self-designed apparatus at an excess pressure of 1-1.5 atm using

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Table I. Preparative Details for the Substitution Derivatives of 1

starting cluster			C <sub>6</sub> H <sub>6</sub> , mL	reagent		chromatography		product no.	yield	
no.	mg	mmol		ligand	mmol	fractn	eluent <sup>a</sup>		mg	%
1	120	0.16	70	<i>p</i> -Tol-NC	0.16	1 (black)	7:1	1	traces	
						2 (black)	6:1	12	125	93
1	130	0.17	100	PMe <sub>3</sub>	0.17	1 (black)	7:1	1	13	10
						2 (black)	5:1	13	116	86
1	85	0.11	50	PMe <sub>2</sub> Ph	0.11	1 (black)	7:1	1	traces	
						2 (black)	5:1	14	84	89
1	100	0.13	100	PPh <sub>3</sub>	0.13	1 (black)	7:1	1	18	19
						2 (black)	5:1	15	91	71
12	120	0.14	100	<i>p</i> -Tol-NC	0.14	1 (black)	6:1	12	traces	
						2 (black)	4:1	16	116	89
12	110	0.13	100	P(OMe) <sub>3</sub>	0.13	1 (black)	5:1	12	traces	
						2 (black)	3:1	17	103	85
12	120	0.14	100	PMe <sub>3</sub>	0.14	1 (black)	6:1	12	traces	
						2 (black)	4:1	18	103	83
1	100	0.13	80	[CH <sub>2</sub> P(OMe) <sub>2</sub> ] <sub>2</sub>	0.13	1 (black)	4:1	1	27	29
						2 (black)	2:1	19	46	39

<sup>a</sup> Hexane/benzene mixture of the given composition.

Table II. Characterization of New Compounds<sup>a</sup>

no.	color	mp, °C	formula	mol wt	anal. calcd (found)		
					C	H	X
2	red	187	C <sub>23</sub> H <sub>10</sub> Fe <sub>3</sub> O <sub>11</sub> P <sub>2</sub> Ru	792.9	34.84 (34.60)	1.27 (1.05)	Fe 21.13 (21.41)
3	green	169	C <sub>23</sub> H <sub>10</sub> Fe <sub>2</sub> O <sub>11</sub> P <sub>2</sub> Ru <sub>2</sub>	838.1	32.96 (33.33)	1.20 (1.20)	Fe 13.32 (13.02)
11	red	164	C <sub>31</sub> H <sub>17</sub> Fe <sub>4</sub> NO <sub>11</sub> P <sub>2</sub>	864.8	43.05 (43.30)	1.98 (2.00)	N 1.75 (1.62)
12	black	169	C <sub>30</sub> H <sub>17</sub> Fe <sub>4</sub> NO <sub>10</sub> P <sub>2</sub>	836.8	43.06 (43.22)	2.04 (2.08)	N 1.67 (1.62)
13	black	162	C <sub>25</sub> H <sub>19</sub> Fe <sub>4</sub> O <sub>10</sub> P <sub>3</sub>	795.7	37.73 (37.64)	2.40 (2.26)	Fe 28.07 (28.31)
14	black	158	C <sub>30</sub> H <sub>21</sub> Fe <sub>4</sub> O <sub>10</sub> P <sub>3</sub>	857.8	42.00 (41.91)	2.46 (2.34)	Fe 26.04 (26.28)
15	black	166	C <sub>40</sub> H <sub>25</sub> Fe <sub>4</sub> O <sub>10</sub> P <sub>3</sub>	982.0	48.92 (48.47)	2.56 (2.46)	Fe 22.75 (22.61)
16	black	157	C <sub>37</sub> H <sub>24</sub> Fe <sub>4</sub> N <sub>2</sub> O <sub>9</sub> P <sub>2</sub>	925.9	47.99 (47.91)	2.61 (2.60)	N 3.02 (3.02)
17	black	158	C <sub>32</sub> H <sub>26</sub> Fe <sub>4</sub> NO <sub>12</sub> P <sub>3</sub>	932.8	41.20 (41.13)	2.80 (2.76)	N 1.50 (1.44)
21	black	211	C <sub>54</sub> H <sub>36</sub> Fe <sub>8</sub> O <sub>24</sub> P <sub>6</sub>	1701.5	38.11 (37.74)	2.13 (2.07)	Fe 26.26 (26.40)
22	black	126 dec	C <sub>52</sub> H <sub>24</sub> Fe <sub>8</sub> N <sub>2</sub> O <sub>20</sub> P <sub>4</sub>	1567.4	39.84 (40.30)	1.54 (1.72)	N 1.78 (1.77)
23	black	117 dec	C <sub>54</sub> H <sub>33</sub> Fe <sub>8</sub> N <sub>2</sub> O <sub>22</sub> P <sub>5</sub>	1663.5	39.98 (39.63)	2.00 (2.28)	N 1.68 (1.71)
25	black	167 dec	C <sub>85</sub> H <sub>62</sub> F <sub>12</sub> O <sub>37</sub> P <sub>10</sub>	2655.3	38.45 (37.96)	2.35 (2.38)	Fe 25.24 (24.97)

<sup>a</sup> 18, 19, and 20 were not analytically pure. 18 (mol wt found 885, calcd 884.8) and 19 (mol wt found 906, calcd 905.7) could be identified by FD-MS.

commercial silica gel columns (Merck LOBAR, LiChroPrep Si 60, 0.040–0.063 mm, size B). IR spectra were recorded on a Perkin-Elmer 782 machine, NMR spectra on Varian EM 360 and (for special cases) Bruker SY 200 machines, UV-vis spectra on a Perkin-Elmer 555, and mass spectra on a Finnigan 4000 machine. Starting materials were prepared according to the published procedures. All phosphine and isonitrile ligands were used as 0.1 M solutions in benzene. For the ligand substituted derivatives of 1 a general preparative procedure is given, the details for which are listed in Table I. All new compounds are characterized in Table II. For the numbering of the compounds see the formula drawings in the text.

**Improved Preparation of 1.** The reaction was performed in an irradiation vessel in which the liquid was allowed to circulate. Pyrex-filtered radiation from an immersed water cooled 150-W high-pressure mercury lamp was used. The vessel was charged with a solution of Fe<sub>2</sub>(CO)<sub>8</sub>(PPh)<sub>2</sub> (600 mg, 1.20 mmol) in benzene (250 mL). A Soxhlet thimble was perforated with a needle 0.5 cm above the bottom, charged with 1 g (2 mmol) of Fe<sub>3</sub>(CO)<sub>12</sub>, and partly immersed in the circulating solution in the side arm of the reaction vessel, thus providing a constant and low concentration of Fe<sub>3</sub>(CO)<sub>12</sub> in solution. The vessel was connected to a reflux condenser via the side arm, the pressure was reduced to ca. 200 mmHg, the solution was warmed to 40–45 °C, and circulation and irradiation were continued for 12 h. The Soxhlet thimble with the remaining Fe<sub>3</sub>(CO)<sub>12</sub> was removed and the irradiation continued until the solution contained no more Fe<sub>3</sub>(CO)<sub>12</sub> (TLC control). Then the solution was filtered and evaporated to dryness. The residue was recrystallized at –27 °C from benzene/hexane (1:5) yielding 600 mg of 1 from the first charge and, after reducing the volume, 210 mg of 1 from the second charge, i.e. a total yield of 90% of 1 containing ca. 1% of Fe<sub>2</sub>(CO)<sub>8</sub>(PPh)<sub>2</sub> as an impurity. By the same procedure and the same scale the clusters Fe<sub>4</sub>(CO)<sub>11</sub>(*P*-*p*-Tol)<sub>2</sub><sup>2</sup> and Fe<sub>4</sub>(CO)<sub>11</sub>(*P*-*t*-

Bu)<sub>2</sub><sup>2</sup> were obtained in 80 and 30% yields, respectively.

