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Preparation of the Triiron Phosphinidene–Imido Clusters $Fe_3(\mu_3\text{-}PBu^t)(\mu_3\text{-}NR)(CO)_9$ (R = Et, Ph) and Their Reactions with Alkynes

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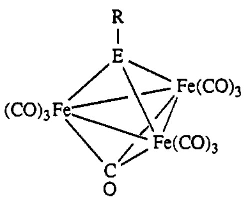
The compounds $Fe_3(\mu_3\text{-}PBu^t)(\mu_3\text{-}NR)(CO)_9$ (R = Ph (**2a**), Et (**2b**)), which are the first examples of clusters possessing both capping imido and phosphinidene ligands, have been prepared in good yield by the photochemical reaction of the corresponding $H_2Fe_3(\mu_3\text{-}NR)(CO)_9$ cluster with Bu^tPCl_2. Cluster **2a** has been crystallographically characterized: $C_{19}H_{14}NO_9PFe_3$, orthorhombic, $Pbc2_1$ (nonstandard $Pca2_1$), $a = 12.109$ (3) Å, $b = 14.793$ (5) Å, $c = 12.982$ (3) Å, $V = 2325.3$ (14) Å^3, $Z = 4$, $R(F) = 7.56\%$. Like $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$, the cluster consists of an isosceles triangle of iron atoms with two Fe–Fe bonds and with capping phosphinidene and imido ligands above and below the metal triangle. Both clusters have been observed to react with alkynes to give a variety of products, the most interesting of which is the binuclear compound $Fe_2(\mu_2,\eta^3\text{-}PhNC(Ph){=}C(Ph)PBu^t)(\mu_2,\eta^4\text{-}PhC{=}C(Ph)C(Ph){=}CPh)(CO)_4$ (**3**) which results from the reaction of $PhC{\equiv}CPh$ with **2a**. This species has been crystallographically characterized and shown to possess a chelating $\mu_2,\eta^3\text{-}PhNC(Ph){=}C(Ph)PBu^t$ ligand formed by insertion of the alkyne between the phosphinidene and imido ligands and also has a ferracyclopentadiene ligand formed by coupling of two additional alkynes: $C_{56}H_{44}NO_4PFe_2$, triclinic, $P\bar{1}$, $a = 10.353$ (3) Å, $b = 14.125$ (4) Å, $c = 20.391$ (7) Å, $\alpha = 83.65$ (2)°, $\beta = 79.20$ (2)°, $\gamma = 68.27$ (2)°, $V = 2718.1$ (15) Å^3, $Z = 2$, $R(F) = 5.83\%$.

Introduction

The chemistry of triiron clusters which possess capping phosphinidene (μ_3-PR) and imido (μ_3-NR) ligands has been extensively investigated in recent years.[1-5] The parent complexes in this family of compounds are the monocapped clusters $Fe_3(\mu_3\text{-}ER)(CO)_{10}$ (I) (E = N, P), which have three metal–metal bonds



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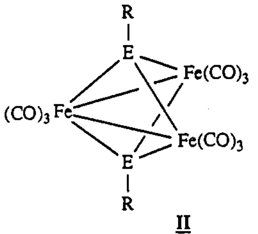
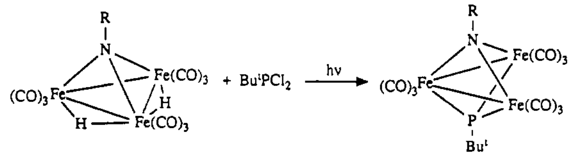


II

and a μ_3-CO ligand and the bicapped clusters $Fe_3(\mu_3\text{-}ER)_2(CO)_9$ (II) which possess only two metal–metal bonds. The capping ligands serve to retain the cluster integrity in a variety of reactions, although examples of alkyne[1i–l,v,3c] and carbene[1p,3a,b] insertion into iron–phosphinidene and iron–imido bonds are known. We have sought the preparation of a *mixed* phosphinidene–imido cluster so as to compare the reactivity of these two different capping ligands on the same molecule. Herein are reported the synthesis of the clusters $Fe_3(\mu_3\text{-}NR)(\mu_3\text{-}PBu^t)(CO)_9$ (R = Et, Ph), the crystallographic characterization of the phenyl derivative, and the reactivity of the compounds with several alkynes.

Results

Synthesis and Spectroscopic Characterization of $Fe_3(\mu_3\text{-}NR)(\mu_3\text{-}PBu^t)(CO)_9$ (R = Ph, Et). A number of strategies and reactions were explored in an attempt to prepare phosphinidene–imido clusters, but the only reaction which led to the desired product is that given in eq 1. This photochemical reaction gave



(1)

1a, R = Ph
1b, R = Et

2a, R = Ph (83%)
2b, R = Et (77%)

high-yield formation of the bicapped clusters **2a** and **2b**, along with a minor product that has not been identified (see Experimental Section). These clusters were isolated as air-stable red-

