Reactivity of Fe_3 and Ru_3 μ_3-Phenylimido Clusters with Alkynes, Allene, and 1,3-Cyclohexadiene

Jeong-Sup Song, Sung-Hwan Han, Sonbinh T. Nguyen, and Gregory L. Geoffroy*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Arnold L. Rheingold

Department of Chemistry, The University of Delaware, Newark, Delaware 19716

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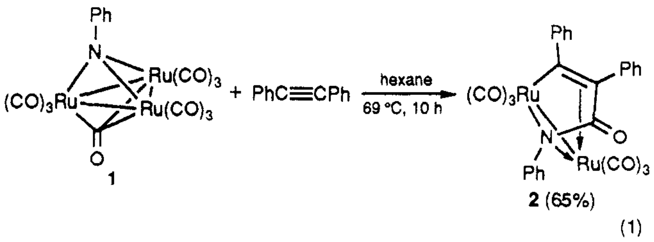
The reactivity of alkynes with the imido clusters $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$, $H_2Ru_3(\mu_3\text{-}NPh)(CO)_9$, $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$, $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$, and $H_2Fe_3(\mu_3\text{-}NPh)(CO)_9$ has been examined. The cluster $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ reacts regiospecifically with a series of alkynes to form the binuclear ferrapyrrolinone complexes $Fe_2(\mu_2\text{-}\eta^3\text{-}RC{=}C(R')C(O)NPh)(CO)_6$, possessing a metallacycle formed by coupling of the alkyne with CO and the imido ligand. These same ferrapyrrolinone complexes also form when $H_2Fe_3(\mu_3\text{-}NPh)(CO)_9$ is allowed to react with PhC≡CPh, EtC≡CEt, and PhC≡CMe. The derivative formed from PhC≡CMe was found to undergo subsequent substitution of one CO ligand by $Bu^tN{\equiv}C$ to form $Fe_2(\mu_2\text{-}\eta^3\text{-}PhC{=}C(Me)C(O)NPh)(CO)_5(CNBu^t)$, which was crystallographically characterized. The bis(imido) cluster $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ reacts with PhC≡CPh to form the tetranuclear cluster $Ru_4(\mu_3\text{-}NPh)_2(\eta^2\text{-}\mu_2\text{-}PhC{\equiv}CPh)(CO)_{10}$, which has been crystallographically shown to possess a butterfly arrangement of the four ruthenium atoms with the alkyne bridging the hinge of the butterfly in a perpendicular fashion and with the imido ligands bridging the open triangular faces of the butterfly. The analogous triiron cluster $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ reacts with PhC≡CPh to give a mixture of products, from which the ferracyclopentadiene $Fe_2(\mu_2\text{-}\eta^4\text{-}PhC{=}C(Ph)C(Ph){=}CPh)(CO)_6$ and the binuclear ferraazetine complex $Fe_2(\mu_2\text{-}\eta^3\text{-}PhC{=}C(Ph)NPh)(CO)_6$ were characterized. The latter compound possesses a four-membered metallacycle formed by coupling of the alkyne with the imido ligand. Treatment of $H_2Ru_3(\mu_3\text{-}NPh)(CO)_9$ with PhC≡CPh results in the formation of the cluster $Ru_4(\mu_4\text{-}NPh)(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)(CO)_{11}$, which has been crystallographically shown to possess a planar arrangement of the four ruthenium atoms bridged on one side by the μ_4-imido ligand and the other by the alkyne. The cluster $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ has also been found to react with 1,3-cyclohexadiene and with allene to respectively form the trinuclear clusters $Fe_3(\mu_3\text{-}NPh)(CO)_8(\eta^4\text{-}1,3\text{-cyclohexadiene})$ and $Fe_3(\mu_3\text{-}NPh)(CO)_8(\mu_2\text{-}\eta^6\text{-}C_6H_8)$. Crystallographic characterization has shown that in the former the diene has replaced two CO's and is coordinated to a single iron atom whereas in the latter two allenes have coupled through their central carbon atoms to form a C_6H_8 ligand that bridges two iron atoms with each C_3H_4 unit of the ligand η^3-bonded to a single iron.

Introduction

The reactions of *phosphinidene* (μ_3-PR, μ_4-PR) clusters of iron and ruthenium with alkynes have been extensively investigated by several research groups.[1] This work has led to the preparation of an impressive series of new compounds, many of which involve coupling of the alkyne and phosphinidene ligands. In contrast, the reactions of alkynes with *imido* (μ_3-NR) clusters has been scarcely examined, and only the mono(imido) cluster $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ (1) and its $Ph_2PCH_2PPh_2$-substituted derivative have been shown to react with alkynes to give mainly the binuclear complex 2 (eq 1)[2a] and its $Ph_2PCH_2PPh_2$ derivative.[2b] As an extension to our investigation of reaction 1, we now report the reactions of the related clusters $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (3), $H_2Ru_3(\mu_3\text{-}NPh)(CO)_9$ (4), $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ (5), $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ (6), and $H_2Fe_3(\mu_3\text{-}NPh)(CO)_9$ (7) with alkynes and where appropriate compare the observed reactivity to the reaction of alkynes with the analogous phosphinidene clusters. The surprising finding is the diversity of products that result from these seemingly related compounds. Also described are reactions of cluster 5 with allene and cyclohexadiene.



1

2 (65%)

(1)

Results and Discussion

Reactivity of $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ with Alkynes. The cluster $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ (5), like its Ru_3 analogue 1, also reacts with alkynes to form metallapyrrolinone complexes (eq 2). The ferrapyrrolinones 8a–g were isolated in good yields and were spectroscopically characterized. Their spectroscopic data indicate their structures to be analogous to those crystallographically determined for the Ru_3 analogue 2 (eq 1) and for the recently reported compounds $Fe_2(CO)_6(\mu_2\text{-}\eta^3\text{-}MeC{=}C(OEt)C(O)N(N{=}CPh_2))$[3a] and $Fe_2(CO)_6(\mu_2\text{-}\eta^3\text{-}MeC{=}C(NEt_2)C(O)NR)$ (R = Et, Ph).[3b] A parent ion was observed in the mass spectrum of each compound, and they displayed similar IR spectra, par-

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[1] (a) Knoll, K.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1986**, *312*, C57. (b) Knoll, K.; Orama, O.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 976. (c) Knoll, K.; Huttner, G.; Zsolnai, L.; Omara, O. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1119. (d) Knoll, K.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1986**, *307*, 237. (e) Lang, H.; Zsolnai, L.; Huttner, G. *Chem. Ber.* **1985**, *118*, 4426. (f) Jaeger, T.; Vahrenkamp, H. *Z. Naturforsch.* **1986**, *B41*, 789. (g) Lunniss, J.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* **1985**, *4*, 2066. (h) Field, J. S.; Haines, R. J.; Minshall, E.; Smit, D. N. *J. Organomet. Chem.* **1986**, *310*, C69. (i) Field, J. S.; Haines, R. J.; Honrath, U.; Smit, D. N. *J. Organomet. Chem.* **1987**, *329*, C25.

[2] (a) Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1987**, *6*, 2380. (b) Pizzotti, M.; Cenini, S.; Crotti, C.; Demartin, F. *J. Organomet. Chem.* **1989**, *375*, 123.

[3] (a) Nuel, D.; Dahan, F.; Mathieu, R. *Organometallics* **1986**, *5*, 1278. (b) Crocq, V.; Daran, J.-C.; Jeannin, Y. *J. Organomet. Chem.* **1989**, *373*, 85.

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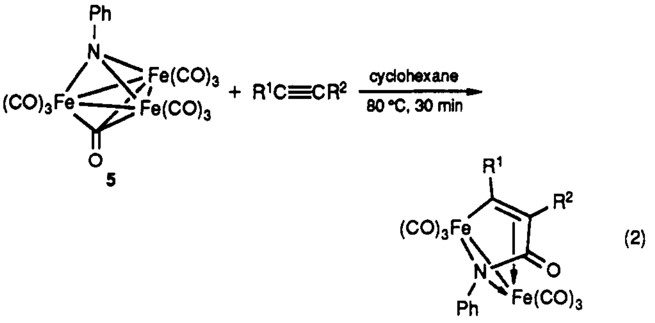


(2)

8a: R^1 = Ph, R^2 = Me (73%)
b: R^1 = R^2 = Ph (79%)
c: R^1 = R^2 = Et (63%)
d: R^1 = R^2 = Me (71%)
e: R^1 = H, R^2 = Me (66%)
f: R^1 = H, R^2 = Et (68%)
g: R^1 = H, R^2 = Ph (74%)

ticularly a ν_{CO} band around 1706 cm^{-1} attributed to the carbonyl group of the metallacycle. The ^{1}H and ^{13}C NMR data, summarized in Table I, indicate that the alkynes add regiospecifically to form only those isomers illustrated in eq 2. Each compound shows a ^{13}C NMR resonance in the δ 171–173 region attributed to the ketonic carbonyl carbon and resonances in the δ 158–187 and 98–111 regions respectively assigned to the α- and β-carbons of the metallacycle, which are derived from the added alkyne. For compounds **8e–g**, which result from terminal alkynes, HC≡CR, the resonances in the δ 155–158 region each appeared as a strong doublet due to coupling to an attached hydrogen atom (e.g., **8e**, δ 158.1, $^1J_{CH}$ = 159.3 Hz), confirming the assignment of this resonance to a carbon atom derived from the added alkyne. That these resonances are due to the α-carbon atoms of the metallacycle was indicated by the ^{13}C NMR resonances for the metallacycle carbonyl carbons, which appeared as doublets of quartets (e.g., **8e**, δ 173.5, $^3J_{CH}$ = 9.8, 3.7 Hz) due to three-bond coupling to both the hydrogen atom on the α-carbon and the three hydrogens of the methyl group attached to the β-carbon. If the alkyne had added in the opposite fashion to yield a product with the hydrogen on the β-carbon, the ketonic carbonyl carbon resonance would have appeared as a doublet with strong two-bond coupling but with weak or nonobservable four-bond coupling to the hydrogens on the methyl group bound to the α-carbon.

The ferrapyrrolinones **8b–d** prepared from the symmetrical alkynes RC≡CR (R = Ph, Et, Me) show distinctive ^{13}C NMR resonances for the alkyne substituent carbon atoms, which are now attached to the α- and β-carbons of the ferrapyrrolinone ring. For example, compound **8b** derived from PhC≡CPh shows ^{13}C NMR resonances at δ 148.4 and 134.6 assigned to the phenyl ipso carbons. The δ 134.6 resonance compares well with the corresponding phenyl ipso resonance at δ 133.8 for the ferrapyrrolinone **8g**, which was derived from PhC≡CH. The phenyl group in the latter compound is attached to the β-carbon of the metallacycle (see above), and therefore, the δ 134.6 resonance of **8b** can logically be attributed to the phenyl group attached to the β-carbon of this metallacycle. The δ 148.4 resonance is then assigned to the phenyl ipso carbon bound to the α-carbon. A similar spectral comparison can be made of **8c** with **8f** and of **8d** with **8e**, leading to the specific assignments given in Table I. A comparison of the positions of all the resonances of **8b–g** then leads to the assignment of the resonances given in Table I for the remaining compound **8a**, derived from the unsymmetrical alkyne MeC≡CPh, and to the conclusion that this alkyne has added regiospecifically to form the ferrapyrrolinone ring with the phenyl group bound to the α-carbon of the metallacycle.