**Improved Preparation of 5.** Ru<sub>3</sub>(CO)<sub>12</sub> (500 mg, 0.78 mmol) was powdered and suspended in toluene (20 mL) at 80 °C. PhPH<sub>2</sub> (110 mg, 1.00 mmol, 0.11 mL) was added at 80 °C and the solution heated under reflux for 3 h. The solution was filtered and evaporated to dryness. The residue was chromatographed over a 2 × 70 cm silica gel column. The first four fractions (yellow, yellow, yellow, green<sup>6</sup>), eluted with benzene/hexane (1:8 to 1:6), were collected and added to the starting compounds in subsequent runs. The fifth fraction, eluted with benzene/hexane (1:5), contained purple 5 together with an unknown brown product.<sup>6</sup> They were separated by medium pressure chromatography over two connected Merck-Lobar silica gel columns with benzene/hexane (5:1). 5 was obtained by recrystallization at –27 °C from the same solvent in 25% yield (104 mg).

**Preparation of the Mixed-Metal Clusters.** Fe<sub>2</sub>(CO)<sub>8</sub>(PPh)<sub>2</sub> (200 mg, 0.40 mmol) and Ru<sub>3</sub>(CO)<sub>12</sub> (380 mg, 0.59 mmol) in benzene (250 mL) were irradiated with quartz-filtered light for 10 h in the circulating vessel as described above for 1. After filtration and evaporation to dryness the residue was chromatographed with benzene/hexane (1:5) over a 2 × 40 cm silica gel column. After some minor yellow and orange fractions a black fraction (130 mg) containing all five clusters 1–5 was collected. Medium-pressure chromatography with benzene/hexane (1:4) and Merck-Lobar silica gel columns (that were changed in a revolving fashion such that the solution had finally passed seven columns) was used to separate the clusters that were eluted in the sequence 1 (black, 10 mg, 3%), 2 (red, mp 187 °C, 30 mg, 9%), 3 (green, mp 169 °C, 30 mg, 9%), 4 (green, mp 192 °C, 15 mg, 4%), 5 (purple, 15 mg, 4%). Of the new clusters, 2 and 3 were analytically pure whereas 4 contained a small amount of 5. All three new clusters were identified by their FD mass spectra which showed the M<sup>+</sup> ions as the only intense peaks with the correct isotopic distribution. <sup>1</sup>H NMR data (δ CDCl<sub>3</sub>, internal TMS, 60 MHz):

2, 7.19 (6 H), 6.64 (4 H); 3, 7.18 (6 H), 6.65 (4 H); 4, 7.09 (6 H), 6.51 (4 H); all multiplets.

**CO Reactions.** Solutions of each of the clusters 1–5 (ca 3 mg in ca. 5 mL of cyclohexane) were stirred under an atmosphere of CO for 30–60 min until the typical color of the solution (red for 1, yellow for 2–5) indicated complete conversion that was verified by the IR spectra. Quick evaporation yielded the solid reaction products that were partly contaminated with the reformed starting materials. Keeping the product solutions overnight attached to an evacuated 1-L flask changed the solution colors back to those of the starting materials which were then identified by their IR spectra. In order to save material for further investigations<sup>9</sup> we refrained from doing the carbonylations of 2–4 on a preparative scale.

**Preparation of the *p*-Tol-NC Addition Product 11.** Under an atmosphere of CO a solution of 1 (105 mg, 0.14 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was treated with 1.4 mL (0.14 mmol) of a 0.1 M CH<sub>2</sub>Cl<sub>2</sub> solution of *p*-Tol-NC at 20 °C. The color of the solution changed immediately from black to red. The volume of the solution was reduced to 15 mL by bubbling CO through it. Pentane (10 mL) was added carefully to form a layer on the CH<sub>2</sub>Cl<sub>2</sub> solution that was allowed to stand at 0 °C whereupon 87 mg (72%) of 11 was obtained.

**Preparation of the Ligand-Substituted Derivatives of 1 (for Details See Table I).** The starting cluster was dissolved in the given amount of benzene. An equimolar amount of the ligand was added as a 0.1 M benzene solution. The solution was heated to 40 °C for the given time. Then the solvent was removed in vacuo and the residue chromatographed with the given hexane/benzene mixture. The substitution product eluted as the main fraction; it was recrystallized from hexane/benzene (5:1) to give the analytical sample.

**Attempted Preparation of 20.** A benzene (100 mL) solution of 1 (95 mg, 0.13 mmol) was stirred with 0.065 mmol of a 0.1 M benzene solution of [CH<sub>2</sub>P(OMe)<sub>2</sub>]<sub>2</sub> for 12 h at room temperature. The solution was filtered and evaporated to dryness. The residue was chromatographed with benzene/hexane (2:1), eluting traces of 1 and then 19 (21 mg, 18%). Adding 10% of THF to the eluent yielded crude 20 (29 mg, 27%) from the third fraction. The purity of 20 was not improved by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:2). The IR spectrum of the product resembled that of 21, but the NMR spectrum showed significant amounts of impurities.

**Preparation of the Double Clusters 21–24.** 21. To a solution of 1 (154 mg, 0.21 mmol) in benzene (100 mL) was added 0.20 mmol of *p*-C<sub>6</sub>H<sub>4</sub>[P(OMe)<sub>2</sub>]<sub>2</sub> as a 0.1 M benzene solution. After 10 s another 154 mg (0.21 mmol) of 1 in benzene (100 mL) was added and the solution stirred for 10 min at room temperature and for 1 h at 40 °C. After filtration and evaporation to dryness the residue was chromatographed: fraction 1 (orange), fraction 2 (red-brown), and fraction 3 (black), eluted with benzene/hexane (1:1), consisted of small amounts of Fe<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>), an unknown compound, and 1, respectively. Fraction 4 (black, eluted with benzene/hexane (1:1) containing 10% of THF) yielded after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:3) 207 mg (58%) of 21.

22. This cluster was prepared in a similar manner to 21 starting from 108 mg (0.14 mmol) of 1 with 0.14 mmol of *p*-C<sub>6</sub>H<sub>4</sub>(NC)<sub>2</sub> and further 108 mg (0.14 mmol) of 1 in a total of 100 mL of benzene. Chromatography: fraction 1 (black) and fraction 2 (red-brown), eluted with benzene/hexane (1:2), contained small amounts of 1 and an unknown compound, respectively. Fraction 3 (black), eluted after adding 10% of THF to the eluent, yielded after crystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:3) 114 mg (52%) of 22.