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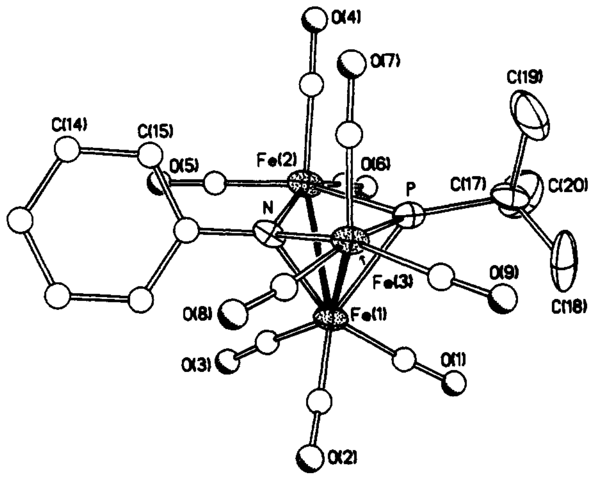

Figure 1. ORTEP drawing of $Fe_3(\mu_3\text{-}NPh)(\mu_3\text{-}PBu^t)(CO)_9$ (**2a**). Thermal ellipsoids are drawn at the 40% probability level.

Table I. Crystallographic Parameters for $Fe_3(\mu_3\text{-}NPh)(\mu_3\text{-}PBu^t)(CO)_9$ (**2a**) and $Fe_2(\mu_2,\eta^3\text{-}PhNC(Ph){=}C(Ph)PBu^t)(\mu_2,\eta^4\text{-}PhC{=}C(Ph)C(Ph){=}CPh)(CO)_4$ (**3**)[a]

	2a	**3**
formula	$C_{19}H_{14}NO_9PFe_3$	$C_{56}H_{44}NO_4PFe_2$
space group	*Pbc*2$_1$ [nonstandard setting for *Pca*2$_1$ (No. 29)]	$P\bar{1}$
a, Å	12.109 (3)	10.353 (3)
b, Å	14.793 (5)	14.125 (4)
c, Å	12.982 (3)	20.391 (7)
α, deg		83.65 (2)
β, deg		79.20 (2)
γ, deg		68.27 (2)
V, Å	2325.3 (14)	2718.1 (15)
Z	4	2
D(calc), g/cm^{-3}	1.710	1.146
temp, °C	23 (1)	23 (1)
T(max)/*T*(min)	1.96	1.081
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
R(*F*), %	7.56	5.83
R$_w$(*F*), %	7.53	6.30

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w(F) = \sum(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $Fe_3(\mu_3\text{-}NPh)(\mu_3\text{-}PBu^t)(CO)_9$ (**2a**)

	x	*y*	*z*	*U*[a]
Fe(1)	1671.5 (17)	5426.4 (15)	2500	42.7 (7)
Fe(2)	1692.3 (17)	5233.8 (17)	4459.5 (19)	46.4 (8)
Fe(3)	3746.1 (16)	5170.3 (14)	2795.7 (21)	41.8 (7)
P	2749 (3)	6195 (3)	3609 (4)	42 (1)
O(1)	771 (13)	7184 (9)	1925 (12)	105 (7)
O(2)	2230 (10)	4912 (9)	408 (8)	76 (5)
O(3)	−506 (11)	4598 (11)	2574 (13)	115 (7)
O(4)	3058 (11)	5148 (11)	6315 (11)	86 (6)
O(5)	191 (10)	3695 (8)	5019 (12)	91 (6)
O(6)	−16 (11)	6497 (9)	5223 (10)	32 (3)
O(7)	5281 (9)	4926 (8)	4483 (10)	79 (5)
O(8)	4464 (10)	3648 (7)	1489 (10)	72 (5)
O(9)	5107 (11)	6409 (9)	1575 (10)	74 (5)
N	2454 (8)	4556 (7)	3364 (9)	36 (4)
C(1)	1096 (16)	6467 (12)	2144 (13)	69 (7)
C(2)	2067 (12)	5109 (13)	1207 (12)	55 (6)
C(3)	370 (14)	4928 (13)	2581 (12)	61 (6)
C(4)	2523 (13)	5187 (12)	5583 (12)	56 (6)
C(5)	755 (14)	4299 (12)	4813 (13)	60 (6)
C(6)	641 (15)	6011 (13)	4956 (15)	70 (7)
C(7)	4697 (10)	4998 (12)	3808 (12)	51 (6)
C(8)	4164 (13)	4282 (10)	1968 (16)	63 (7)
C(9)	4550 (14)	5928 (14)	2039 (14)	68 (8)
C(11)	1986 (7)	3109 (7)	2541 (6)	63 (7)
C(12)	2000	2166	2547	63 (7)
C(13)	2455	1704	3382	90 (10)
C(14)	2895	2184	4211	88 (9)
C(15)	2881	3127	4205	56 (6)
C(16)	2427	3589	3370	39 (5)
C(17)	3052 (11)	7400 (12)	3832 (11)	52 (6)
C(18)	3315 (16)	7875 (11)	2823 (15)	106 (10)
C(19)	4009 (23)	7413 (16)	4591 (26)	181 (17)
C(20)	2068 (18)	7904 (16)	4319 (18)	114 (11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Fe_3(\mu_3\text{-}NPh)(\mu_3\text{-}PBu^t)(CO)_9$ (**2a**)