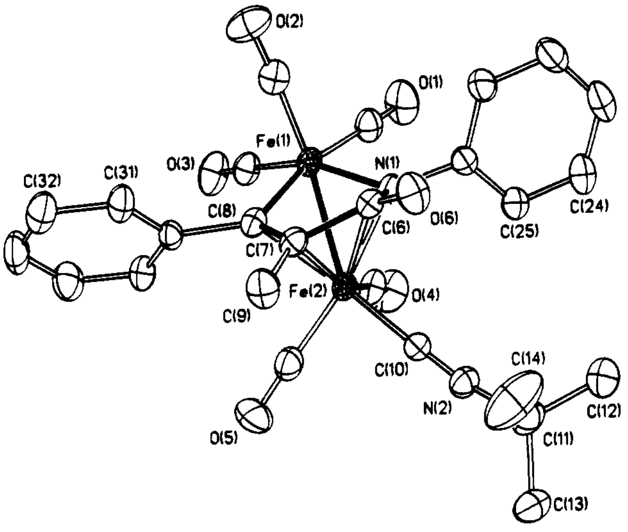
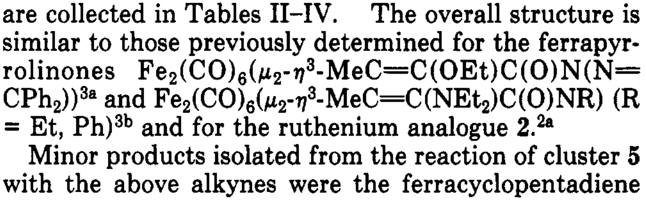


Figure 1. ORTEP drawing of Fe$_2$(μ_2-η^3-PhC=C(Me)C(O)NPh)(CO)$_5$(CNBu^t) (**9**).

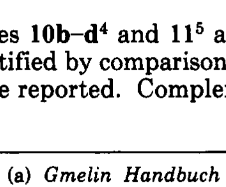
The latter assignment is supported by the crystallographic characterization of compound **9**, which resulted from substitution of Bu^{t}N≡C for one of the carbonyl carbons of **8a** (eq 3). An ORTEP drawing of the molecule



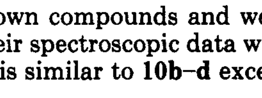
(3)

is shown in Figure 1, and relevant crystallographic data are collected in Tables II–IV. The overall structure is similar to those previously determined for the ferrapyrrolinones Fe$_2$(CO)$_6$(μ_2-η^3-MeC=C(OEt)C(O)N(N=CPh$_2$))[3a] and Fe$_2$(CO)$_6$(μ_2-η^3-MeC=C(NEt$_2$)C(O)NR) (R = Et, Ph)[3b] and for the ruthenium analogue **2**.[2a]

Minor products isolated from the reaction of cluster **5** with the above alkynes were the ferracyclopentadiene complexes **10a–d** and the dinuclear complex **11**. Com-



10a: R^1 = Ph, Me
b: R^1 = R^2 = Ph
c: R^1 = R^2 = Et
d: R^1 = R^2 = Me



11

plexes **10b–d**[4] and **11**[5] are known compounds and were identified by comparison of their spectroscopic data with those reported. Complex **10a** is similar to **10b–d** except

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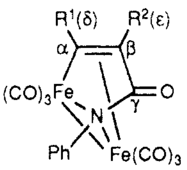
(4) (a) *Gmelin Handbuch der Anorganischen Chemie*, 8th ed., Springer-Verlag: Berlin, 1980; Fe, Organoiron Compounds, Binuclear Compounds 3. (b) King, R. B.; Ackermann, M. N. *J. Organomet. Chem.* **1973**, *60*, C57.

(5) Dekker, M.; Knox, G. R. *Chem. Commun.* **1967**, 1243.

Table I. Selected NMR Resonances for the Ferrapyrrolinone Complexes 8a–g

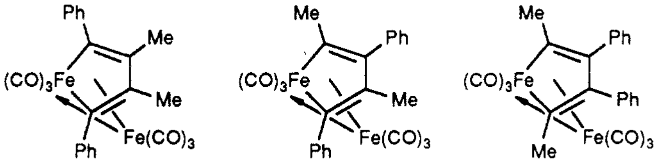


compd			^{13}C NMR, ppm					^{1}H NMR, ppm		
	R^1	R^2	C$_\alpha$	C$_\beta$	C$_\gamma$	C$_\delta$	C$_\epsilon$	H (C$_\alpha$)	H (C$_\delta$)	H (C$_\epsilon$)
8a	Ph	Me	182.1	98.4	172.4	146.6	17.1			2.15
8b	Ph	Ph	183.5	103.2	172.0	148.4	134.6			
8c	Et	Et	187.3	108.8	172.9	37.0	21.5		2.52	1.41
8d	Me	Me	181.1	101.8	173.3	30.4	14.7		2.67	2.16
8e	H	Me	158.1	103.9	173.5		18.7	8.14		2.24
8f	H	Et	155.6	111.1	173.2		25.9	8.17		2.57
8g	H	Ph	155.2	104.0	172.2		133.8	8.87		

Table II. Crystallographic Parameters for 9, 15, 22, and 23

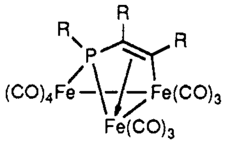
	9	15	22	23
		(a) Crystal Parameters		
formula	$C_{26}H_{22}O_6N_2Fe_2$	$Ru_4C_{36}H_{20}N_2O_{10}$	$Fe_3C_{20}H_{13}NO_8$	$Fe_3C_{19}H_{13}NO_7$
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
a, Å	12.354 (2)	12.506 (3)	13.750 (4)	8.511 (2)
b, Å	12.264 (2)	12.789 (3)	10.929 (3)	8.609 (2)
c, Å	17.949 (5)	22.432 (6)	14.461 (5)	14.209 (4)
α, deg				96.06 (2)
β, deg	96.87 (2)	92.30 (2)	103.19 (3)	91.22 (2)
γ, deg				107.31 (2)
V, Å^3	2700 (1)	3585 (2)	2116 (1)	986.9 (4)
Z	4	4	4	2
cryst dimens, mm	0.32 × 0.21 × 0.28	0.22 × 0.22 × 0.22	0.24 × 0.26 × 0.36	0.29 × 0.36 × 0.47
cryst color	red	red	deep red	deep red
D(calcd), g cm^{-3}	1.402	1.936	1.767	1.800
temp, °C	23	22	23	22
T(max)/T(min)	1.1	1.17	1.10	1.21
		(b) Data Collection		
diffractometer		Nicolet R3m/μ		
monochromator		graphite		
scan technique		Wyckoff		
radiation		Mo Kα (λ = 0.71073 Å)		
2θ scan range, deg	4–43	4–48	4–48	4–55
data collected	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm h,\pm k,+l$
no. of rflns collected	3246	6073	3675	4702
no. of indpt rflns	2944	5617	3320	4519
R(merg), %	2.40	1.8	2.5	1.8
no. of indpt rflns obsd	2121 ($F_o \geq 5\sigma(F_o)$)	4681 ($F_o \geq 5\sigma(F_o)$)	2563 ($F_o \geq 4\sigma(F_o)$)	3638 ($F_o \geq 5\sigma(F_o)$)
std rflns	3 stds/197 rflns			
var in stds, %	<1	<1	<1	<1
		(c) Refinement		
$R(F)$, %	3.92	2.61	3.14	3.39
$R(wF)$, %	4.14	3.17	3.46	3.85
Δ/σ(max)	0.027	0.10	0.07	0.05
$\Delta(\rho)$, e Å^{-3}	0.336	0.38	0.31	0.51
N_o/N_v	7.05	9.33	9.25	12.5
GOF	1.105	0.97	0.99	1.17

that the ^{1}H NMR data imply formation of a mixture of the regioisomers



but these isomers did not separate upon chromatographic workup.

It is interesting that the reactivity of $Fe_3(\mu_3\text{-NPh})(CO)_{10}$ with alkynes is significantly different from the corresponding reactivity of its phosphinidene analogues $Fe_3(\mu_3\text{-PR})(CO)_{10}$ (R = Bu^t, aryl),[1b] which gave the three different clusters 12–14, depending upon whether thermal



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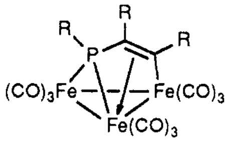

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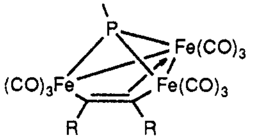

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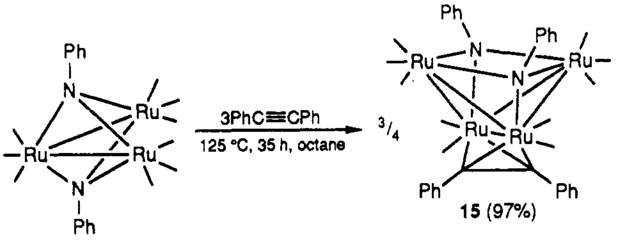
Table III. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for 9

	x	y	z	U^a
Fe(1)	1242.5 (6)	8523.2 (6)	7835.2 (4)	36.4 (3)
Fe(2)	−387.9 (6)	7371.3 (6)	7527.3 (4)	35.8 (3)
N(1)	934 (3)	7524 (3)	6981 (2)	35 (1)
N(2)	−1519 (3)	5860 (3)	6362 (2)	45 (2)
O(1)	1302 (4)	10483 (3)	6885 (2)	80 (2)
O(2)	3567 (3)	8106 (3)	8272 (3)	73 (2)
O(3)	843 (4)	10050 (3)	9016 (2)	74 (2)
O(4)	−1450 (4)	9458 (3)	7149 (2)	79 (2)
O(5)	−1943 (4)	6775 (4)	8546 (3)	90 (2)
O(6)	1443 (3)	5741 (3)	6708 (2)	53 (1)
C(1)	1270 (5)	9722 (4)	7237 (3)	51 (2)
C(2)	2677 (4)	8312 (4)	8091 (3)	46 (2)
C(3)	1021 (5)	9426 (5)	8582 (3)	50 (2)
C(4)	−994 (5)	8649 (4)	7299 (3)	52 (2)
C(5)	−1318 (5)	7034 (5)	8151 (3)	53 (2)
C(6)	1167 (4)	6404 (4)	7145 (3)	36 (2)
C(7)	875 (4)	6218 (4)	7904 (3)	36 (2)
C(8)	925 (4)	7168 (4)	8355 (3)	38 (2)
C(9)	722 (5)	5065 (4)	8141 (3)	51 (2)
C(10)	−1132 (4)	6464 (4)	6805 (3)	40 (2)
C(11)	−1818 (4)	5060 (4)	5762 (3)	49 (2)
C(12)	−1681 (6)	5634 (6)	5026 (3)	82 (3)
C(13)	−2982 (5)	4729 (5)	5787 (4)	73 (3)
C(14)	−1043 (6)	4131 (6)	5903 (5)	109 (4)
C(21)	2090 (2)	7943 (3)	5999 (2)	50 (2)
C(22)	2221	8336	5286	58 (3)
C(23)	1311	8647	4796	59 (3)
C(24)	271	8564	5018	57 (2)
C(25)	139	8171	5731	46 (2)
C(26)	1049	7861	6222	38 (2)
C(31)	1825 (3)	6393 (3)	9549 (2)	50 (2)
C(32)	1941	6280	10328	63 (3)
C(33)	1232	6825	10750	70 (3)
C(34)	406	7483	10393	64 (3)
C(35)	290	7596	9614	48 (2)
C(36)	999	7051	9192	37 (2)

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

or photochemical conditions were used.[1a–c] No compounds analogous to the ferrapyrrolinones **8a–g** have ever been observed in any of the phosphinidene reactions, although nitrogen analogues of clusters **12–14** may be intermediates en route to the ferrapyrrolinones.