23 and 24. Preparation as for 21 starting from 120 mg (0.14 mmol) of Fe<sub>3</sub>(CO)<sub>10</sub>(PPh<sub>2</sub>)<sub>2</sub>[P(OMe)<sub>3</sub>] with 0.14 mmol of *p*-C<sub>6</sub>H<sub>4</sub>(NC)<sub>2</sub> and 106 mg (0.14 mmol) of 1 in a total of 150 mL of benzene/THF (1:1). Chromatography: fraction 1 (black) and fraction 2 (black), eluted with benzene/hexane (1:1), contained small amounts of 1 and Fe<sub>4</sub>(CO)<sub>5</sub>(PPh<sub>2</sub>)<sub>2</sub>[P(OMe)<sub>3</sub>]<sub>2</sub>. Fractions 3 (black), 4 (black), and 5 (black), eluted with benzene/hexane (1:1) containing 10% of THF, yielded 22 (30 mg, 13%), 23 (103 mg, 55%), and 24 (30 mg, 12%), respectively. Compounds 23 and 24 were recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:2), rendering 23, but not 24, analytically pure.

**Preparation of the Triple Cluster 25.** Compound 1 (88 mg, 0.12 mmol) in THF (50 mL) was treated with 0.12 mmol of

*p*-C<sub>6</sub>H<sub>4</sub>[P(OMe)<sub>2</sub>]<sub>2</sub> as a 0.1 M benzene solution. The solution turned red immediately, and a solution of 21 (200 mg, 0.12 mmol) in THF (100 mL) was added immediately. The mixture was stirred for 1 h at room temperature and for 2 h at 40 °C. After filtration and evaporation to dryness the residue was chromatographed with benzene/THF (10:1). Fraction 1 (black) consisted of small amounts of 1 and fraction 2 (black) of 34 mg (17%) of 21. Fraction 3 (black) yielded, after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:2), 118 mg (38%) of 25.

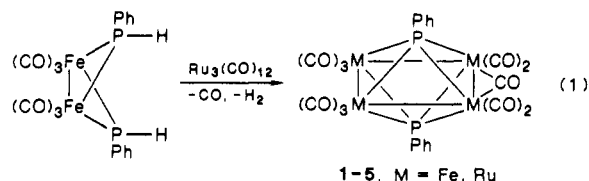
All recrystallized compounds were kept under high vacuum before analysis whereby any solvent of crystallization was removed.

**Crystal Structure Determination.** A crystal of 21 (0.45 × 0.20 × 0.18 mm) was obtained by slow evaporation from toluene/CH<sub>2</sub>Cl<sub>2</sub> (5:1). It belonged to the space group *P* $\bar{1}$  with *a* = 1135.5 (6) pm, *b* = 1005.8 (6) pm, *c* = 1615.2 (7) pm,  $\alpha$  = 103.78 (7)°,  $\beta$  = 91.38 (6)°,  $\gamma$  = 68.34 (6)°, *V* = 1.660 (1) nm<sup>3</sup>, *Z* = 1, *d*<sub>calcd</sub> = 1.72, *d*<sub>obsd</sub> = 1.72 g cm<sup>-3</sup>, and *F*(000) = 892. The quality of the crystal was checked by photographic methods; the data set was obtained at room temperature with a Nonius CAD4 diffractometer using Ag K $\alpha$  radiation and a graphite monochromator. In the 2 $\theta$  range 2–42° a total of 4184 observed reflections of the ( $\pm h, \pm k, +l$ ) set were obtained with  $\omega$ -2 $\theta$  scans making two intensity checks every 30 min. No absorption correction was applied ( $\mu$  = 10.9 cm<sup>-1</sup>). The structure was solved with Patterson and Fourier methods<sup>14,15</sup> which revealed a molecule of CH<sub>2</sub>Cl<sub>2</sub> per asymmetric unit (atoms C11, C12, and C33). Refinement, using unit weights, using anisotropic temperature factors for the Fe, P, C (phenyl), C (carbonyl), and O (carbonyl) atoms, including H atoms with fixed C–H geometry and common temperature factors, and making a total of 340 variables, resulted in a *R* value of 0.051 with maximum residual electron densities of +0.7 and –0.6 e-10<sup>-6</sup> pm<sup>-3</sup>. Table III lists the atomic positions with the *U*<sub>eq</sub> values.

## Results and Discussion

One goal of the present work has been achieved in making the parent clusters 1 and 5, whose yields were not satisfying before<sup>3,7,16</sup> available in research quantities. The major preparative modifications have been the maintenance of a low concentration of Fe<sub>3</sub>(CO)<sub>12</sub> in the formation of 1 and starting the reaction at high temperature for 5. Whereas 1 can now be obtained on a 1-g scale in a day, the synthesis of 5 is still tedious due to the laborious chromatographic procedure. The derivative chemistry of 1 continues to be facile and prolific. Its application leading to double and triple clusters may result in cluster compounds with unusual physical properties.<sup>9</sup>

**The Mixed-Metal Clusters 2–4.** The approach to the mixed-metal compounds in this system was disappointing and favorable at the same time: disappointing because the identity of the Fe<sub>2</sub>P<sub>2</sub> building block of Fe<sub>2</sub>(CO)<sub>6</sub>(PPh)<sub>2</sub> is lost during the cluster buildup reaction, eq 1, which does



not lead to a single product as in the case of the reaction with Fe<sub>3</sub>(CO)<sub>12</sub> but instead to the whole range of clusters 1–5 and favorable because the product mixture has provided access to the two other mixed-metal species 2 (Fe<sub>3</sub>Ru) and 4 (FeRu<sub>3</sub>) in addition to the expected complex 3 (Fe<sub>2</sub>Ru<sub>2</sub>). This reaction outcome repeats an observation

(14) Programs SHELX (G. Sheldrick, University of Cambridge, 1976) and SCHAAL (E. Keller, Universität Freiburg, 1984).

(15) Scattering factors from Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* 1968, A24, 321.

(16) Lang, H.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* 1985, 282, 23.