Bond Distances			
Fe(1)–Fe(2)	2.560 (2)	Fe(1)–Fe(3)	2.569 (3)
Fe(1)–P	2.251 (4)	Fe(2)–P	2.209 (5)
Fe(3)–P	2.207 (5)	Fe(1)–N	1.953 (11)
Fe(2)–N	1.969 (12)	Fe(3)–N	1.954 (10)
P–C(17)	1.843 (18)	N–C(16)	1.431 (15)
Bond Angles			
Fe(2)–Fe(1)–Fe(3)	80.0 (1)	Fe(1)–P–Fe(2)	70.0 (1)
Fe(1)–P–Fe(3)	70.4 (1)	Fe(2)–P–Fe(3)	96.5 (2)
Fe(1)–N–Fe(2)	81.5 (4)	Fe(1)–N–Fe(3)	82.3 (4)
Fe(2)–N–Fe(3)	114.3 (5)	P–Fe(1)–N	71.6 (3)
P–Fe(2)–N	72.3 (3)	P–Fe(3)–N	72.6 (3)
Fe(2)–Fe(1)–P	54.2 (1)	Fe(3)–Fe(1)–P	54.0 (1)
Fe(2)–Fe(1)–N	49.5 (3)	Fe(3)–Fe(1)–N	48.9 (3)
Fe(1)–P–C(17)	134.8 (5)	Fe(2)–P–C(17)	131.3 (5)
Fe(3)–P–C(17)	129.1 (5)	Fe(1)–N–C(16)	130.6 (8)
Fe(2)–N–C(16)	119.6 (8)	Fe(3)–N–C(16)	119.0 (7)

brown solids which are readily soluble in CH_2Cl_2, THF, and hydrocarbon solvents. The structure of **2a** has been confirmed by an X-ray diffraction study (see Figure 1 and below), and the spectroscopic data for the compounds (see Experimental Section) are fully consistent with the determined structure. Cluster **2a** also formed from the addition of $AgBF_4$ to a CH_2Cl_2 solution of **1a** and Bu^tPCl_2, although the yield was low (23%). The mechanisms of these reactions have not been investigated, but it is important to note that reaction 1 proceeds well only under photochemical, but not thermal, conditions.

An ORTEP drawing of **2a** is shown in Figure 1, and pertinent crystallographic details are given in Tables I–III. The structure of the molecule is similar to that previously determined for the bis(imido) cluster $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$[5j] except that a μ_3-phosphinidene ligand has replaced one of the μ_3-imido ligands. There are two Fe–Fe bonds with distances of 2.560 (2) and 2.569 (3) Å, which are slightly longer than the 2.45-Å average Fe–Fe distance in $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$.[5j] Similarly, the Fe(2)–Fe(1)–Fe(3) angle of 80.0 (1)° is slightly larger than the 76.7 (1)° angle reported for $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$.[5j] The capping μ_3-NPh and

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Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Parameters (Å^2 $\times 10^3$) for $Fe_2(\mu_2,\eta^3$-PhNC(Ph)=C(Ph)PBu^t)(μ_2,η^4-PhC=C(Ph)C(Ph)=CPh)$(CO)_4$ (**3**)

	x	*y*	*z*	U^a
Fe(1)	4301.6 (10)	3553.4 (7)	2432.8 (5)	37.9 (4)
Fe(2)	6127.1 (10)	3561.7 (7)	3085.2 (5)	38.3 (4)
P	5498 (2)	2228 (1)	3090 (1)	39 (1)
N	4894 (5)	2419 (4)	1773 (3)	40 (2)
O(7)	1747 (6)	3120 (4)	2956 (3)	74 (3)
O(8)	3064 (6)	5223 (4)	1491 (3)	75 (3)
O(9)	9121 (5)	2479 (4)	2931 (3)	82 (3)
O(10)	6244 (6)	3658 (4)	4486 (3)	77 (3)
C(1)	6084 (6)	3928 (5)	2086 (3)	36 (3)
C(2)	6063 (7)	4809 (5)	2363 (3)	36 (3)
C(3)	4947 (7)	5172 (5)	2921 (3)	36 (3)
C(4)	3999 (7)	4628 (5)	3066 (3)	42 (3)
C(5)	6303 (7)	1253 (5)	2526 (3)	40 (3)
C(6)	5842 (7)	1510 (5)	1893 (3)	39 (3)
C(7)	2757 (8)	3303 (6)	2761 (4)	52 (4)
C(8)	3547 (7)	4553 (5)	1843 (4)	47 (3)
C(9)	7925 (7)	2898 (5)	2984 (4)	52 (3)
C(10)	6172 (8)	3611 (5)	3933 (4)	54 (4)
C(11)	8126 (5)	2620 (3)	1406 (2)	47 (3)
C(12)	9033	2348	803	63 (4)
C(13)	8848	3024	246	70 (5)
C(14)	7755	3971	292	70 (5)
C(15)	6848	4243	895	53 (4)
C(16)	7033	3567	1452	41 (3)
C(21)	8477 (5)	4876 (3)	2024 (3)	61 (4)
C(22)	9351	5427	1772	84 (5)
C(23)	8764	6465	1600	86 (6)
C(24)	7305	6951	1680	73 (5)
C(25)	6431	6400	1932	57 (4)
C(26)	7018	5362	2104	42 (3)
C(31)	5919 (4)	6021 (3)	3617 (2)	53 (4)
C(32)	5816	6878	3934	66 (4)
C(33)	4624	7763	3928	74 (5)
C(34)	3535	7791	3605	74 (4)
C(35)	3638	6935	3288	58 (4)
C(36)	4830	6050	3294	41 (3)
C(41)	1405 (6)	5317 (4)	3363 (2)	55 (4)
C(42)	171	5763	3807	72 (4)
C(43)	242	5920	4461	85 (5)
C(44)	1548	5630	4671	77 (5)
C(45)	2782	5183	4227	56 (4)
C(46)	2710	5027	3573	44 (3)
C(51)	8437 (6)	174 (4)	2984 (3)	59 (4)
C(52)	9355	−765	3197	83 (5)
C(53)	9103	−1655	3142	90 (5)
C(54)	7933	−1606	2874	76 (5)
C(55)	7015	−666	2662	60 (4)
C(56)	7267	224	2717	47 (3)
C(61)	5442 (4)	372 (4)	1151 (3)	54 (4)
C(62)	5946	−383	683	64 (4)
C(63)	7385	−800	445	69 (4)
C(64)	8321	−462	674	66 (4)
C(65)	7817	293	1142	52 (4)
C(66)	6377	710	1380	45 (3)
C(71)	2893 (5)	2902 (4)	1196 (2)	57 (4)
C(72)	2280	3214	618	78 (5)
C(73)	3107	3299	7	83 (5)
C(74)	4549	3072	−27	75 (5)
C(75)	5162	2760	551	58 (4)
C(76)	4334	2675	1163	46 (3)
C(81)	4829 (8)	1666 (5)	3910 (3)	51 (3)
C(82)	3688 (8)	2550 (6)	4321 (4)	61 (4)
C(83)	6020 (9)	1110 (7)	4316 (4)	71 (4)
C(84)	4140 (9)	942 (6)	3761 (4)	69 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