Reactivity of $Fe_3(\mu_3\text{-NPh})_2(CO)_9$ and $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ with PhC≡CPh. The bis(imido) cluster $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (**3**) was found to react with diphenylacetylene in refluxing octane over the course of 35 h to form the new cluster $Ru_4(\mu_3\text{-NPh})_2(\mu_2\text{-}\eta^2\text{-PhC}{\equiv}\text{CPh})(CO)_{10}$ (**15**) (eq 4). Cluster **15** was isolated as an



3 **15** (97%) (4)

orange solid in 97% yield based on the amount of **3** consumed and was spectroscopically and crystallographically characterized. An ORTEP drawing of the cluster is shown in Figure 2, and the important crystallographic parameters are given in Tables II, V, and VI. The structure consists of a butterfly arrangement of the four Ru atoms with two μ_3-NPh ligands capping the open sides of the butterfly between one hinge and two wingtip atoms. Although a number of compounds are known to have butterfly structures with μ_3 ligands arranged in this fashion,[6] to our

Table IV. Bond Distances and Angles for 9

Bond Distances (Å)			
Fe(1)–Fe(2)	2.468 (1)	Fe(1)–N(1)	1.964 (4)
Fe(1)–C(8)	1.969 (5)	Fe(2)–N(1)	2.011 (4)
Fe(2)–C(6)	2.425 (5)	Fe(2)–C(7)	2.154 (5)
Fe(2)–C(8)	2.080 (5)	Fe(2)–C(10)	1.865 (5)
N(1)–C(6)	1.427 (6)	N(2)–C(10)	1.149 (6)
C(6)–C(7)	1.467 (7)	C(7)–C(8)	1.416 (7)
Bond Angles (deg)			
Fe(2)–Fe(1)–N(1)	52.5 (1)	Fe(2)–Fe(1)–C(8)	54.5 (1)
N(1)–Fe(1)–C(8)	79.2 (2)	Fe(1)–Fe(2)–N(1)	50.8 (1)
Fe(1)–Fe(2)–C(6)	72.0 (1)	N(1)–Fe(2)–C(6)	36.0 (2)
Fe(1)–Fe(2)–C(7)	76.4 (1)	N(1)–Fe(2)–C(7)	158.1 (2)
C(6)–Fe(2)–C(7)	36.8 (2)	Fe(1)–Fe(2)–C(8)	50.4 (1)
N(1)–Fe(2)–C(8)	75.5 (2)	C(6)–Fe(2)–C(8)	64.3 (2)
C(7)–Fe(2)–C(8)	39.0 (2)	Fe(1)–N(1)–C(6)	115.1 (3)
Fe(1)–C(8)–C(7)	114.9 (4)	N(1)–C(6)–C(7)	106.0 (4)
C(6)–C(7)–C(8)	113.8 (4)	Fe(2)–C(10)–N(2)	174.8 (4)

Table V. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $Ru_4(\mu_3\text{-NPh})_2(\mu_2\text{-}\eta^2\text{-PhC}{\equiv}\text{CPh})(CO)_{10}$ (15)

	x	y	z	U^a
Ru(1)	1643.3 (3)	4784.7 (3)	2898.9 (1)	25.9 (1)
Ru(2)	3857.4 (3)	4399.2 (3)	2976.2 (2)	26.7 (1)
Ru(3)	2089.9 (3)	2591.6 (3)	2932.2 (2)	25.9 (1)
Ru(4)	2315.1 (3)	4120.5 (3)	3869.5 (1)	24.6 (1)
N(1)	2661 (3)	3784 (3)	2390 (2)	26 (1)
N(2)	3362 (3)	3106 (3)	3504 (2)	28 (1)
C(1)	1734 (4)	5995 (4)	2330 (3)	48 (2)
O(1)	1733 (4)	6704 (4)	2026 (2)	82 (2)
C(2)	251 (4)	4646 (4)	2456 (2)	41 (2)
O(2)	−611 (3)	4618 (4)	2264 (2)	65 (2)
C(3)	4042 (4)	5543 (4)	2442 (2)	42 (2)
O(3)	4171 (4)	6197 (3)	2115 (2)	71 (2)
C(4)	5182 (4)	3761 (4)	2756 (3)	44 (2)
O(4)	5978 (3)	3428 (3)	2634 (2)	73 (2)
C(5)	4586 (4)	5235 (4)	3566 (2)	37 (2)
O(5)	5034 (3)	5810 (3)	3876 (2)	63 (2)
C(6)	831 (4)	2414 (4)	2420 (2)	37 (2)
O(6)	108 (3)	2270 (3)	2111 (2)	64 (2)
C(7)	2828 (4)	1478 (4)	2550 (2)	37 (1)
O(7)	3285 (3)	836 (3)	2327 (2)	63 (2)
C(8)	1453 (4)	1709 (4)	3515 (2)	41 (2)
O(8)	1041 (3)	1175 (3)	3838 (2)	68 (2)
C(9)	3148 (4)	4707 (4)	4508 (2)	42 (2)
O(9)	3643 (3)	5084 (4)	4886 (2)	76 (2)
C(10)	1576 (4)	3368 (4)	4456 (2)	37 (1)
O(10)	1083 (3)	2956 (3)	4795 (2)	61 (1)
C(11)	842 (3)	4935 (3)	3651 (2)	30 (1)
C(12)	1590 (3)	5644 (3)	3647 (2)	30 (1)
C(13)	−915 (2)	5650 (2)	3918 (2)	39 (2)
C(14)	−2004	5528	4013	48 (2)
C(15)	−2472	4539	3970	55 (2)
C(16)	−1851	3673	3832	50 (2)
C(17)	−763	3794	3737	42 (2)
C(18)	−295	4783	3780	30 (1)
C(19)	1423 (3)	7008 (3)	4406 (1)	49 (2)
C(20)	1619	8017	4621	71 (2)
C(21)	2238	8707	4299	69 (2)
C(22)	2662	8389	3762	69 (2)
C(23)	2466	7380	3547	53 (2)
C(24)	1847	6690	3869	37 (1)
C(25)	1966 (2)	3981 (3)	1351 (1)	56 (2)
C(26)	2090	3869	739	73 (3)
C(27)	3025	3431	530	62 (2)
C(28)	3837	3107	933	55 (2)
C(29)	3714	3219	1545	46 (2)
C(30)	2778	3657	1754	35 (1)
C(31)	3990 (2)	1364 (2)	3845 (1)	39 (2)
C(32)	4712	742	4176	50 (2)
C(33)	5538	1205	4519	56 (2)
C(34)	5641	2291	4532	55 (2)
C(35)	4918	2914	4201	46 (2)
C(36)	4093	2450	3858	29 (1)

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

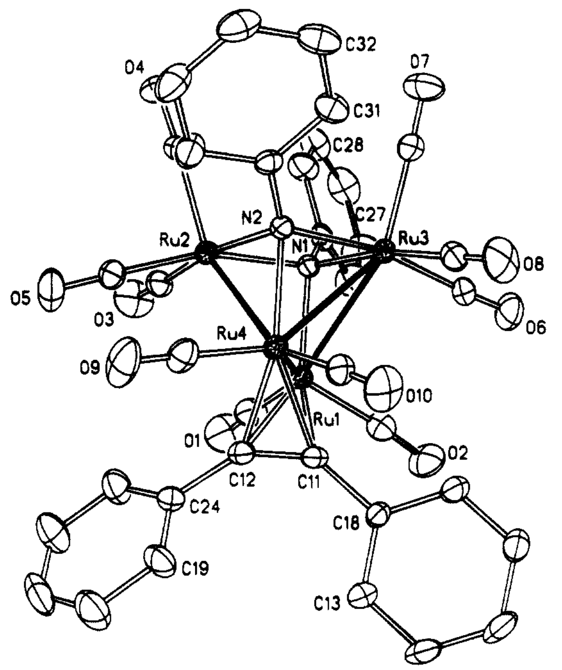


Figure 2. ORTEP drawing of $Ru_4(\mu_3\text{-}NPh)_2(\mu_2\text{-}\eta^2\text{-}PhC{\equiv}CPh)(CO)_{10}$ (**15**).