Table III. Atomic Coordinates for 21

atom	x	y	z	$U_{eq}, \text{\AA}^2$
Fe1	0.1881 (1)	0.0184 (1)	0.1889 (1)	0.0321 (6)
Fe2	0.2182 (1)	0.2705 (1)	0.2693 (1)	0.0339 (7)
Fe3	0.2424 (1)	0.2003 (1)	0.4102 (1)	0.0399 (7)
Fe4	0.2181 (1)	-0.0455 (1)	0.3467 (1)	0.0333 (6)
P1	0.3394 (1)	0.0364 (2)	0.2780 (1)	0.032 (1)
P2	0.0904 (1)	0.1678 (2)	0.3150 (1)	0.031 (1)
P3	0.3157 (2)	-0.1224 (2)	0.0783 (1)	0.037 (1)
O11	0.2298 (5)	-0.1501 (6)	0.0024 (3)	0.055 (4)
C11	0.2817 (9)	-0.236 (1)	-0.0820 (6)	0.073 (3)
H111	0.2063 (9)	-0.232 (1)	-0.1245 (6)	0.0800 (0)
H112	0.3300 (9)	-0.347 (1)	-0.0758 (6)	0.0800 (0)
H113	0.3483 (9)	-0.200 (1)	-0.1077 (6)	0.0800 (0)
O12	0.4174 (5)	-0.2823 (6)	0.0795 (4)	0.055 (4)
C12	0.377 (1)	-0.388 (1)	0.1045 (7)	0.078 (3)
H121	0.463 (1)	-0.483 (1)	0.1038 (7)	0.0800 (0)
H122	0.315 (1)	-0.420 (1)	0.0592 (7)	0.0800 (0)
H123	0.329 (1)	-0.346 (1)	0.1677 (7)	0.0800 (0)
C14	0.5772 (4)	0.0524 (4)	0.2737 (3)	0.047 (2)
C15	0.7096 (4)	-0.0067 (4)	0.2640 (3)	0.052 (2)
C16	0.7748 (4)	-0.1593 (4)	0.2448 (3)	0.055 (2)
C17	0.7076 (4)	-0.2528 (4)	0.2353 (3)	0.060 (2)
C18	0.5752 (4)	-0.1938 (4)	0.2450 (3)	0.051 (2)
C13	0.5100 (4)	-0.0411 (4)	0.2642 (3)	0.034 (1)
H14	0.5267 (4)	0.1706 (4)	0.2886 (3)	0.0700 (0)
H15	0.7616 (4)	0.0657 (4)	0.2713 (3)	0.0700 (0)
H16	0.8773 (4)	-0.2050 (4)	0.2372 (3)	0.0700 (0)
H17	0.7581 (4)	-0.3710 (4)	0.2204 (3)	0.0700 (0)
H18	0.5232 (4)	-0.2662 (4)	0.2376 (3)	0.0700 (0)
C20	-0.1568 (4)	0.3358 (5)	0.2872 (2)	0.046 (2)
C21	-0.2878 (4)	0.4018 (5)	0.3065 (2)	0.056 (2)
C22	-0.3411 (4)	0.3868 (5)	0.3790 (2)	0.049 (2)
C23	-0.2633 (4)	0.3058 (5)	0.4322 (2)	0.048 (2)
C24	-0.1323 (4)	0.2398 (5)	0.4128 (2)	0.041 (2)
C19	-0.0790 (4)	0.2548 (5)	0.3403 (2)	0.032 (1)
H20	-0.1155 (4)	0.3474 (5)	0.2310 (2)	0.0700 (0)
H21	-0.3480 (4)	0.4646 (5)	0.2654 (2)	0.0700 (0)
H22	-0.4425 (4)	0.4379 (5)	0.3940 (2)	0.0700 (0)
H23	-0.3046 (4)	0.2942 (5)	0.4883 (2)	0.0700 (0)
H24	-0.0721 (4)	0.1770 (5)	0.4540 (2)	0.0700 (0)
C25	0.4225 (6)	-0.0566 (8)	0.0342 (4)	0.036 (5)
C26	0.4463 (6)	0.1123 (8)	-0.0434 (5)	0.043 (5)
C27	0.3705 (6)	0.0539 (9)	-0.0089 (5)	0.044 (5)
C11	-0.129 (1)	0.552 (1)	0.0316 (7)	0.152 (4)
C12	0.1383 (8)	0.59 (1)	1.0149 (6)	0.121 (3)
C33	0.010 (3)	0.432 (3)	0.964 (2)	0.108 (8)
C1	0.1033 (7)	0.137 (1)	0.1256 (5)	0.057 (6)
O1	0.0416 (6)	0.2076 (8)	0.0834 (4)	0.090 (6)
C2	0.0968 (8)	-0.092 (1)	0.1726 (5)	0.069 (8)
O2	0.0352 (8)	-0.160 (1)	0.1603 (5)	0.121 (9)
C3	0.3264 (7)	0.2929 (8)	0.2021 (5)	0.047 (5)
O3	0.3952 (6)	0.3120 (7)	0.1614 (4)	0.077 (6)
C4	0.2547 (9)	0.3757 (9)	0.3695 (5)	0.058 (7)
O4	0.2783 (9)	0.4768 (9)	0.4029 (5)	0.110 (9)
C5	0.0951 (8)	0.4275 (9)	0.2489 (6)	0.054 (6)
O5	0.0193 (7)	0.5305 (8)	0.2372 (5)	0.095 (6)
C6	0.1405 (7)	0.3224 (9)	0.5002 (5)	0.047 (5)
O6	0.0761 (6)	0.3983 (7)	0.5593 (4)	0.076 (5)
C7	0.3781 (8)	0.192 (1)	0.4687 (5)	0.060 (6)
O7	0.4625 (6)	0.1920 (9)	0.5067 (5)	0.104 (7)
C8	0.2370 (6)	0.0196 (9)	0.4602 (5)	0.045 (5)
O8	0.2490 (6)	0.0052 (7)	0.5288 (4)	0.072 (5)
C9	0.0937 (7)	-0.1072 (9)	0.3633 (5)	0.049 (6)
O9	0.0192 (6)	-0.1498 (8)	0.3751 (5)	0.086 (6)
C10	0.3312 (7)	-0.2270 (9)	0.3356 (5)	0.051 (6)
O10	0.4011 (6)	-0.3441 (7)	0.3299 (5)	0.083 (5)

that we have made in cluster syntheses by metal exchange<sup>17</sup> and by cluster buildup<sup>18</sup> and which has often been reported in other cases,<sup>11</sup> namely, that under thermolytic conditions complete cluster fragmentation and statistical recombination are not uncommon. The new clusters 2, 3, and 4 have been obtained in quantities sufficient for

Table IV. IR Data ( $C_6H_{12}$ ,  $cm^{-1}$ ) for 1–5

no.	$\nu(CO)$				
	1	2070 w	2025 s	2010 m	1986 m
2	2078 w	2037 s	2012 m	1989 m	1839 w
3	2080 w	2039 s	2017 m	1990 m	1842 w
4	2060 w	2042 s	2018 m	1988 m	1839 w
5	2075 m	2035 s	2018 m	1980 m	1838 w

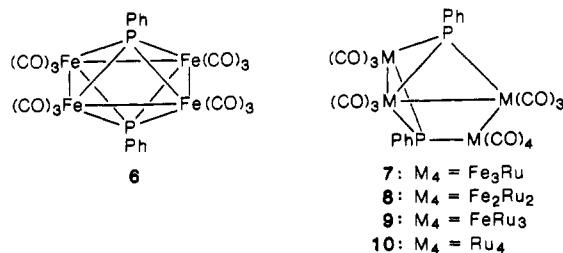
Table V. IR Data ( $C_6H_{12}$ ,  $cm^{-1}$ ) for 6–10

no.	$\nu(CO)$				
	6	2033 vs	2011 m	2000 s	1971 w
7	2110 w	2070 s	2058 vs	2041 vs	2030 s
	2007 s	1998 s	1978 m	1972 sh	
8	2118 w	2102 s	2058 vs	2042 vs	2031 s
	2010 s	1997 s	1975 m	1960 sh	
9	2115 w	2077 s	2055 vs	2043 vs	2018 s
	2002 s	1995 s	1978 sh	1971 m	
10	2110 w	2080 s	2062 vs	2044 vs	2035 s
	1995 s	1985 m	1980 m	1970 m	

identification and preliminary chemical investigation, but their small yields (4–9%) and their cumbersome separation by medium-pressure chromatography pose a serious limitation to their preparative use.