μ_3-PBu^t ligands in **2a** lie above and below the Fe_3 plane, with the nitrogen atom being essentially equidistant from the three iron atoms (average 1.96 Å). However, the phosphorus atom is slightly closer to Fe(1) and Fe(2) [average 2.208 Å] than it is to Fe(3) [2.251 (4) Å].

Reaction of 2a and 2b with PhC≡CPh and EtC≡CEt. Cluster **2a** has been observed to slowly react with PhC≡CPh in refluxing cyclohexane to give the unusual binuclear complex **3**, the known ferracyclopentadiene complex **4a**[6] (eq 2), and two other minor

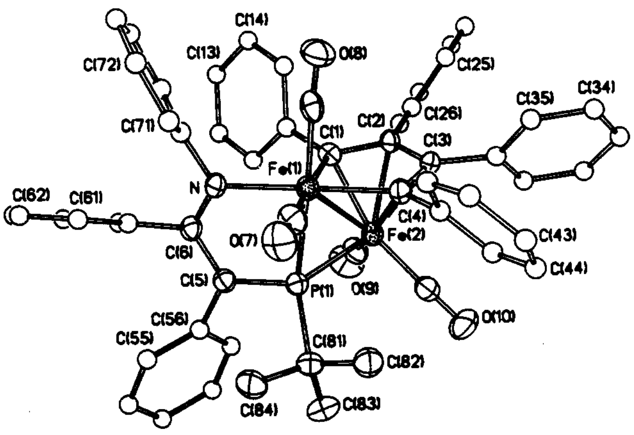
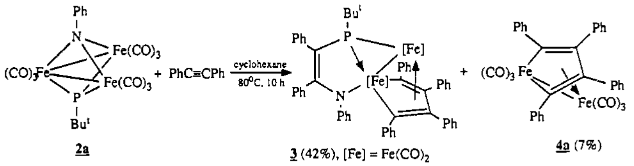


Figure 2. ORTEP drawing of $Fe_2(\mu_2,\eta^3$-PhNC(Ph)=C(Ph)PBu^t)(μ_2,η^4-PhC=C(Ph)C(Ph)=CPh)$(CO)_4$ (**3**). Thermal ellipsoids are drawn at the 40% probability level.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Fe_2(\mu_2,\eta^3$-PhNC(Ph)=C(Ph)PBu^t)(μ_2,η^4-PhC=C(Ph)C(Ph)=CPh)-$(CO)_4$ (**3**)

Bond Distances			
Fe(1)–Fe(2)	2.511 (2)	Fe(1)–P	2.277 (2)
Fe(2)–P	2.208 (3)	Fe(1)–N	2.048 (6)
Fe(1)–C(1)	2.083 (7)	Fe(1)–C(4)	2.001 (7)
Fe(2)–C(1)	2.050 (7)	Fe(2)–C(2)	2.156 (6)
Fe(2)–C(3)	2.169 (6)	Fe(2)–C(4)	2.165 (6)
P–C(5)	1.749 (7)	P–C(81)	1.894 (7)
N–C(6)	1.326 (7)	N–C(76)	1.424 (8)
C(1)–C(2)	1.413 (10)	C(2)–C(3)	1.445 (8)
C(3)–C(4)	1.427 (11)	C(5)–C(6)	1.423 (10)
Bond Angles			
Fe(1)–P–Fe(2)	68.1 (1)	Fe(1)–Fe(2)–P	57.3 (1)
Fe(2)–Fe(1)–P	54.7 (1)	Fe(1)–Fe(2)–C(1)	53.2 (2)
Fe(1)–Fe(2)–C(4)	50.0 (2)	Fe(1)–P–C(5)	102.1 (2)
Fe(1)–N–C(6)	102.6 (5)	P–Fe(1)–N	81.6 (2)
P–Fe(1)–C(1)	92.0 (2)	P–Fe(1)–C(4)	95.1 (2)
P–Fe(2)–C(1)	94.9 (2)	P–Fe(2)–C(4)	92.6 (2)
C(1)–Fe(1)–C(4)	79.8 (3)	C(1)–Fe(2)–C(4)	76.9 (2)
Fe(1)–C(1)–C(2)	114.0 (4)	Fe(1)–C(4)–C(3)	116.0 (4)
P–C(5)–C(6)	113.6 (4)	N–C(6)–C(5)	120.5 (6)