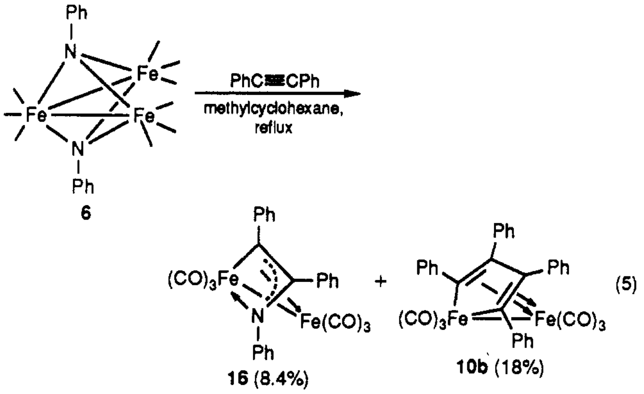
Table VI. Selected Bond Distances and Angles for $Ru_4(\mu_3\text{-}NPh)_2(\mu_2\text{-}\eta^2\text{-}PhC{\equiv}CPh)(CO)_{10}$ (15)

(a) Bond Distances (Å)			
Ru(1)–Ru(2)	2.8229 (6)	Ru(4)–C(11)	2.155 (4)
Ru(1)–Ru(3)	2.8711 (6)	Ru(1)–C(12)	2.181 (4)
Ru(1)–Ru(4)	2.6319 (5)	Ru(4)–C(12)	2.199 (4)
Ru(2)···Ru(3)	3.1970 (7)	C(11)–C(12)	1.303 (6)
Ru(2)–Ru(4)	2.8589 (6)	Ru(1)–C(1)	1.889 (5)
Ru(3)–Ru(4)	2.8770 (6)	Ru(1)–C(2)	1.892 (5)
Ru(2)–N(1)	2.105 (3)	Ru(2)–C(3)	1.911 (5)
Ru(3)–N(1)	2.095 (3)	Ru(2)–C(4)	1.928 (5)
Ru(2)–N(2)	2.140 (3)	Ru(2)–C(5)	1.905 (5)
Ru(3)–N(2)	2.109 (3)	Ru(3)–C(6)	1.925 (5)
N(1)···N(2)	2.755 (5)	Ru(3)–C(7)	1.918 (5)
Ru(1)–N(1)	2.058 (3)	Ru(3)–C(8)	1.923 (5)
Ru(4)–N(2)	2.039 (3)	Ru(4)–C(9)	1.892 (5)
Ru(1)–C(11)	2.182 (4)	Ru(4)–C(10)	1.900 (5)
(b) Bond Angles (deg)			
N(1)–Ru(2)–N(2)	80.9 (1)	C(1)–Ru(1)–C(2)	85.1 (2)
N(1)–Ru(3)–N(2)	81.9 (1)	C(9)–Ru(4)–C(10)	86.9 (2)
Ru(2)–N(1)–Ru(3)	99.2 (1)	C(3)–Ru(2)–C(4)	92.1 (2)
Ru(2)–N(2)–Ru(3)	97.6 (1)	C(3)–Ru(2)–C(5)	86.5 (2)
Ru(1)–N(1)–C(30)	127.5 (2)	C(4)–Ru(2)–C(5)	91.4 (2)
Ru(4)–N(2)–C(36)	124.0 (2)	C(6)–Ru(3)–C(7)	92.4 (2)
Ru(2)–Ru(1)–Ru(3)	68.3 (1)	C(6)–Ru(3)–C(8)	89.2 (2)
Ru(2)–Ru(4)–Ru(3)	67.8 (1)	C(7)–Cu(3)–C(8)	95.1 (2)
Ru(1)–Ru(2)–Ru(4)	55.2 (1)	all Ru–C–O	177 ± 1.5
Ru(1)–Ru(3)–Ru(4)	54.5 (1)		

knowledge this is the first bis(imido) cluster to have this structure. The alkyne ligand bridges the two hinge atoms as a perpendicular 4e donor, although the C(11)–C(12) bond length of 1.303 (6) Å is close to a typical C–C double bond value and is 0.12 Å shorter than the corresponding C–C distance of 1.424 Å found in cluster **19** described below. The Ru–N distances in the Ru_2N_2 rhombus of **15** average 2.11 Å and are somewhat longer than the average Ru–N distance of 2.05 Å to the butterfly-hinge Ru atoms. Both are similar to the 2.053-Å average Ru–N distances in the μ_3-imido cluster $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$.[7] The Ru–Ru distances to the wingtips of **15** average 2.856 Å, similar to the 2.8541-Å average Ru–Ru distance in $Ru_3(CO)_{12}$.[8] The unique Ru(1)–Ru(4) distance in the hinge of the butterfly is 2.6319 (5) Å. The Ru(2)–Ru(3) distance is 3.1970 (7) Å, suggesting some degree of Ru–Ru bonding across the Ru_2N_2 rhombus.

The conversion of **3** into **15** requires the loss of $^3/_2$ CO's and formation of $^1/_2$ equiv of "NPh", but the form of the lost imido ligand was not determined. No IR bands characteristic of PhNCO (ν_{CO} = 2260 cm^{-1}), its dimer (ν_{CO} = 1778 cm^{-1}), or its trimer (ν_{CO} = 1709 cm^{-1})[9] were detected in the IR spectrum of the reaction mixture, and no azobenzene was detected by TLC. Interestingly, reaction 4 occurred only under thermal conditions and did not proceed upon photolysis or upon opening of a coordination site through the use of Me_3NO. These latter reactions gave mainly decomposition of the starting complex **3**. In contrast, the reaction of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ (**1**) with alkynes occurred readily upon photolysis or by using Me_3NO to give products similar to those in the thermal reaction shown in eq 1.[2a]

The cluster $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ (**6**) reacts with PhC≡CPh in a dramatically different fashion than its Ru_3 analogue. In refluxing methylcyclohexane, cluster **6** and PhC≡CPh gave a low-yield mixture of the ferraazetine complex **16** and the ferracyclopentadiene compound **10b**[4] (eq 5), along with two other products that have not been identified. Complex **16** was isolated as an orange microcrystalline solid and was spectroscopically characterized. It is analogous to the known derivatives **17**[10] and **18**,[11] which were prepared by quite different means. The IR spectrum of **16** is similar to those of **17** and **18**, and **16** shows a parent ion in its mass spectrum at m/z = 549, consistent with the given formulation. Its ^{13}C NMR spectrum shows two resonances at δ 125.3 and 117.1, assigned to the carbon atoms in the metallacycle, and these

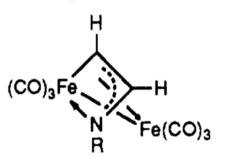


6

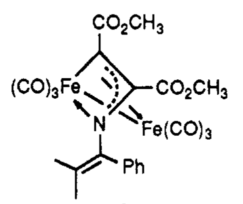
16 (8.4%)

10b (18%)

(5)



17 (R = Ph, Bu^t)



18

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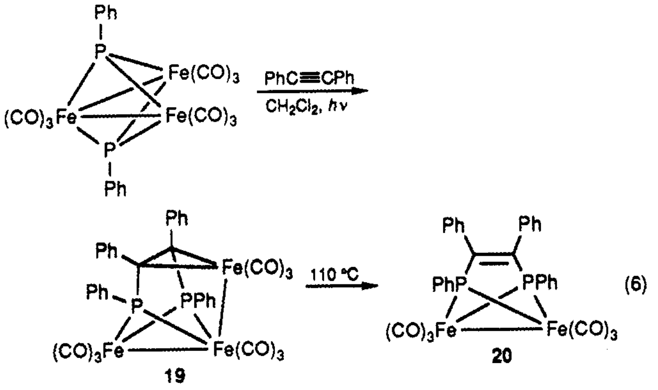
(11) Nakamura, Y.; Bachmann, K.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta* **1978**, *61*, 589.

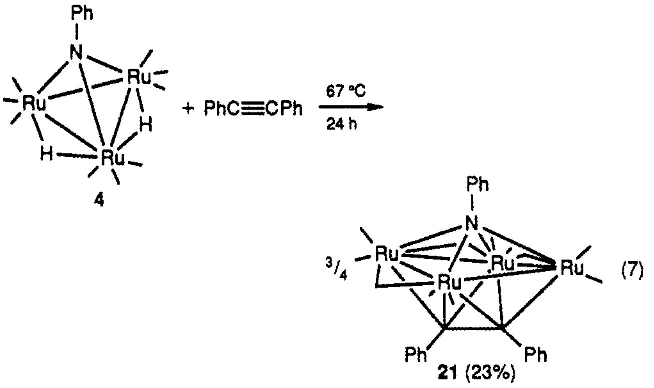
compare well with corresponding resonances at δ 113.3 and 109.3 reported for 17 (R = Ph).

Different still from the reactions of alkynes with either of the imido $M_3(\mu_3\text{-NPh})_2(CO)_9$ clusters described above is the reported reactivity of the phosphinidene analogue of 6. This species reacts with PhC≡CPh under photochemical conditions to first give cluster 19, which upon heating loses a $Fe(CO)_x$ fragment to form the binuclear compound 20 (eq 6).[1d,e] To our knowledge, the reactivity of alkynes with the corresponding $Ru_3(\mu_3\text{-PPh})_2(CO)_9$ cluster has not been reported.

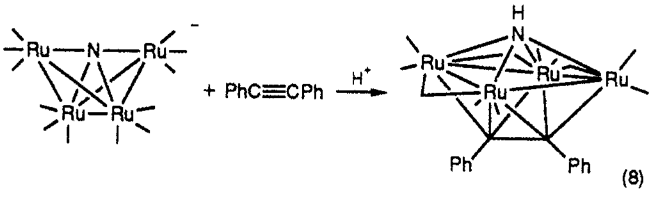


19 20 (6)

Reactivity of $H_2Ru_3(\mu_3\text{-NPh})(CO)_9$ and $H_2Fe_3(\mu_3\text{-NPh})(CO)_9$ with Alkynes. The cluster $H_2Ru_3(\mu_3\text{-NPh})(CO)_9$ (4) reacts with diphenylacetylene to give as the main product the tetraruthenium cluster 21 (eq 7), which was isolated as an orange solid in 23% yield based upon the amount of 4 consumed. Complex 21 was spectroscopically and crystallographically characterized. An ORTEP drawing of the cluster framework is shown in Figure 3, although details of its structure determination have been published elsewhere.[12] The similar cluster $Ru_4(\mu_4\text{-NPh})(CO)_{11}(PhC{\equiv}CPh)$ has been prepared by Gladfelter et al.,[13] but by the quite different route shown in eq 8. The reaction of eq 7 is obviously a complex transformation involving loss of H_2, incorporation of the alkyne ligand, and scavenging of an additional ruthenium atom. The overall yield of 21 is accordingly modest. Two other fractions were separated upon chromatographic workup of the reaction mixture, but the spectroscopic data were inconclusive as to their structures.



4 21 (23%) (7)



(8)

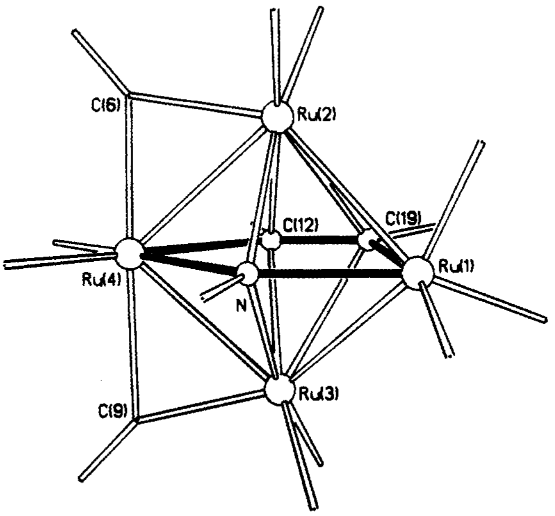
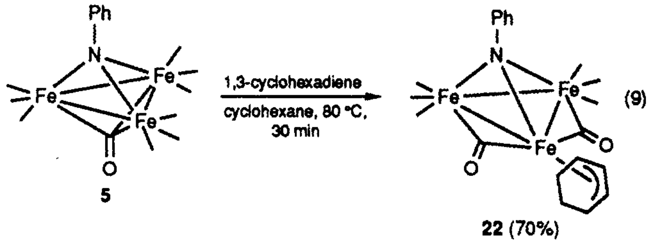


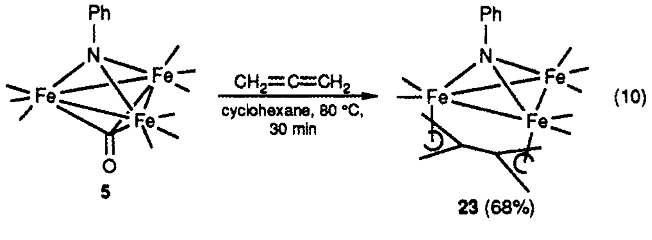
Figure 3. Drawing of the cluster framework for $Ru_4(\mu_4\text{-NPh})(\mu_4\text{-}\eta^2\text{-PhC{\equiv}CPh})(CO)_{11}$ (21), emphasizing the equatorial plane of the pentagonal-bipyramidal structure.