Elementary analysis and IR and  $^1H$ -NMR spectra would have failed to establish that the five-component product mixture of 1–5 obtained after the first chromatographic run is not the pure  $Fe_2Ru_2$  cluster 3. The  $^1H$  NMR spectra (cf. Experimental Section) showing the phenyl multiplets are inconclusive, and the IR spectrum of the mixture is extremely similar to those of 1 and 5 as are, in fact, the IR spectra of all three mixed clusters 2–4 (cf. Table IV). It was only after FD mass spectrometry that the product was found to be a mixture and the purity of the single components was ascertained.

The most obvious difference in reactivity between the  $Fe_4$  cluster 1 and the  $Ru_4$  cluster 5, both being unsaturated according to the 18-electron rule, shows up in their reversible CO additions.<sup>2,6</sup> While 1 adds 1 equiv of CO to form saturated 6 without significant structural change, 5 adds 2 equiv with concomitant loss of one metal–metal bond and formation of the unusually shaped 10. The IR spectra of 5 and 10 are distinctively different. It was therefore to be expected that the CO reaction products of 2, 3, and 4 should be identifiable as belonging to 6-type or 10-type clusters. The mixed-metal systems 2–4 thereby offered a simple means of learning about the factors governing hetero metal reactivity.



Solutions of 2, 3, and 4 quickly changed their color to yellow under an atmosphere of CO, and they slowly reverted to the starting compounds in a vacuum. This indicates that CO is added reversibly in all three cases. IR spectra of the reaction solutions gave no evidence for intermediates in the forward or reverse reactions. The IR spectra of the addition products are all very similar to that of 10 (cf. Table V). Thus, although the small amounts of products were not analytically characterized, it can be concluded that 2, 3, and 4 add 2 equiv of CO to form the clusters 7, 8, and 9 with a structure analogous to that of

(17) Richter, F.; Vahrenkamp, H. *Chem. Ber.* 1982, 115, 3224.

(18) Müller, M.; Vahrenkamp, H. *Chem. Ber.* 1983, 116, 2311.

Table VI. IR (C<sub>6</sub>H<sub>12</sub>) and <sup>1</sup>H NMR (CDCl<sub>3</sub>) Spectra of Single-Cluster Derivatives

no.	$\nu(\text{CO}), \text{cm}^{-1}$						$\delta(\text{CH}_3)$	$\delta(\text{arom})$	
11 <sup>a</sup>	2059 w	2030 vs	2019 s	1992 m	1985 s	1970 sh	1954 m	2.31	6.9–8.5 (m)
12 <sup>a</sup>	2059 m	2020 vs	1985 m	1977 sh	1970 s	1944 sh	1822 w	2.32	7.2–8.8 (m)
13	2055 m	2010 vs	1992 m	1986 sh	1965 s	1947 m	1805 w	1.28 <sup>b</sup>	6.7–7.2 (m)
14	2058 w	2015 vs	2005 vs	1975 s	1964 m	1820 w		1.67 <sup>b</sup>	6.5–7.4 (m)
15	2050 m	2010 vs	1982 s	1970 sh	1805 w				6.3–7.3 (m)
16 <sup>a</sup>	2035 m	2005 s	1994 vs	1966 sh	1923 sh	1800 w		2.30	6.7–7.1 (m)
17 <sup>a</sup>	2024 m	1990 vs	1972 sh	1962 m	1953 m	1915 w	1798 w	3.58 <sup>b,c</sup>	6.7–7.3 (m)
18 <sup>a</sup>	2030 m	1995 vs	1985 sh	1962 sh	1955 s	1814 w		1.35 <sup>b,d</sup>	6.6–7.1 (m)
19	2052 m	2017 vs	2005 vs	1967 s	1915 sh	1808 w		3.74 <sup>b,e</sup>	6.8–7.0 (m)

<sup>a</sup> $\nu(\text{CN})$  absorptions (cm<sup>-1</sup>): 11, 2130 m; 12, 2130 w; 16, 2120 m; 17, 2120 m; 18, 2119 m. <sup>b</sup>Doublet splittings (Hz): 13, 9.8; 14, 9.6; 17, 11.6; 18, 9.0; 19, 11.3. <sup>c</sup> $\delta(\text{Me}(\text{Tot}))$  2.62. <sup>d</sup> $\delta(\text{Me}(\text{Tot}))$  2.30. <sup>e</sup> $\delta(\text{CH}_2)$  1.79 (d,  $J = 14.0$  Hz).

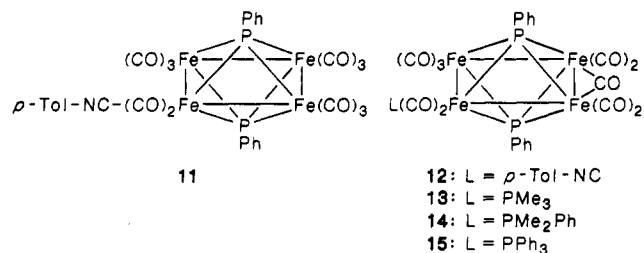
10. Mass spectra of 7–9, due to the facile CO loss, showed only the parent ions of 2–4.

In an attempt to understand the different reactivity of 1 and 5 toward CO the MO schemes<sup>19</sup> can be invoked which focus attention on an empty  $b_u$  orbital located in the gap between the bonding and antibonding states. In the Fe<sub>4</sub> case the energy of this orbital is such that providing two electrons for it (e.g. by adding CO) does not destabilize the system. In the Ru<sub>4</sub> case the  $b_u$  orbital is higher in energy, filling it makes the system labile, the chemical consequence of which is the significant rearrangement in the formation of 10. It is hard to understand how replacing just one iron atom by ruthenium, i.e., going from 1 to 2, should result in such a significant change of the  $b_u$  orbital energy as to make 2 (and 3 and 4) only similar to 5. Accordingly, other explanations must be considered. Among these are thermodynamic ones (i.e. Ru–P bonds being weaker than Fe–P bonds), steric ones (i.e. Ru(CO)<sub>n</sub> units requiring more space and thereby labilizing the M<sub>4</sub>P<sub>2</sub> core), and kinetic ones (i.e. ruthenium centers being more labile than Fe centers in mixed Fe–Ru carbonyls<sup>20</sup>). However, the lack of kinetic data or of detailed structural information for 7–9 which, for instance, does not allow assignment of the M(CO)<sub>n</sub> units to Fe or Ru renders any interpretation speculative at the moment.