(2)

products that have not been identified (see Experimental Section). Complex **3** was isolated as a crystallographically characterized brown solid, and its spectroscopic data (see Experimental Section) are fully consistent with the determined structure. An ORTEP drawing of **3** is shown in Figure 2, and pertinent crystallographic data are given in Tables I, IV, and V. The molecule consists of two $Fe(CO)_2$ units joined by an Fe–Fe bond [2.511 (2) Å] and bridged by μ_2,η^2-$C_4(Ph)_4$ and μ_2,η^3-PhNC(Ph)=C(Ph)PBu^t ligands. The former has formed by the coupling of two alkynes, whereas the latter results from insertion of the alkyne between the imido and the phosphinidene ligands. The data given in Tables IV and V indicate that the ferracyclopentadiene ring is similar

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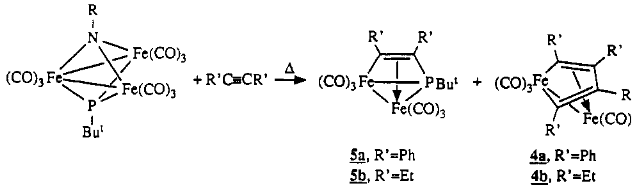
(6) (a) *Gmelin Handbuch der Anorganischen Chemie*, 8th ed.; Fe, Organoiron Compounds, Binuclear Compounds 3; Springer-Verlag: Berlin, 1980; pp 24–61. (b) Fehlhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol 4, p 548ff. (c) King, R. B.; Ackermann, M. N. *J. Organomet. Chem.* **1973**, *60*, C57. (d) Hubel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250.

Scheme I



Reaction A: **2a** + $EtC\equiv CEt$ → **5b** (35%) + **4b** (5%)

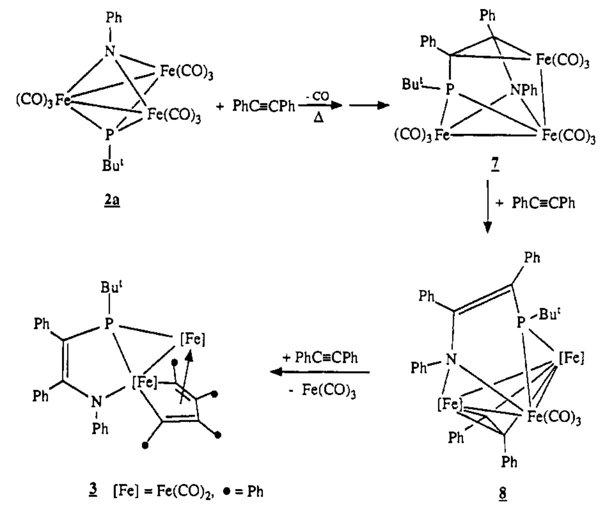
Reaction B: **2b** + $PhC\equiv CPh$ → **5a** (28%) + **4a** (3%)

to that found in many other ferracyclopentadiene complexes (e.g., $Fe_2(CO)_6(\mu_2,\eta^4\text{-}C_4(Ph)_4)$).[6] It is particularly noteworthy that although the valences of the nitrogen and phosphorus atoms are identical, the phosphorus atom binds in a bridging fashion as a μ_2-phosphido ligand whereas the nitrogen atom bonds to a single iron as a terminal amido ligand. The P–Fe(2) distance of 2.208 (3) Å is slightly shorter than the P–Fe(1) distance of 2.277 (2) Å, although their 2.243-Å average is close to the 2.222-Å average reported for 67 other iron–phosphido bonds.[7a] The Fe(1)–N distance of 2.048 (6) Å compares well to the 2.038-Å average Fe–N distance found in 78 Schiff base (σ-RN=CR$_2$) complexes.[7b] The coordination geometry about the amido ligand is trigonal planar (the sum of the angles about N is 359.8°), implying that the nitrogen lone pair is delocalized through π-bonding to the adjacent carbon atom and possibly to the iron atom. Consistent with this interpretation is the C(6)–N distance of 1.326 (7) Å, which compares well to the 1.337-Å average C–N distance found in pyridine and substituted pyridines.[8] The C(5)–C(6) distance of 1.423 (10) Å corresponds to a bond order between 1 and 2,[8,9] and the P–C(5) distance of 1.749 (7) Å is slightly shorter than normal P—C single-bond distances of 1.83–1.84 Å[1m] but is not as short as a typical P=C double-bond distance of 1.68–1.74 Å.[1m] Notably, the five-membered metallacycle Fe(1)–P–C(5)–C(6)–N is nearly planar [maximum deviation (Å): Fe(1), 0.076; P, –0.078; C(5), 0.060; C(6), 0.029; N, –0.087].