The cluster $H_2Fe_3(\mu_3\text{-NPh})(CO)_9$ (7) was found to react quite differently with the alkynes PhC≡CPh, EtC≡CEt, and PhC≡CMe than its Ru_3 analogue described above. The main products of these reactions were the above-described ferrapyrrolinone complexes **8a–c** along with small amounts of the ferracyclopentadienyl complexes **10b–d** and the azobenzene complex 11. The reactivity of alkynes with the phosphinidene clusters $H_2Ru_3(\mu_3\text{-PPh})(CO)_9$ and $H_2Fe_3(\mu_3\text{-PPh})(CO)_9$ has not been reported, and thus a comparison of the reactivity of alkynes with phosphinidene and imido clusters cannot be made for this family of compounds.

Reaction of $Fe_3(\mu_3\text{-NPh})(CO)_{10}$ with 1,3-Cyclohexadiene and with Allene. The mono(imido) cluster $Fe_3(\mu_3\text{-NPh})(CO)_{10}$ (5) was also observed to react with 1,3-cyclohexadiene to yield cluster 22 (eq 9), in which the diene has replaced two CO's and is coordinated to a single iron atom. The surprising product of the reaction of cluster 5 with allene is compound 23 (eq 10), which possesses an $\eta^6\text{-}C_6H_8$ ligand that results from coupling of two allene molecules. Each C_3H_4 unit of the $\eta^6\text{-}C_6H_8$ ligand is η^3-bonded to a single iron atom, with the entire ligand bridging two iron atoms. Both clusters 22 and 23 were isolated as dark brown solids and were spectroscopically and crystallographically characterized. ORTEP drawings are shown in Figures 4 and 5, and relevant crystallographic



5 22 (70%) (9)



5 23 (68%) (10)

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[12] Rheingold, A. L.; Staley, D. L.; Han, S.-H.; Geoffroy, G. L. *Acta Crystallogr.* **1988**, *C44*, 570.

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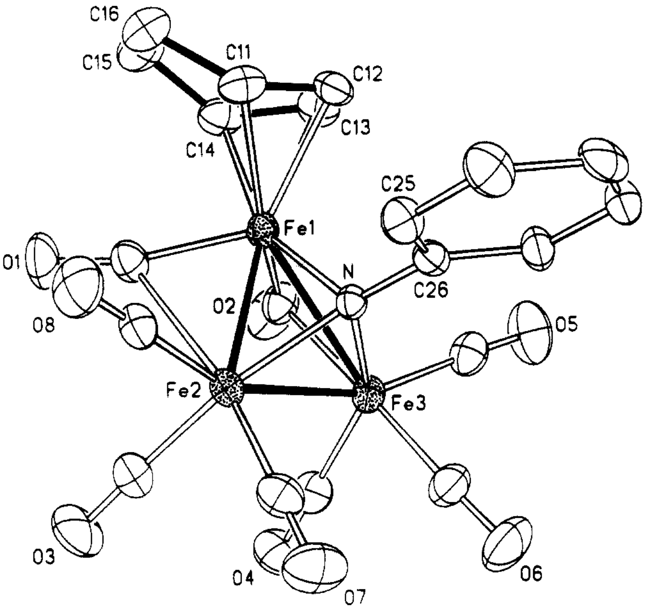


Figure 4. ORTEP drawing of $Fe_3(\mu_3\text{-}NPh)(\eta^4\text{-}C_6H_8)(CO)_8$ (**22**).

Table VII. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $Fe_3(\mu_3\text{-}NPh)(\eta^4\text{-}C_6H_8)(CO)_8$ (22)

	x	y	z	U^a
Fe(1)	2221.3 (4)	8830.4 (5)	4881.6 (4)	29.9 (2)
Fe(2)	2041.8 (4)	6561.4 (5)	5251.6 (4)	31.0 (2)
Fe(3)	1220.7 (4)	7369.8 (5)	3624.2 (4)	32.8 (2)
O(1)	1770 (3)	8688 (3)	6757 (2)	63 (1)
O(2)	198 (2)	9730 (3)	4041 (2)	65 (1)
O(3)	266 (2)	6113 (3)	6025 (3)	74 (1)
O(4)	−861 (2)	6847 (3)	3738 (3)	69 (1)
O(5)	981 (3)	8721 (4)	1811 (2)	79 (2)
O(6)	1386 (3)	5081 (3)	2631 (2)	77 (1)
O(7)	2210 (2)	3991 (3)	4714 (3)	66 (1)
O(8)	3614 (2)	6252 (3)	6997 (2)	63 (1)
C(1)	1915 (3)	8580 (4)	6005 (3)	42 (1)
C(2)	909 (3)	9125 (4)	4232 (3)	44 (1)
C(3)	956 (3)	6304 (4)	5732 (3)	45 (1)
C(4)	−66 (3)	7067 (4)	3694 (3)	47 (1)
C(5)	1077 (3)	8224 (4)	2519 (3)	47 (1)
C(6)	1312 (3)	5961 (4)	3029 (3)	48 (2)
C(7)	2129 (3)	4995 (4)	4907 (3)	43 (1)
C(8)	3015 (3)	6386 (4)	6324 (3)	40 (1)
C(11)	3735 (3)	9327 (4)	5569 (3)	43 (1)
C(12)	3459 (3)	9725 (4)	4627 (3)	44 (1)
C(13)	2624 (3)	10506 (4)	4400 (3)	48 (2)
C(14)	2190 (3)	10780 (4)	5172 (3)	49 (2)
C(15)	2832 (4)	11061 (4)	6135 (3)	61 (2)
C(16)	3727 (3)	10192 (4)	6384 (3)	61 (2)
N	2587 (2)	7340 (3)	4309 (2)	27 (1)
C(21)	3482 (2)	7269 (2)	3026 (1)	40 (1)
C(22)	4342	7014	2704	47 (2)
C(23)	5188	6554	3331	53 (2)
C(24)	5173	6350	4280	51 (2)
C(25)	4313	6605	4602	39 (1)
C(26)	3467	7065	3975	32 (1)

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

data are given in Tables II and VII–X.

Table VIII. Selected Bond Distances and Angles for $Fe_3(\mu_3\text{-}NPh)(\eta^4\text{-}C_6H_8)(CO)_8$ (22)

	(a) Bond Distances (Å)		
Fe(1)–Fe(2)	2.561 (1)	Fe(1)–C(11)	2.162 (4)
Fe(1)–Fe(3)	2.570 (1)	Fe(1)–C(12)	2.068 (4)
Fe(2)–Fe(3)	2.526 (1)	Fe(1)–C(13)	2.079 (4)
Fe(1)–N	1.944 (3)	Fe(1)–C(14)	2.174 (4)
Fe(2)–N	1.900 (3)	C(11)–C(12)	1.398 (6)
Fe(3)–N	1.913 (3)	C(12)–C(13)	1.407 (6)
Fe(1)–C(1)	1.790 (4)	C(13)–C(14)	1.413 (7)
Fe(2)–C(1)	2.484 (4)	C(14)–C(15)	1.500 (6)
Fe(1)–C(2)	1.862 (4)	C(15)–C(16)	1.531 (7)
Fe(3)–C(2)	2.193 (4)	C(16)–C(11)	1.513 (6)
	(b) Bond Angles (deg)		
Fe(1)–Fe(2)–Fe(3)	60.71 (5)	Fe(1)–C(2)–O(2)	152.4 (3)
Fe(2)–Fe(3)–Fe(1)	60.30 (5)	Fe(3)–C(2)–O(2)	129.3 (3)
Fe(3)–Fe(1)–Fe(2)	59.02 (5)	Fe–C(3–8)–O(3–8)	177 ± 1.5
Fe(1)–N–Fe(2)	83.5 (1)	C(11)–C(12)–C(13)	116.3 (4)
Fe(1)–N–Fe(3)	83.6 (1)	C(12)–C(13)–C(14)	114.4 (4)
Fe(2)–N–Fe(3)	83.0 (1)	C(13)–C(14)–C(15)	120.8 (4)
Fe(1)–C(1)–Fe(2)	71.5 (1)	C(14)–C(15)–C(16)	111.2 (4)
Fe(1)–C(1)–O(1)	164.9 (4)	C(15)–C(16)–C(11)	110.7 (3)
Fe(2)–C(1)–O(1)	123.2 (3)	C(16)–C(11)–C(12)	121.0 (4)
Fe(1)–C(2)–Fe(3)	78.2 (2)		

Table IX. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $Fe_3(\mu_3\text{-}NPh)(\eta^6\text{-}C_6H_8)(CO)_7$ (23)

	x	y	z	U^a
Fe(1)	2688 (1)	1422 (1)	3037 (1)	33 (1)
Fe(2)	995 (1)	3443 (1)	3211 (1)	33 (1)
Fe(3)	−168 (1)	668 (1)	2224 (1)	29 (1)
N	1745 (3)	2431 (3)	2112 (2)	29 (1)
O(1)	4340 (4)	−842 (4)	2124 (2)	85 (1)
O(2)	640 (4)	−1136 (4)	4078 (2)	73 (1)
O(3)	−1940 (3)	1723 (3)	4149 (2)	52 (1)
O(4)	−875 (4)	5582 (4)	2629 (2)	77 (1)
O(5)	−2819 (3)	−1899 (3)	2996 (2)	60 (1)
O(6)	−2536 (3)	1673 (4)	1082 (2)	63 (1)
O(7)	676 (3)	−1591 (3)	769 (2)	73 (1)
C(1)	3690 (4)	49 (5)	2474 (3)	51 (1)
C(2)	1306 (4)	−135 (4)	3620 (2)	45 (1)
C(3)	−795 (4)	2221 (4)	3727 (2)	37 (1)
C(4)	−131 (4)	4755 (4)	2860 (3)	48 (1)
C(5)	−1791 (4)	−911 (4)	2710 (2)	38 (1)
C(6)	−1914 (4)	1269 (4)	1514 (2)	39 (1)
C(7)	289 (4)	−741 (4)	1326 (2)	45 (1)
C(8)	4142 (4)	3397 (4)	3893 (2)	48 (1)
C(9)	3927 (5)	2059 (5)	4416 (3)	57 (1)
C(10)	5019 (4)	3289 (5)	3058 (3)	51 (1)
C(11)	3141 (4)	4531 (4)	4014 (3)	49 (1)
C(12)	1856 (5)	4350 (5)	4659 (3)	59 (1)
C(13)	3084 (4)	5616 (4)	3331 (3)	59 (1)
C(21)	1833 (3)	4267 (2)	893 (1)	46 (1)
C(22)	2277	4743	4	56 (1)
C(23)	3199	3949	−556	62 (1)
C(24)	3677	2679	−226	54 (1)
C(25)	3233	2203	664	43 (1)
C(26)	2311	2997	1223	34 (1)