**Simple Donor Derivatives of 1.** CO substitutions of 1 have been shown to proceed by ligand addition forming saturated intermediates of the type Fe<sub>4</sub>(CO)<sub>11</sub>L(PPh)<sub>2</sub> followed by a reversible CO elimination.<sup>3</sup> In order to extend the scope of this reaction and to lay a foundation for the intended double-cluster synthesis (by collecting spectroscopic material for simple derivatives and by learning about suitable linking ligands), a few more addition/substitution reactions of 1 were performed. The ligands used were *p*-Tol-NC (as a model for bidentate *p*-phenylenebis(isonitrile), PMe<sub>3</sub>, PMe<sub>2</sub>Ph, and PPh<sub>3</sub> (as models for the various diphos ligands), combinations thereof, and (MeO)<sub>2</sub>P–CH<sub>2</sub>CH<sub>2</sub>–P(OMe)<sub>2</sub> (as an easily accessible and, due to the experience with P(OMe)<sub>3</sub>, seemingly suitable ligand of the bis(phosphino)ethane type).

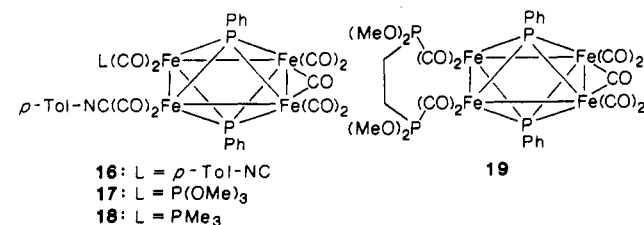
Only with *p*-Tol-NC, like other isonitrile ligands,<sup>3</sup> could an addition product, 11, be obtained. Compound 11 is quite labile and could only be isolated under an atmosphere of CO; working without precautions or raising the temperature of the reaction solutions resulted in the preferred formation of the substitution product 12. With the organophosphine ligands PMe<sub>3</sub>, PMe<sub>2</sub>Ph, and PPh<sub>3</sub> the addition products were not detected, not even as reaction intermediates. The typical color change from black to red upon addition of the ligands did not take place, the re-

actions were slow, and the only isolable products were the substituted clusters 13, 14, and 15. Furthermore these



products were unstable at room temperature under nitrogen. It seems that both the higher electron densities and the higher cone angles of these ligands, compared with isonitrile or phosphite type ligands, induce a weakening of the bonding in the cluster core. The application of alkyl- or aryl-substituted R<sub>2</sub>P–X–PR<sub>2</sub> linking ligands for double-cluster synthesis was thereby eliminated.

Cluster 12 which was easiest to handle was used to study the introduction of a second ligand. As observed before,<sup>3</sup> substitution rather than addition occurred in this second reaction step. Thereby *p*-Tol-NC and P(OMe)<sub>3</sub> were introduced to form 16 and 17. The introduction of PMe<sub>3</sub> was also possible, but the product 18 was again labile and could not be obtained analytically pure. In an attempt to form a double-cluster building block the bidentate ligand (MeO)<sub>2</sub>P–CH<sub>2</sub>CH<sub>2</sub>–P(OMe)<sub>2</sub> was reacted with 1 in a 1:1 ratio. But although an intermediate red color of the solution indicated monodentate addition, the only product that could be isolated was impure 19 which according to its FD-MS contains nine CO groups and according to its <sup>1</sup>H NMR spectrum a symmetrical environment of the diphos ligand, thereby supporting the proposed structure. Accordingly, the use of (MeO)<sub>2</sub>P–CH<sub>2</sub>CH<sub>2</sub>–P(OMe)<sub>2</sub> as a linking ligand for double clusters was questionable as well.



The constitutions of clusters 11–19 could be assigned by their IR and <sup>1</sup>H NMR spectra (cf. Table VI) which can be related to those of Fe<sub>4</sub>(CO)<sub>11</sub>(*P-p*-Tol)<sub>2</sub>[P(OMe)<sub>3</sub>] and Fe<sub>4</sub>(CO)<sub>10</sub>(*P-p*-Tol)<sub>2</sub>[P(OMe)<sub>3</sub>] of which the crystal structures have been determined.<sup>3</sup> All their IR spectra have a typical appearance with one prominent central absorption, the position of which shifts to lower wavenumbers with increasing number of donor ligands present. The unsaturated systems 12–19 are different from their saturated counterpart 11 in their color (black vs red) and

(19) Halet, J. F.; Hoffmann, R.; Saillard, J. Y. *Inorg. Chem.* 1985, 24, 1695. Halet, J. F.; Saillard, J. Y. *Nouv. J. Chim.* 1987, 11, 315.

(20) Shojaie, R.; Atwood, J. D. *Inorg. Chem.* 1987, 26, 2199.

Table VII. IR ( $C_6H_{12}$ ) and  $^1H$  NMR ( $CDCl_3$ ) Spectra of the Double and Triple Clusters

no.	$\nu(CO)$ , $cm^{-1}$				$\delta/J(L)$ , Hz		$\delta(arom)$
21	2055 w	2012 vs	1980 sh	1972 s	1812 m	3.48/11.8 <sup>c</sup>	6.6–7.5 (m)
22 <sup>a</sup>	2052 s	2018 vs	1990 sh	1968 s	1810 w	7.45 (s, 4 H) <sup>c</sup>	6.6–7.1 (m)
23 <sup>a,b</sup>	2058 m	2019 vs	2002 vs	1970 s	1800 w	3.60/11.5 <sup>d</sup>	6.7–7.1 (m)
24 <sup>a</sup>	2058 m	2012 vs	1995 vs	1970 sh	1805 w	3.47/11.9 <sup>d</sup>	6.6–7.6 (m)
25 <sup>b</sup>	2050 w	2015 vs	1989 sh	1970 s	1810 w	3.47/11.7, <sup>c</sup> 3.28/10.7 <sup>c</sup>	6.6–7.5 (m)

<sup>a</sup>  $\nu(CN)$  absorptions ( $cm^{-1}$ ): 22, 2122 m; 23, 2130 sh, 2110 m; 24, 2110 w. <sup>b</sup> IR spectrum recorded in  $CH_2Cl_2$ . <sup>c</sup> Bidentate ligand. <sup>d</sup> Terminal  $P(OMe)_3$  ligand.

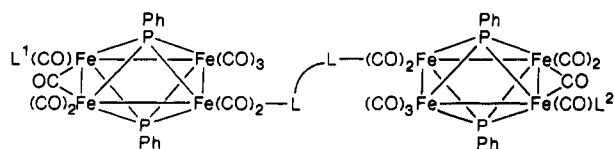
in having a  $\nu(CO)$  absorption around 1800  $cm^{-1}$  due to the bridging CO ligand. The FD mass spectra of 18 and 19 confirmed the assigned constitutions.

All clusters 11–19 allow several isomers: L can be axial or equatorial, L can be adjacent to or distant from the CO bridge, and two L's can be vic, gem, cis, or trans. The structural assignments in the formula drawings must, therefore, be arbitrary. Those given for 12–15 correspond to the one found for  $Fe_4(CO)_{10}(P-p-Tol)_2[P(OMe)_3]$ .<sup>3</sup> Furthermore, as we have shown by a comprehensive NMR study before,<sup>3</sup> such systems show a high fluxionality involving the Fe–Fe “double bond”, the CO ligands, and even the donor ligands L.