In contrast to the above reaction with $PhC\equiv CPh$, cluster **2a** was observed to react with $EtC\equiv CEt$ to give mainly the known[1v] binuclear complex $Fe_2(\mu_2,\eta^3\text{-}EtC{=}C(Et)PBu^t)(CO)_6$, (**5a**) (see reaction A in Scheme I) along with the ferracyclopentadiene complex **4b**[6] and two other minor products that have not been identified (see Experimental Section). The conversion of **2a** into **5a** requires the loss of an imido ligand, but the fate of this moiety was not determined. Aniline and azobenzene would be likely products, but they were not detected in the reaction mixture by gas chromatographic analysis. Cluster **2b** gave similar products in its reaction with $PhC\equiv CPh$ (see reaction B in Scheme I). The spectroscopic data for **5b** indicate it to be similar to the known compound **5a**.[1v] The IR spectra of the two compounds are similar, and **5b** shows a parent ion in its mass spectrum at m/z = 434, consistent with the given formulation. The singlet at δ 132.1 observed in its $^{31}P\{^1H\}$ NMR spectrum compares well to the corresponding resonance at δ 131 for **5a**.[1v] The ^{13}C NMR spectrum of **5b** showed two resonances at δ 128.2 and 119.2, assigned to the ring carbons, in addition to resonances due to the carbonyls, the phenyls, and the *tert*-butyl group.

Discussion

Scheme II



Although intermediates were not observed in the reactions described above, it is reasonable to suggest that in each case thermally-induced CO extrusion occurs to provide a coordination site for the added alkyne, followed by coupling of the μ_3-capping ligands with the alkyne. Product **3** may form by the sequence of reactions shown in Scheme II, which involves intermediates **7** and **8** that are analogous to clusters that have been shown to form as stable products from the reaction of the related cluster $Fe_3(\mu_3\text{-}PR)_2(CO)_9$ with $PhC\equiv CPh$.[1e,i] The last step in Scheme II involves displacement of an $Fe(CO)_3$ unit by a third alkyne and coupling of the alkynes to form a ferracyclopentadiene ring, a reaction with considerable literature precedent.[6] Complexes **5a,b** must form by a different mechanism since the NR ligand is not incorporated into the products. We do not know at which stage degradation of the cluster framework occurs to form these complexes, but it is not likely that this reaction proceeds via decay of the intermediates **7** and **8**.

Experimental Section

The compounds $H_2Fe_3(\mu_3\text{-}NPh)(CO)_9$ and $H_2Fe_3(\mu_3\text{-}NEt)(CO)_9$ were prepared by literature methods.[5h] The reagents $PhC\equiv CPh$, $EtC\equiv CEt$, and $AgBF_4$ (Aldrich Chemical Co.) and Bu^tPCl_2 (Strem Chemicals, Inc.) were purchased from the indicated sources and used as received. Solvents were dried by standard methods, and all manipulations of compounds were performed under N_2 using standard Schlenk techniques unless otherwise specified. IR spectra were recorded on an IBM FT-IR 32 spectrometer operated in the absorption mode, NMR spectra were obtained on a Bruker AM 300 FT-NMR spectrometer, and electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on an AEI-MS9 mass spectrometer. Photolyses were conducted in Pyrex Schlenk vessels using an unfiltered Hanovia 450-W medium-pressure Hg discharge lamp (Ace Glass, Inc.) in a Pyrex water-cooled immersion well. Gas chromatographic analyses were conducted on a Hewlett Packard 5890 gas chromatograph using a 3% SP-2100 prepacked column (Supelco, Inc.). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Synthesis of $Fe_3(\mu_3\text{-}NPh)(\mu_3\text{-}PBu^t)(CO)_9$ (2a). Method A. A solution of $Fe_3(\mu\text{-}H)_2(\mu_3\text{-}NPh)(CO)_9$ (**1a**) (930 mg, 1.81 mmol) and Bu^tPCl_2 (330 mg, 2.1 mmol) in anhydrous THF (100 mL) was irradiated for 1 h using the above-described lamp with constant stirring during which time the solution turned from dark brown to dark red. The solvent was removed under vacuum, and the residue was chromatographed on neutral alumina (activated, Brockmann I, ~150 mesh) with pentane as eluent to give first a yellow band of an uncharacterized compound (3 mg; IR(pentane) ν_{CO} = 2064 (m), 2028 (vs), 2002 (s), 1976 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.68 (br)) followed by a red-brown band of the bicapped cluster **2a** (902 mg, 83%).

2a. Anal. Calcd for $C_{19}H_{14}Fe_3NO_9P$: C, 38.11; H, 2.36. Found: C, 38.04; H, 2.91. IR (pentane): 2078 (w), 2048 (s), 2020 (vs), 2006 (s), 1988 (s), 1975 (m), 1944 (w) cm^{-1}. MS (EI): m/z = 599 (M$^+$, ^{56}Fe). ^1H NMR (CD_2Cl_2): δ 7.35–6.81 (m, 5 H, Ph), 1.56 (d, 9 H, J_{P-H} = 17 Hz, Bu^t). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 307.9.