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

The structures of **22** and **23** are both based on nearly equilateral triangles of Fe atoms. In both cases the μ_3-NPh capping group is slightly displaced away from the coordinated organic molecules. In **22**, two carbonyl groups (1 and 2) adopt semibridging positions, forming closer attachments to Fe(1). The unbridged Fe(2)–Fe(3) bond is significantly shorter (2.526 (1) Å) than the average of the other two (2.566 Å). These semibridging bonds result from the fractional electron deficiency (formally $17^1/_3$ electrons) at Fe(2) and Fe(3). A similar, but smaller, effect is seen in **23**, in which carbonyl groups 2 and 3 are slightly inclined toward Fe(3). In **23** the tetramethyleneethylene-bridged Fe(1)–Fe(2) distance, 2.566 (1) Å, is slightly longer than the 2.544 (1) Å average of the other two. In **22**, the η^4-cyclohexadiene molecule makes shorter Fe–C bonds (average 2.074 (4) Å) to the interior atoms of the conjugated system than to the outer atoms (average 2.166 (4) Å). The η^6-tetramethyleneethylene ligand in **23** symmetrically bridges the Fe(1)–Fe(2) bond; the central C(8)–C(11) bond is essentially parallel to the Fe–Fe bond. The η^6 ligand is planar, and the C–C–C and H–C–H angles all suggest the assemblage of six sp^2-hybridized carbon atoms, al-

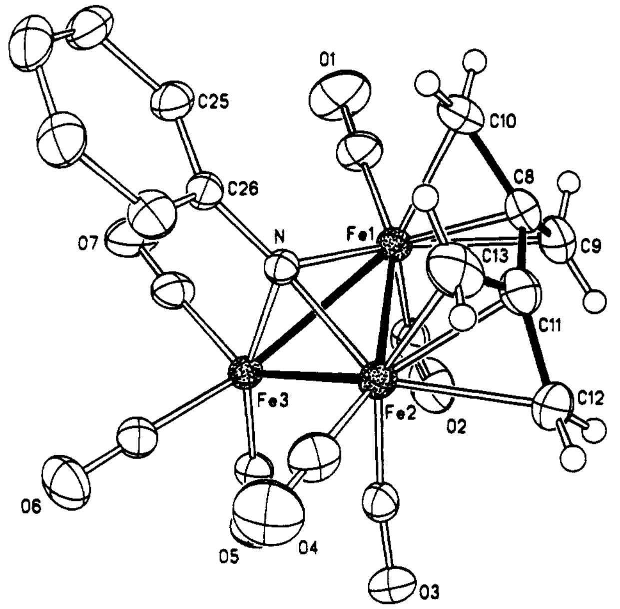
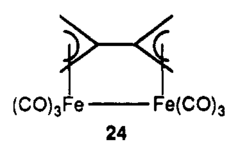


Figure 5. ORTEP drawing of $Fe_3(\mu_3\text{-}NPh)(\mu_2\text{-}\eta^6\text{-}C_6H_8)(CO)_7$ (**23**).

Table X. Selected Bond Distances and Angles for $Fe_3(\mu_3\text{-}NPh)(\eta^6\text{-}C_6H_8)(CO)_7$ (23)

	(a) Bond Distances (Å)		
Fe(1)–Fe(2)	2.566 (1)	Fe(2)–C(11)	2.044 (3)
Fe(1)–Fe(3)	2.539 (1)	Fe(2)–C(12)	2.152 (3)
Fe(2)–Fe(3)	2.546 (1)	Fe(2)–C(13)	2.151 (3)
Fe(1)–N	1.933 (3)	C(8)–C(9)	1.405 (6)
Fe(2)–N	1.922 (2)	C(8)–C(10)	1.424 (5)
Fe(3)–N	1.890 (2)	C(8)–C(11)	1.474 (6)
Fe(1)–C(8)	2.037 (3)	C(11)–C(12)	1.426 (5)
Fe(1)–C(9)	2.143 (4)	C(11)–C(13)	1.425 (6)
Fe(1)–C(10)	2.147 (3)		
	(b) Bond Angles (deg)		
Fe(1)–Fe(2)–Fe(3)	59.63 (6)	C(1)–Fe(1)–C(2)	93.6 (2)
Fe(2)–Fe(3)–Fe(1)	60.57 (6)	C(3)–Fe(2)–C(4)	90.5 (2)
Fe(3)–Fe(1)–Fe(2)	59.81 (6)	C(5)–Fe(3)–C(6)	93.1 (1)
Fe(1)–N–Fe(2)	83.5 (1)	C(5)–Fe(3)–C(7)	94.4 (1)
Fe(1)–N–Fe(3)	83.2 (1)	C(6)–Fe(3)–C(7)	97.2 (1)
Fe(2)–N–Fe(3)	83.8 (1)	C(9)–C(8)–C(10)	114.0 (4)
Fe(1)–C(2)–O(2)	169.0 (3)	C(12)–C(11)–C(13)	113.4 (4)
Fe(2)–C(3)–O(3)	166.8 (3)	H–C(9,10,12,13)–H (av)	113 (3)
other Fe–C–O	177.5 ± 1.5		

though the length of the C(8)–C(11) bond, 1.474 (6) Å, suggests only weak conjugation between the allylic coordinated ends. The binuclear complex **24**, possessing a η^6-C_6H_8 ligand similar to that found in cluster **23**, has been reported to result from the reaction of allene with $Fe_3(CO)_{12}$.[14]



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Concluding Remarks

The surprising finding of this study is the diversity of products that result from the reactions of the trinuclear imido clusters with alkynes. Also remarkable is the total lack of any correspondence between the reactions of alkynes with analogous imido and phosphinidene clusters. Particularly notable is the absence of phosphorus analogues of metallapyrrolinone products such as **2** and **8** that result from combining alkynes with imido clusters. The metallapyrrolinones all have a carbonyl group in the metallacycle bonded to the nitrogen atom, and the lack of phosphinidene analogues may simply reflect the weaker RP–C(O) bond as compared to a RN–C(O) bond. We were also surprised that the reactions of $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ with 1,3-cyclohexadiene and with allene did not lead to products in which the imido ligand had coupled in some fashion with the added organic species, in contrast to the reactivity of this cluster with alkynes. It was our expectation that these various imido clusters would prove useful as imido-transfer reagents to produce nitrogen-containing organic products, but it appears that the metal–nitrogen bonds are simply too strong for that to be easily realized.

Experimental Section

The compounds $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$,[15] $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$,[16] $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$,[17] $H_2Ru_3(\mu_3\text{-}NPh)(CO)_9$,[18] and $H_2Fe_3(\mu_3\text{-}NPh)(CO)_9$[17] were prepared by literature methods. The alkynes PhC≡CPh, EtC≡CEt, PhC≡CMe, MeC≡CMe, and HC≡CPh and 1,3-cyclohexadiene were purchased from Aldrich Chemical Co. and used as received. Propyne, 1-butyne, and allene were obtained from Liquid Carbonic Co. and were used without further purification. Solvents were dried by standard methods, and all manipulations of compounds were done with use of standard Schlenk techniques. Instruments used in this research have been previously described.[2a] Elemental analyses were obtained by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Reaction of $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ (5) with PhC≡CMe. A solution of **5** (108 mg, 0.20 mmol) and PhC≡CMe (35 mg, 0.30 mmol) in cyclohexane (50 mL) was heated under reflux for 30 min, during which time the solution turned from dark brown to dark red-brown. The solvent was evaporated, and the residue was dissolved in a minimum of CH_2Cl_2. Chromatography on Florisil with 10:1 (v/v) pentane/CH_2Cl_2 gave in order of elution a dark purple band of $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ (8 mg, 7%), a yellow band of the ferracyclopentadiene complex **10a** (21 mg, 21%), and an orange band of the ferrapyrrolinone complex **8a** (75 mg, 73%).

8a: Anal. Calcd for $C_{22}H_{13}O_7NFe_2$: C, 51.30; H, 2.54. Found: C, 52.09; H, 2.90. IR (cyclohexane): ν_{CO} 2079 (m), 2048 (vs), 2010 (vs), 1998 (s), 1976 (w), 1707 (m) cm^{-1}. MS (EI): *m/z* 487 (M^+ – CO, ^{56}Fe). ^{1}H NMR (CD_2Cl_2): δ 7.39–6.89 (br, 10 H, Ph), 2.15 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 208.9 (Fe—CO), 182.1 (Fe—CPh), 172.3 (C=O), 148.5, 146.6, 130.5, 128.9, 128.6, 128.2, 127.7, 126.7, 125.6 (Ph), 98.4 (CH_3), 17.1 (CH_3).

10a: Anal. Calcd for $C_{24}H_{16}O_6Fe_2$: C, 56.29; H, 3.15. Found: C, 55.70; H, 3.28. IR (cyclohexane): ν_{CO} 2065 (m), 2026 (vs), 1995 (s), 1987 (vs), 1943 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.52–7.01 (br, Ph), 2.23 (s, CH_3), 2.16 (s, CH_3), 1.71 (s, CH_3). ^{13}C NMR (CD_2Cl_2): δ 215.9, 214.6, 213.2, 210.1, 206.3, 202.9 (Fe–CO), 169.6, 169.3 (Fe–CPh, Fe–CMe), 139.8, 135.2, 130.7, 128.9, 128.7, 128.6, 128.2, 128.1, 127.8, 126.4, 126.2, 125.7, 123.6 (Ph, CPh, CMe), 30.9, 30.6, 17.5 (CH_3). MS (EI): *m/z* 512 (M^+).

Reaction of $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ (5) with PhC≡CPh. A solution of **5** (108 mg, 0.20 mmol) and PhC≡CPh (39 mg, 0.22 mmol) in cyclohexane (50 mL) was heated under reflux for 20 min and then worked up as described above for the reaction of **5** with PhC≡CMe to give $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ (6 mg, 5%), the ferracyclopentadiene complex **10b** (16 mg, 13%; *m/z* (EI) 636 (M^+); ν_{CO}(cyclohexane) 2064 (m), 2023 (s), 1984 (vs), 1939 (w) cm^{-1}), and the ferrapyrrolinone complex **8b** (91 mg, 79%).