**Double and Triple Clusters.** The accumulated experience with the derivative chemistry of 1 indicated that phosphite and isonitrile type bidentate ligands should be suited for linking  $Fe_4P_2$  cluster units together due to ease of reaction and stability of products. The formation of 19 in the reaction with  $(MeO)_2P-CH_2CH_2-P(OMe)_2$  had shown, in addition, that the distance and orientation of the two donor sites would be of significance as well. For this reason the rigid *p*-phenylenebis(ligand) compounds  $(MeO)_2P-C_6H_4-P(OMe)_2$  and  $CN-C_6H_4-NC$  were chosen as linking units.

Attempts to link two cluster molecules with  $(MeO)_2P-CH_2CH_2-P(OMe)_2$  met with limited success. Prolonged reaction with 1 in a 1:2 ratio at room temperature resulted in the formation of 19 as well as an impure compound which may be 20 due to the similarity of its IR spectrum with that of 21 (see below). Its slow decomposition in solution prevented the isolation of a pure compound. It seems that the shortness of the linking unit in this double cluster creates too much steric hindrance between the two half-molecules and that a rigid backbone of the linking ligand is necessary to keep the two clusters apart.

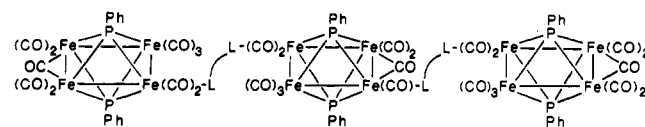
Accordingly, the rigid and longer bidentate ligands *p*- $(MeO)_2P-C_6H_4-P(OMe)_2$  and *p*- $CN-C_6H_4-NC$  allowed the linkage of two  $Fe_4P_2$  units forming the stable double clusters 21 and 22 in good yields. In a stepwise reaction first the addition products of 1 with the bidentate ligands L–L were formed which were used immediately to add the second cluster unit to the second donor site of L–L after which CO elimination was completed by warming. The crystalline compounds 21 and 22 can be stored for prolonged times at room temperature under nitrogen.



- 20:  $L^1 = L^2 = CO$ ,  $\widehat{L-L} = (MeO)_2P-CH_2CH_2-P(OMe)_2$   
 21:  $L^1 = L^2 = CO$ ,  $\widehat{L-L} = (MeO)_2P-C_6H_4-P(OMe)_2$   
 22:  $L^1 = L^2 = CO$ ,  $\widehat{L-L} = CN-C_6H_4-NC$   
 23:  $L^1 = CO$ ,  $L^2 = P(OMe)_3$ ,  $\widehat{L-L} = CN-C_6H_4-NC$   
 24:  $L^1 = L^2 = P(OMe)_3$ ,  $\widehat{L-L} = CN-C_6H_4-NC$

The stepwise reaction sequence allowed the formation of the unsymmetrically substituted double cluster 23 by

starting with  $Fe_4(CO)_{10}(PPh)_2P(OMe)_3$  and adding  $CN-C_6H_4-NC$  and 1 sequentially to it. The formation of 23 was not unambiguous, however. It was accompanied by formation of the redistribution products 22 and 24 of which the bis(phosphite)-substituted double cluster 24 was obtained in quantities which were only sufficient for spectroscopic identification. A certain lability of the double clusters in solution is thereby indicated. In an extension of the applied buildup sequence the triple cluster 25 could also be obtained in reasonable yield starting from 1, by adding  $(MeO)_2P-C_6H_4-P(OMe)_2$ , followed by the double cluster 21. 25 is crystalline and stable up to 160 °C. It is the first compound containing three cluster units linked together systematically and sequentially. It may be compared with the cyclic triple-cluster systems  $[Co_3(CO)_8P]_3$ <sup>21</sup> and  $[H_2Ru_3(CO)_8S]_3$ .<sup>22</sup>



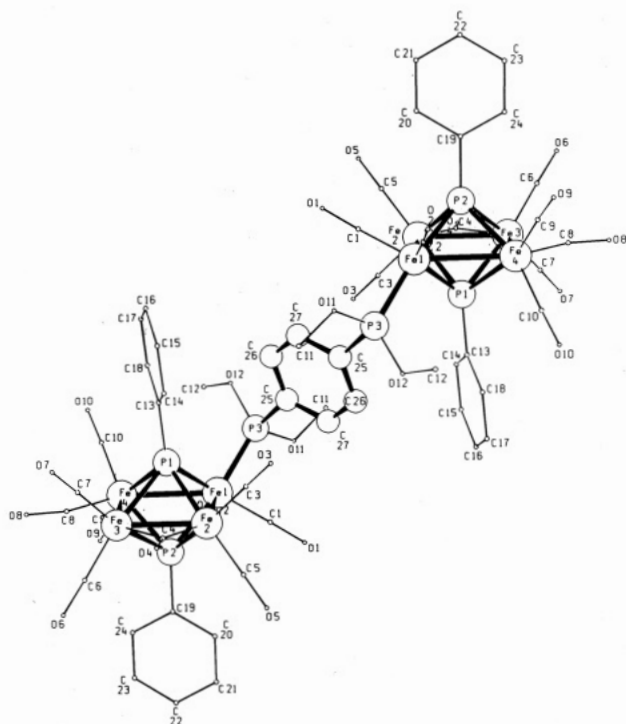
25:  $\widehat{L-L} = (MeO)_2P-C_6H_4-P(OMe)_2$

Of the double and triple clusters, 21 was confirmed by structure determination. On the basis of this and on the IR and NMR data (cf. Table VII) the structures of the other complexes can be assigned with confidence (but note the possibilities for isomerism as discussed above for 11–19). The  $^1H$  NMR spectra give the correct H atom ratios. The IR spectra of 21 and 22 resemble those of the corresponding singly substituted derivatives of 1.<sup>3</sup> The IR spectra of 23 and 24 have but a rough resemblance with those of mixed disubstituted derivatives of 1, but their  $^1H$  NMR spectra show the expected patterns, and the  $\nu(CN)$  absorption in the IR spectrum of 23 is split corresponding to the unsymmetrical neighborhood of the bis(isonitrile) ligand. The  $^1H$  NMR spectrum of the triple cluster 25 shows, as expected, two doublets of equal intensity corresponding to the inner and outer  $P(OMe)_2$  units of the linking ligands. All double and triple clusters have an IR absorption near 1800  $cm^{-1}$ , indicating a CO bridge and thereby the unsaturated nature of the  $Fe_4$  units.