Method B. To a solution of **1a** (103 mg, 0.20 mmol) and Bu^tPCl_2 (48 mg, 0.30 mmol) in dry CH_2Cl_2 (50 mL) was added $AgBF_4$ (156 mg, 0.80 mmol). The solution was stirred for 15 h during which time the initial dark brown color changed to dark red. The solution was filtered through Celite, and the solvent was evaporated under vacuum. The residue was chromatographed on neutral alumina (activated, Brockmann I, ~150 mesh) with pentane as eluent to give a red-brown band of the bicapped cluster **2a** in low yield (28 mg, 23%).

Synthesis of $Fe_3(\mu_3\text{-}NEt)(\mu_3\text{-}PBu^t)(CO)_9$ (2b). A solution of **1b** (93 mg, 0.20 mmol) and Bu^tPCl_2 (48 mg, 0.30 mmol) in dry THF (50 mL)

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(7) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1: (a) entry 8.3.1.2 in Table 3; (b) entry 4.12 in Table 3.

(8) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1987**, S1.

(9) Nyburg, S. C. *X-ray Analysis of Organic Structures*; Academic Press: New York, 1961.

was irradiated for 1 h using the above described lamp and with constant stirring. The solution was worked up as described above for the preparation of **2a** to give upon chromatography a yellow band of an uncharacterized compound (2 mg; IR(pentane) ν_{CO} = 2065 (m), 2028 (vs), 2000 (s), 1975 (w) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.68–1.32 (br)) followed by a red-brown band of the bicapped cluster **2b** (85 mg, 77%).

2b. Anal. Calcd for $C_{15}H_{14}Fe_3NO_9P$: C, 32.71; H. 2.56. Found: C, 32.60; H, 2.64. IR (pentane): 2074 (w), 2040 (vs), 2023 (s), 1996 (vs), 1978 (m), 1962 (w) cm^{-1}. MS (EI): m/z = 551 (M$^+$, ^{56}Fe). ^{1}H NMR ($CDCl_3$): δ 3.64 (q, 2 H, J_{H-H} = 6.8 Hz, NCH_2CH_3), 1.58 (t, 3 H, J_{H-H} = 6.8 Hz, NCH_2CH_3), 1.48 (d, 9 H, J_{P-H} = 17.2 Hz, Bu^t). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 323.8.

Reaction of $Fe_3(\mu_3\text{-}NPh)(\mu_3\text{-}PBu^t)(CO)_9$ (2a) with PhC≡CPh. A 100-mL Schlenk flask was charged with **2a** (60 mg, 0.10 mmol) and diphenylacetylene (36 mg, 0.20 mmol) to which was added 60 mL of dry cyclohexane. The solution was refluxed under N_2 with stirring for 10 h, during which time the color changed from red-brown to dark brown. The solvent was removed under vacuum, and chromatographic workup of the residue (SiO_2, TLC, hexane/CH_2Cl_2 = 7/1) gave first a yellow band of the ferracyclopentadiene complex **4a** (4.5 mg, 7%), a red-brown band of unreacted **2a** (17 mg, 28%), and a brown band of the binuclear complex **3** (40 mg, 42%). These were followed by an additional yellow-brown band (6 mg; IR(CH_2Cl_2) ν_{CO} = 2065 (s), 2026 (vs), 1998 (sh), 1988 (s), 1905 (w) cm^{-1}) and a dark green band (9 mg; IR(CH_2Cl_2) ν_{CO} = 2015 (s), 1993 (vs), 1966 (s), 1836 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.33–6.81 (m, Ph), 1.06 (d, J_{P-H} = 16.5 Hz, Bu^t)) of compounds which were isolated but not identified.

3. Anal. Calcd for $C_{56}H_{44}Fe_2NO_4P$: C, 71.73; H, 4.73. Found: C, 71.12; H, 4.20. IR (pentane): ν_{CO} = 2038 (w), 2014 (m), 1981 (vs), 1964 (s), 1939 (m), 1591 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.35–6.79 (m, 35 H, Ph), 1.16 (d, 9 H, J_{P-H} = 16.3 Hz, Bu^t). MS (FAB): m/z = 937 (M$^+$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 167.4.

4a. IR (pentane): ν_{CO} = 2065 (m), 2023 (s), 1985 (vs), 1941 (w) cm^{-1} (lit.[6d] ν_{CO} (hexane) = 2074, 2026, 1981, 1929 cm^{-1}). MS (EI): m/z = 636 (M$^+$).

Reaction of $Fe_3(\mu_3\text{-}NPh)(\mu_3\text{-}PBu^t)(CO)_9$ (2a) with EtC≡CEt. A 100-mL Schlenk flask was charged with **2a** (60 mg, 0.10 mmol) and EtC≡CEt (20 mg, 0.24 mmol) to which was added 60 mL of dry cyclohexane. The solution was refluxed under N_2 with stirring for 10 h and then worked up as described above for the reaction of **2a** with PhC≡CPh to give first a yellow band of the ferracyclopentadiene complex **4b** (2 mg, 5%), a yellow band of the known complex **5b** (16 mg, 35%), and a red-brown band of unreacted **2a** (22 mg, 37%). These were followed by an additional dark brown band (2 mg; IR (CH_2Cl_2) ν_{CO} = 2049 (w), 2034 (m), 1988 (s, sh), 1971 (vs), 1957 (s), 1932 (s), 1882 (w) cm^{-1}) and a green band (5 mg; IR (CH_2Cl_2) ν_{CO} = 2038 (m), 2011 (w), 1976 (m), 1965 (vs), 1951 (s), 1920 (m) cm^{-1}) of unidentified compounds.