8b: Anal. Calcd for $C_{27}H_{15}O_7NFe_2$: C, 56.19; H, 2.62. Found: C, 56.91; H, 3.02. IR (cyclohexane): ν_{CO} 2078 (m), 2048 (s), 2009 (vs), 1995 (m), 1983 (w), 1706 (m) cm^{-1}. MS (FAB): *m/z* 577 (M^+, ^{56}Fe). ^{1}H NMR (CD_2Cl_2): δ 7.50–6.95 (br, 15 H, Ph). ^{13}C NMR ($CDCl_3$): δ 208.3 (Fe—CO), 183.5 (Fe—CPh), 171.9 (C=O), 148.4, 147.5, 134.5, 130.1, 128.9, 128.3, 127.7, 127.2, 126.8, 125.9 (Ph), 103.2 (CPh).

Reaction of $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ (5) with EtC≡CEt. A solution of **5** (108 mg, 0.20 mmol) and EtC≡CEt (25 mg, 0.30 mmol)

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in cyclohexane (50 mL) was heated under reflux for 30 min and then worked up as described above for the reaction of **5** with PhC$\equiv$CMe to give $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ (13 mg, 11%), the ferracyclopentadiene **9c** (19 mg, 21%; m/z (EI) 444 (M^+); ν_{CO}(hexane) 2060 (m), 2023 (s), 1984 (vs), 1939 (w) cm^{-1}; lit.[4] ν_{CO} 2069, 2031, 1984, 1930 cm^{-1}), and the ferrapyrrolinone complex **8c** (61 mg, 63%).

8c: Anal. Calcd for $C_{19}H_{15}O_7NFe_2$: C, 47.44; H, 3.14. Found: C, 47.53; H, 3.24. IR (cyclohexane): ν_{CO} 2076 (m), 2042 (vs), 2006 (vs), 1998 (s), 1954 (w), 1706 (m), cm^{-1}. MS (EI): m/z 481 (M^+, ^{56}Fe). ^{1}H NMR (CD_2Cl_2): δ 7.28–6.79 (br, 5 H, Ph), 2.52 (q, 2 H, $C\mathit{H}_2CH_3$), 1.41 (q, 2 H, $C\mathit{H}_2CH_3$), 1.31 (t, 3 H, $CH_2C\mathit{H}_3$), 0.88 (t, 3 H, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): δ 209.38, 208.29 (Fe—*C*O), 187.28 (Fe—*C*Et), 172.88 (*C*=O), 148.37, 128.88, 126.74, 126.06 (Ph), 108.77 (*C*Et), 36.95, 21.53, 17.83, 15.95 (Et).

Reaction of $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ (5) with MeC$\equiv$CMe. A solution of **5** (108 mg, 0.20 mmol) and 2-butyne (33 mg, 0.61 mmol) in cyclohexane (40 mL) was heated under reflux for 20 min and then worked up as described above for the reaction of **5** with PhC$\equiv$CMe to give the ferracyclopentadiene complex **10d** (8 mg, 10%; m/z (EI) 389 (M^+); ν_{CO}(hexane) 2063 (m), 2023 (vs), 1988 (sh), 1981 (s), 1941 (w) cm^{-1}; lit.[4] ν_{CO} 2069, 2031, 1984, 1930 cm^{-1}), and the ferrapyrrolinone complex **8d** (64 mg, 71%).

8d: Anal. Calcd for $C_{17}H_{11}O_7NFe_2$: C, 45.07; H, 2.45. Found: C, 44.85; H, 2.75. IR (hexane): ν_{CO} 2079 (m), 2049 (vs), 2006 (vs), 1989 (s), 1961 (w), 1713 (m) cm^{-1}. MS (EI): m/z 453 (M^+). ^{1}H NMR (CD_2Cl_2): δ 7.32–6.80 (br, 5 H, Ph), 2.67 (s, 3 H, $C\mathit{H}_3$), 2.16 (s, 3 H, $C\mathit{H}_3$). ^{13}C NMR (CD_2Cl_2): δ 209 (br, Fe—*C*O), 181.1 (Fe—*C*Me), 173.3 (*C*=O), 149.1, 129.1, 127.1, 126.9 (Ph), 101.8 (*C*Me), 30.4 (*C*H$_3$), 14.7 (*C*H$_3$).

Reaction of $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ (5) with HC$\equiv$CMe. A solution of **5** (108 mg, 0.20 mmol) in cyclohexane (50 mL) was charged with 25 psi of propyne in a 370-mL Fischer–Porter bottle and heated to 80 °C for 1 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel with 10:1 (v/v) hexane/CH_2Cl_2 to give a yellow band of $Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}PhN{=}NPh)$ (**11**, 7 mg, 8%) and an orange band of the ferrapyrrolinone complex **8e** (60 mg, 66%).

8e: Anal. Calcd for $C_{16}H_9NO_7Fe_2$: C, 43.78; H, 2.07. Found: C, 43.04; H, 2.54. IR (hexane): ν_{CO} 2084 (m), 2050 (vs), 2016 (vs), 1995 (s), 1963 (w), 1718 (m) cm^{-1}. MS (EI): m/z 439 (M^+). ^{1}H NMR (CD_2Cl_2): δ 8.14 (s, 1 H, H), 7.33–6.82 (br, 5 H, Ph), 2.24 (s, 3 H, $C\mathit{H}_3$). ^{13}C NMR ($CDCl_2$): δ 208.7 (br, Fe—CO), 173.5 (*C*=O, $^3J_{C\text{-}H} = 9.8$ Hz, $^3J_{C\text{-}H} = 3.7$ Hz), 158.1 (Fe—*C*H, $^1J_{C\text{-}H} = 159.3$ Hz, $^3J_{C\text{-}H} = 3.9$ Hz), 149.0, 129.1, 127.1, 126.9 (Ph), 103.9 (*C*Me, $^2J_{C\text{-}H} = 6.1$ Hz, $^2J_{C\text{-}H} = 3.9$ Hz), 18.7 (*C*H$_3$).

Reaction of $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ (5) with HC$\equiv$CEt. A solution of **5** (108 mg, 0.20 mmol) in cyclohexane (50 mL) was charged with 25 psi of 1-butyne in a 370-mL Fischer–Porter bottle and heated to 80 °C for 1 h. After the mixture was cooled to room temperature, the solvent was evaporated and the residue was chromatographed on silica gel with 10:1 (v/v) hexane/CH_2Cl_2 to give a yellow band complex **11** (5 mg, 5%) and an orange band of the ferrapyrrolinone complex **8f** (61 mg, 68%).

8f: Anal. Calcd for $C_{17}H_{11}NO_7Fe_2$: C, 45.07; H, 2.45. Found: C, 44.85; H, 2.75. IR (cyclohexane): ν_{CO} 2082 (m), 2048 (vs), 2011 (s), 1994 (s), 1961 (w), 1711 (m) cm^{-1}. MS (EI): m/z 453 (M^+). ^{1}H NMR (CD_2Cl_2): δ 8.17 (s, 1 H), 7.42–6.78 (br, 5 H, Ph), 2.57 (q, 2 H, $C\mathit{H}_2CH_3$), 1.26 (t, 3 H, $CH_2C\mathit{H}_3$). ^{13}C NMR (CD_2Cl_2): δ 208.6 (br, Fe—*C*O), 173.23 (C=O, $^3J_{C\text{-}H} = 10$ Hz, $^3J_{C\text{-}H} = 5$ Hz), 155.57 (Fe—*C*H, $^1J_{C\text{-}H} = 159$ Hz, $^3J_{C\text{-}H} = 4.5$ Hz), 148.94, 129.14, 127.04, 126.89 (Ph), 111.17 (*C*Et), 25.87, 13.81 (Et).

Reaction of $Fe_3(\mu_3\text{-}NPh)(CO)_{10}$ (5) with HC$\equiv$CPh. A solution of **5** (108 mg, 0.20 mmol) and HC$\equiv$CPh (31 mg, 0.30 mmol) in cyclohexane (50 mL) was heated under reflux for 30 min and then worked up as described above for the reaction of **5** with PhC$\equiv$CMe to give complex **11** (8 mg, 10%) and the ferrapyrrolinone complex **8g** (74 mg, 74%).

8g: Anal. Calcd for $C_{21}H_{11}NO_7Fe_2$: C, 50.34; H, 2.21. Found: C, 50.77; H, 2.44. IR (pentane): 2082 (m), 2050 (vs), 2016 (vs), 1997 (m), 1961 (w), 1715 (m) cm^{-1}. MS (EI): m/z 502 (M^+). ^{1}H NMR (CD_2Cl_2): δ 8.87 (s, 1 H, CH), 8.03–6.93 (br, 10 H, Ph). ^{13}C NMR (CD_2Cl_2): δ 209.4 (br, Fe—*C*O), 172.2 (*C*=O, $^3J_{C\text{-}H} = 9.7$ Hz), 155.2 (Fe—*C*H, $^1J_{C\text{-}H} = 110.1$ Hz), 149.0, 133.8, 129.6, 129.6, 129.2, 129.1, 127.5, 127.2, 127.1 (Ph), 103.9 (*C*Ph).

Photolysis of $Fe_2(\mu_2\text{-}\eta^3\text{-}PhC{=}C(Me)C(O)NPh)(CO)_6$ (8a) in the Presence of Bu^{t}N$\equiv$C. A 50-mL Schlenk tube was charged with **8a** (51 mg, 0.10 mmol), Bu^{t}NC (50 μL, 0.44 mmol), and dry THF (30 mL). The solution was irradiated for 1 h with a medium-pressure Hg discharge lamp. The solvent was removed from the resultant burgundy red solution, and the residue was chromatographed on Florisil with 1:1 (v/v) hexane/CH_2Cl_2 to give unreacted **8a** (5 mg, 10%) and a red-brown band of complex **9** (49 mg, 86%).

9: Anal. Calcd for $C_{26}H_{22}O_6N_2Fe_2$ (%): C, 54.77; H, 3.89. Found: C, 54.57; H, 3.82. IR (Et_2O): ν_{CO} 2129 (m), 2075 (w), 2043 (vs), 2033 (m), 2022 (w), 2007 (w), 1983 (s), 1938 (s), 1920 (w), 1666 (m), 1592 (w). MS (EI): m/z 570 (M^+, ^{56}Fe). ^{1}H NMR (CD_2Cl_2): δ 7.50–6.65 (br, 10 H, Ph), 1.92 (s, 3 H, Me), 1.43 (s, 9 H, Bu^t).