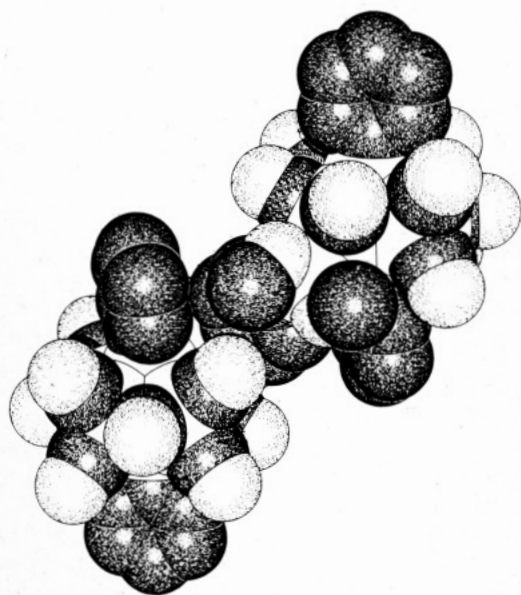
**Structure Determination.** A qualitative view of the double cluster 21 with hydrogen atoms omitted for clarity is given in Figure 1. Figure 2 gives a space-filling model on the same scale. All structural details including a drawing giving the atom numbering are deposited with the supplementary material. The double-cluster molecule has a crystallographic center of symmetry in the center of the aromatic ring. All bond distances involving the iron atoms of 21 ( $Fe-Fe$  bonds see below,  $Fe-\mu_4-P = 230 \pm 6$  (0.02) pm,  $Fe-P(external) = 216.9$  (2) pm) are equal to within a few picometers to those of the single-cluster derivative  $Fe_4(CO)_{10}(P-p-Tol)_2P(OMe)_3$ .<sup>3</sup> This similarity extends to

(21) Vizi-Orosz, A.; Galamb, V.; Palyi, G.; Marko, L.; Bor, G.; Natile, G. *J. Organomet. Chem.* 1976, 107, 235.

(22) Adams, R. D.; Männig, D.; Segmüller, B. E. *Organometallics* 1983, 2, 149.



**Figure 1.** Schematic drawing of the molecular structure of **21**: open circles, C atoms of the central aromatic ring; small circles, C and O atoms.



**Figure 2.** Space-filling plot of the molecular structure of **21**, drawn at the same scale as Figure 1: Fe and P atoms unshaded; C atoms with dark shading; O atoms with light shading.

the overall geometry of one  $\text{Fe}_4$  unit in **21**, with the linking ligand attached in an axial position, with one CO bridged and one CO semibridged Fe–Fe bond opposite to the linking ligand, with all iron atoms being within  $\pm 0.4$  pm of a common plane, and with a rather short contact distance of 265.4 (3) pm between the two  $\mu_4$ -phosphorus atoms.

While Figure 1 is meant to draw attention to the cluster cores and the linking situation, Figure 2 demonstrates the close packing of ligand groups within the molecule of **21**. Several molecular features seem to result from this crowded situation: the Fe–Fe bonds adjacent to the linking ligand (269.8 (1) and 275.7 (1) pm) are longer than the two

others (251.8 (2) pm CO bridged, 255.3 (2) pm semi-bridged); the Fe–P–C angle at the linking phosphorus atom (119.5 (2) $^\circ$ ) is significantly larger than the tetrahedral value; and the  $\mu_4$ -P-phenyl group on the side of the linking ligand is bent away from the linking iron atom (P–C vector 7 $^\circ$  away from the normal of the  $\text{Fe}_4$  plane). From these findings it becomes obvious that the *p*-phenylenebis(donor) ligands are about the shortest ligands possible to link two  $\text{Fe}_4\text{P}_2$  clusters, thereby justifying the expansion given above for the instability of **20**.

With respect to the electronic situation of the double cluster **21** two observations are relevant: As already discussed for the corresponding single clusters,<sup>3</sup> a possible Fe–Fe double bond in the unsaturated  $\text{Fe}_4$  cores cannot be located from the structural data, leaving cyclic delocalization within the  $\text{Fe}_4$  unit a possibility. On the other hand, the extension of this delocalization across the ligand L–L over both  $\text{Fe}_4$  units seems unlikely due to the tetrahedral nature of the linking phosphorus atoms and their axial position with respect to the  $\text{Fe}_4$  rings. This limitation of possible electronic interactions between the two  $\text{Fe}_4$  units may not exist for the bis(isonitrile)-linked double cluster **22** for which the molecular geometry is not known.

### Conclusions

This work has provided access to a complete series of mixed-metal clusters  $\text{M}_4(\text{CO})_{11}(\text{PPh})_2$  with  $\text{M} = \text{Fe}$  and  $\text{Ru}$  due to a facile cluster fragmentation process. This series of clusters **1–5** has yielded one new piece of information concerning heterometal reactivity in that the  $\text{Fe}_4$  system reacts differently with CO than all four Ru-containing systems. Using the unsaturated nature of the  $\text{Fe}_4\text{P}_2$  compounds, it has been possible to extend cluster construction beyond the cluster core and to obtain interconnected polymetallic units by a systematic step by step procedure. The approach used may be related to the methods used to anchor clusters to supports,<sup>23</sup> but the compounds obtained are molecular entities that can be fully characterized. The resulting possibilities of unidimensional interactions between metal-rich building blocks should be worth investigating with respect to optical as well as electrical properties. We have tried to do the first step in this direction by addressing the question of electronic interactions between the ligand-linked tetrairon units.<sup>9</sup>

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**Registry No.** **1**, 81534-73-8; **5**, 81988-72-9; **6**, 81191-38-0; **10**, 84204-14-8; **11**, 115161-27-8; **12**, 115160-40-2; **13**, 115160-41-3; **14**, 115161-30-3; **15**, 115160-42-4; **16**, 115160-43-5; **17**, 115161-31-4; **18**, 115160-46-8; **19**, 115161-26-7; **21**, 115161-32-5; **22**, 115161-33-6; **23**, 115161-28-9; **24**, 115161-29-0; **25**, 115161-34-7;  $\text{Fe}_2(\text{CO})_6(\text{PPh})_2$ , 39049-79-1;  $\text{Fe}_3(\text{CO})_{12}$ , 17685-52-8;  $\text{Fe}_2(\text{CO})_6(\text{Ph-}i\text{-}p\text{-}tol)_2$ , 81191-74-4;  $\text{Fe}_2(\text{CO})_6(\text{Ph-}t\text{-}Bu)_2$ , 81191-40-4;  $\text{Fe}_4(\text{CO})_{11}(\text{P-}i\text{-}tol)_2$ , 81534-74-9;  $\text{Fe}_4(\text{CO})_{11}(\text{P-}t\text{-}Bu)_2$ , 81534-72-7;  $\text{Ru}_3(\text{CO})_{12}$ , 15243-33-1;  $\text{Fe}_4(\text{CO})_{10}(\text{PPh})_2[\text{P}(\text{OMe})_3]$ , 99376-29-1.

**Supplementary Material Available:** A drawing of **21** giving the atom numbering, a table of positional and all thermal parameters, and a table of all distances and angles (15 pages); the  $F_o/F_c$  listing (18 pages). Ordering information is given on any current masthead page.

(23) Gates, B. C., Guzzi, L., Knözinger, H., Eds. *Metal Clusters in Catalysis*; Elsevier: Amsterdam, 1986.