5b. IR (pentane): ν_{CO} = 2057 (s), 2015 (s), 1989 (s), 1973 (vs), 1961 (m), 1933 (w) cm^{-1}. MS (EI): m/z = 450 (M$^+$). ^{1}H NMR (CD_2Cl_2): δ 2.51 (dq, 2 H, J_{H-H} = 7.5 Hz, J_{H-P} = 3.0 Hz, CH_2CH_3), 2.06 (dq, 2 H, J_{H-H} = 7.4 Hz, J_{H-P} = 14.8 Hz, CH_2CH[illegible] 1.47 (d, 9 H, J_{P-H} = 18.3 Hz, Bu^t), 1.39–1.21 (m, 6 H, CH_2CH_3). [illegible]$P\{^1H\}$ NMR (CD_2Cl_2): δ 131.2 (lit.[1v] ν_{CO} (pentane) = 2059 (s), 2017 (vs), 1990 (s), 1974 (s), 1962 (w), 1928 (vw) cm^{-1}; $^{31}P\{^1H\}$ NMR (toluene) δ 131).

4b. IR (pentane): ν_{CO} = 2062 (m), 2023 (s), 1986 (vs), 1938 (w) cm^{-1} (lit.[6] ν_{CO} (hexane) = 2069, 2031, 1984, 1930 cm^{-1}). MS (EI): m/z = 444 (M$^+$).

Reaction of $Fe_3(\mu_3\text{-}NEt)(\mu_3\text{-}PBu^t)(CO)_9$ (2b) with PhC≡CPh. A 100-mL Schlenk flask was charged with **2b** (52 mg, 0.10 mmol) and PhC≡CPh (36 mg, 0.20 mmol) to which was added 50 mL of dry *n*-hexane. The solution was refluxed under N_2 with stirring for 15 h and then worked up as described above for the reaction of **2a** with PhC≡CPh to give first a yellow band of the ferracyclopentadiene complex **4a** (2 mg, 3%), a yellow band of the binuclear complex **5a** (12 mg, 28%), and a red brown band of unreacted **2b** (24 mg, 55%). These were followed by an additional orange band (5 mg; IR(pentane) ν_{CO} = 2051 (m), 2008 (vs), 1994 (s), 1970 (w), 1940 (w), 1846 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.52–6.97 (m, Ph)) of an as of yet unidentified product.

5a. Anal. Calcd for $C_{24}H_{19}Fe_2O_6P$: C, 66.36; H, 4.41. Found: C, 66.14; H, 4.01. IR (pentane): ν_{CO} = 2057 (s), 2019 (vs), 1991 (s), 1966 (s), 1957 (m), 1932 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.26–7.05 (br, 10 H, Ph), 1.39 (d, 9 H, H_{P-H} = 19 Hz, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 212.9, 209.6 (Fe–CO), 136.1, 130.7, 130.6. 130.3, 128.5, 127.7, 127.2 (Ph), 128.2 (d, J_{P-C} = 14.6 Hz), 119.2 (*C*Ph), 36.5 (d, J_{P-C} = 12.2 Hz, $PC(CH_3)_3$), 29.6 (d, J_{P-H} = 4.9 Hz, $PC(CH_3)_3$). ^{31}P NMR (CD_2Cl_2): δ 132.1. MS (EI): m/z = 434 (M$^+$).

Crystal and Molecular Structures of 2a and 3. Crystallographic data for both structures are presented in Table I. Weakly diffracting specimens of both were mounted on glass fibers. Photographic characterization revealed *mmm* and $\bar{1}$ Laue symmetry for **2a** and **3**, respectively. *E* statistics for **2a** suggested the noncentrosymmetric alternative of the two space groups (*Pbc*2$_1$ and *Pbcm*) indicated by systematic absences in the diffraction data. The potential mirror plane in the structure of **2a** is not perpendicular to the *c* axis; refinement suggested that the noncentrosymmetric alternative was preferable. **3** was assumed to be centrosymmetric and was well-behaved. Empirical corrections for absorption were applied to both data sets.

Both structures were solved by direct methods. For **3**, two groups of atoms were found that probably represent disordered solvent molecules. These atoms are labeled CA and CG and were arbitrarily refined as full occupancy carbon atoms, but no chemical identity could be assigned from the crystallographic data. These contributions were not included in the calculated density. For both structures, all non-hydrogen atoms were refined with anisotropic thermal parameters, and the phenyl rings were constrained as rigid planar hexagons.

All computations used the SHELXTL (Version 5.1) program library (G. Sheldrick, Nicolet (Siemens), Madison, WI).

Acknowledgment. We thank the Department of Energy for support of this research and the National Science Foundation for partial support for the purchase of the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: For **2a** and **3**, tables of crystallographic parameters, bond lengths and angles, anisotropic and isotropic thermal parameters, and H atom coordinates (11 pages); tables of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.