Reaction of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (3) with PhC$\equiv$CPh. A 100-mL Schlenk flask was charged with $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (124 mg, 0.17 mmol), diphenylacetylene (17 mg, 0.097 mmol), and 40 mL of dry octane. The solution was refluxed under N_2 with stirring for 35 h, during which time the dark orange color changed to dark red. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation, and the residue was chromatographed on silica gel. With hexane as eluent, the first fraction was an orange band of unreacted **3** (72 mg), and this was followed by a yellow band of cluster **15** (53 mg, 29%, 97% based on consumed **3**). An additional dark yellow band (4 mg) came off the column with pure CH_2Cl_2 as eluent, but this species was not identified (IR (CH_2Cl_2) ν_{CO} 2054 (s), 2002 (m), 1970 (m), 1892 (w), 1788 (w) cm^{-1}; MS (EI) m/z 1130).

15: Anal. Calcd for $C_{36}H_{20}O_{10}N_2Ru_4$: C, 41.38; H, 1.92. Found: C, 41.27; H, 1.39. IR (CH_2Cl_2): ν_{CO} 2085 (w), 2068 (s), 2020 (vs), 1966 (w) cm^{-1}. MS (FD): m/z 1044 (M^+, ^{101}Ru).

Reaction of $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ (6) with PhC$\equiv$CPh. A 100-mL Schlenk flask was charged with **6** (94 mg, 0.16 mmol) and diphenylacetylene (57 mg, 0.32 mmol), to which was added 40 mL of dry methylcyclohexane. The solution was refluxed under N_2 with stirring for 8 h, during which time the color changed from purple to dark red. Vacuum evaporation of the solvent followed by chromatography on silica gel with pentane as eluent gave first a purple band of unreacted **6** (41.5 mg, 0.068 mmol, 44%) followed by an orange band of compound **16** (6 mg, 0.011 mmol, 8%), and a yellow/brown band (30 mg) of a mixture of two chromatographically inseparable compounds, one of which was **10b**. Compound **10b** is less soluble in pentane than the other compound, and after multiple recrystallizations from pentane, it was obtained in pure form (15 mg, 0.024 mmol, 18%). One other dark brown band came off the column with a 1:4 CH_2Cl_2/hexane eluent, but this species was not identified (IR (CH_2Cl_2) ν_{CO} 2058 (m), 2012 (vs), 2006 (s), 1973 (m), 1865 (m), 1856 (m) cm^{-1}; MS (EI) m/z 720).

16: Anal. Calcd for $C_{26}H_{15}Fe_2NO_6$: C, 56.87; H, 2.75. Found: C, 56.71; H, 2.64. IR (pentane): ν_{CO} 2066 (m), 2039 (m), 2028 (vs), 1997 (s), 1980 (s), 1973 (w, sh) cm^{-1}. MS (EI): m/z 549 (M^+). ^{13}C NMR (CD_2Cl_2): δ 210.5 (*C*O), 148.0, 143.3, 140.0, 131.6, 130.2, 129.7, 128.9, 128.3, 128.1, 127.4, 126.9, 126.2 (Ph), 125.3, 117.1 (CPh).

Reaction of $H_2Ru_3(\mu_3\text{-}NPh)(CO)_9$ (4) with PhC$\equiv$CPh. A solution of **4** (80 mg, 0.11 mmol) and PhC$\equiv$CPh (29 mg, 0.016 mmol) in THF (30 mL) was refluxed for 24 h under N_2 to give a dark red solution. Rotary evaporation of the solvent followed by column chromatography on silica gel with hexane as eluent gave first a yellow fraction of unreacted **4** (34 mg) followed by a yellow band of $Ru_4(\mu_4\text{-}NPh)(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)(CO)_{11}$ (**21**; 12 mg, 11%, 23% based on consumed Ru). Two more green (IR (hexane) ν_{CO} 2089 (w), 2081 (m), 2062 (m), 2037 (s, sh), 2029 (vs), 2008 (m), 1999 (m), 1988 (m, sh), 1929 (w), 1880 (w), 1860 (w) cm^{-1}; MS (EI) m/z 671; ^{1}H NMR (CD_2Cl_2) δ −16.29 (s, Ru–*H*) and dark yellow bands (IR (hexane) ν_{CO} 2043 (vs), 2014 (s), 2004 (s), 1979 (m), 1963 (m), 1954 (m) cm^{-1}) were eluted with 3:1 hexane/CH_2Cl_2 as eluent, but these complexes were not completely characterized.

21: Anal. Calcd for $C_{31}H_{15}O_{11}NRu_4$: C, 37.92; H, 1.53. Found: C, 38.09; H, 1.49. IR (hexane): ν_{CO} 2089 (w), 2064 (m), 2049 (m), 2033 (vs), 2016 (m), 2008 (m), 1983 (m), 1898 (w), 1852 (m) cm^{-1}.

Reaction of $H_2Fe_3(\mu_3\text{-}NPh)(CO)_9$ (7) with PhC$\equiv$CMe. A solution of **7** (103 mg, 0.20 mmol) and PhC$\equiv$CMe (35 mg, 0.30 mmol) in cyclohexane (50 mL) was heated under reflux for 20 min, during which time the solution turned from dark brown to dark red-brown. The solvent was evaporated, and the residue was dissolved in a minimum of CH_2Cl_2. Chromatography on silica gel with 10:1 (v/v) pentane/CH_2Cl_2 gave in order of elution a brown band of **7** (3 mg, 3%), a trace amount of complex **11**, a yellow band of the ferracyclopentadiene complex **10a** (19 mg, 19%), and an orange band of the ferrapyrrolinone complex **8a** (76 mg, 73%).

Reaction of $H_2Fe_3(\mu_3\text{-NPh})(CO)_9$ with EtC≡CEt. A solution of **7** (103 mg, 0.20 mmol) and EtC≡CEt (25 mg, 0.30 mmol) in methylcyclohexane (50 mL) was heated at 80 °C for 25 min, during which time the solution turned from dark brown to dark yellow. The solvent was evaporated under vacuum, and the residue was dissolved in a minimum of CH_2Cl_2. Chromatography on silica gel with 10:1 (v/v) pentane/CH_2Cl_2 gave in order of elution a yellow-brown band of complex **11** (5 mg, 5%), a yellow band of the ferracyclopentadiene complex **10c** (12 mg, 14%), and an orange band of the ferrapyrrolinone complex **10c** (54 mg, 56%).

Reaction of $H_2Fe_3(\mu_3\text{-NPh})(CO)_9$ with PhC≡CPh. A solution of **7** (103 mg, 0.20 mmol) and PhC≡CPh (54 mg, 0.30 mmol) in cyclohexane (50 mL) was heated under reflux for 30 min and then worked up as described above for the reaction of **5** with EtC≡CEt to yield complex **10** (5 mg, 5%), the ferracyclopentadiene complex **9b** (21 mg, 17%), and the ferrapyrrolinone complex **8b** (79 mg, 69%).

Reaction of $Fe_3(\mu_3\text{-NPh})(CO)_{10}$ (5) with 1,3-Cyclohexadiene. A solution of **5** (108 mg, 0.20 mmol) and 1,3-cyclohexadiene (24 mg, 0.30 mmol) in cyclohexane (50 mL) was heated under reflux for 20 min, during which time the solution turned from dark brown to black. The solvent was evaporated, and the residue was dissolved in a minimum amount of CH_2Cl_2. Chromatography on silica gel with 2:1 (v/v) hexane/CH_2Cl_2 gave in order of elution a dark purple band of $Fe_3(\mu_3\text{-NPh})_2(CO)_9$ (14 mg, 12%) and a dark brown band of cluster **22** (79 mg, 70%).

22: Anal. Calcd for $C_{20}H_{13}NO_8Fe_3$: C, 42.68; H, 2.33. Found: C, 42.12; H, 2.31. IR (cyclohexane): ν_{CO} 2065 (5), 2023 (vs), 2006 (vs), 1977 (s), 1964 (s), 1923 (m), 1865 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.41–7.17 (br, Ph), 4.66 (2 H), 3.12 (2 H), 2.07 (2 H), 1.74 (2 H). ^{13}C NMR (CD_2Cl_2): δ 228.0, 209.6 (br, Fe–CO), 167.0, 129.2, 128.6, 126.5 (Ph), 97.7, 83.2, 24.0 (C_6H_8). MS (FAB): *m/z* 563 (M$^+$).

Reaction of $Fe_3(\mu_3\text{-NPh})(CO)_{10}$ (5) with Allene. A solution of **5** (108 mg, 0.20 mmol) in cyclohexane (50 mL) was charged with 20 psi of allene in a 370-mL Fischer–Porter bottle and heated to 80 °C for 30 min. After the mixture was cooled to room temperature, the solvent was evaporated and the residue was dissolved in a minimum amount of CH_2Cl_2. Chromatography on silica gel with 2:1 (v/v) hexane/CH_2Cl_2 gave in order of elution a dark purple band of $Fe_3(\mu_3\text{-NPh})_2(CO)_9$ (12 mg, 10%) and a dark brown band of cluster **23** (77 mg, 68%).

23: Anal. Calcd for $C_{19}H_{13}NO_7Fe_3$: C, 42.67; H, 2.45. Found: C, 43.04; H, 2.54. IR (CH_2Cl_2): ν_{CO} = 2067 (s), 1997 (vs), 1960 (s), 1935 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.33–7.02 (br, 5 H, Ph), 2.57 (q, 2 H), 2.36 (q, 2 H), 2.24 (q, 2 H), 1.85 (q, 2 H). ^{13}C NMR (CD_2Cl_2): δ 223.9, 211.0, 207.9 (Fe–CO), 166.9, 128.7, 128.3, 125.3 (Ph), 87.1, 53.6, 47.3 (C_6H_8). MS (EI): *m/z* 535 (M$^+$).

Crystal Structure Determinations. Crystallographic data are collected in Table II. Crystals suitable for diffraction studies were grown by slow evaporation of solvent (pentane, hexane) from saturated solutions and were mounted on glass fibers. The space groups for **9**, **15**, and **22** were unambiguously determined from photographic evidence and systematic absences in the diffraction data. TRACER revealed no symmetry higher than triclinic for **23**, and the centrosymmetric alternative was assumed throughout solution and refinement of the structure. The transmission ratios did not suggest that absorption corrections were needed for any of the structures.

The structures were solved by direct methods. Phenyl rings were constrained to rigid, planar hexagons during refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were idealized for **9**, **22**, and **23** except for those of C atoms 8–13 in **23**, which were found and isotropically refined. All hydrogen atoms in **15** were found and isotropically refined. All software used in the calculations and sources of scattering factors are contained in the SHELXTL program library, version 5.1 (G. Sheldrick, Nicolet XRD, Madison, WI).

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Supplementary Material Available: Tables of atomic positional and thermal parameters and complete bond lengths and angles for **9**, **15**, **22**, and **23** (17 pages); listings of structure factors for **9**, **15**, **22**, and **23** (78 pages). Ordering information is given on any current masthead page.