Comparison of the Closo Trigonal-Bipyramidal Structures of μ_3-η^2-$\perp$-Acetylene and -Acetylide Clusters: Synthesis of (η^5-C_5H_5)$NiFe_2(CO)_6$(μ_3-η^2-C≡CPr^i) and X-ray Structures of (η-C_5H_5)$NiFe_2(CO)_5$(L)(μ_3-η^2-C≡CR) (R = Pr^i, L = CO; R = Bu^t, L = PPh_3)

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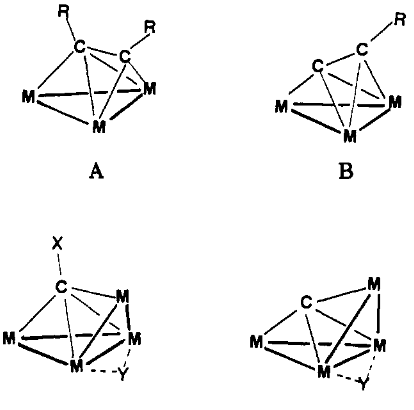
A comparison between the structures of closo trigonal-bipyramidal acetylene and acetylide clusters with M_3C_2 frameworks is made. The synthesis of (η^5-C_5H_5)$NiFe_2(CO)_6$(μ_3-η^2-C≡CPr^i) (1) from [(η^5-C_5H_5)Ni(CO)]$_2$, Ph_2PC≡CPr^i, and $Fe_2(CO)_9$ is described. X-ray structural analyses of (η^5-C_5H_5)$NiFe_2(CO)_5$(L)(μ_3-η^2-C≡CR) (L = CO, R = Pr^i, **1**; L = PPh_3, R = Bu^t, **2**) are described. Crystal data: **1**, $C_{16}H_{12}Fe_2NiO_6$, M_r = 470.67, triclinic space group $P\bar{1}$, a = 14.769 (7) Å, b = 14.824 (6), c = 8.708 (4), α = 91.77 (2)°, β = 96.45 (2)°, γ = 109.27 (2)°, V = 1784 (1) Å^3, Z = 4; **2**, $C_{35}H_{29}Fe_2NiO_5P\cdot 0.5C_7H_{16}$, M_r = 781.10, space group $P2_1/c$, a = 10.058 (3) Å, b = 13.225 (6) Å, c = 26.906 (8) Å, β = 96.08 (2)°, V = 3559 (2) Å^3, Z = 4. The structures of **1** and **2** were solved and refined on the basis of 5143 and 3289 observed intensities measured on Siemens AED and Syntex $P2_1$ diffractometers. Final R and R_w values were 0.048 and 0.054 for **1** and 0.056 and 0.066 for **2**. There are significant structural differences between the closo trigonal-bipyramidal M_3C_2 skeletons of the acetylide and acetylene clusters. In particular the M–C_α distances are much shorter in the acetylides, perhaps indicating substantial π-character to the metal–σ-acetylide bond. The intrapolyhedral M–C_α–C_β angles are much larger in the acetylides than in the acetylenes. The C_α–R fragments in the μ_3-η^2-$\perp$-acetylene clusters approximate more closely to an equatorial component of a trigonal bipyramid than the "bare" C_α in the μ_3-η^2-acetylides. The acetylides show a closer structural resemblance to the M_4 cluster carbides.

Introduction

The iron group carbonyls $M_3(CO)_{12}$ react with alkynes to give a diverse array of organometallic compounds whose structures are a function of the metal, the nature of the alkyne, and the reaction conditions.[1] Among the first products observed in the reactions of $Fe_3(CO)_{12}$ with internal alkynes are the monoalkyne complexes $Fe_3(CO)_9$(μ_3-η^2-$\perp$-RC≡CR), which have been the subject of intense study because of the unusual bonding of the alkyne in a perpendicular fashion on the Fe_3 edge,[2,3] and the violet bis(alkyne) compounds $Fe_3(CO)_8$(μ_3-η^2-$\|$-RC≡CR)$_2$.[4] With ruthenium and osmium, on the other hand, internal alkynes afford tetranuclear $M_4(CO)_{10}$(μ_4-η^2-RC≡CR) clusters via metal fragment condensation,[5] trinuclear complexes from oxidative addition,[6] and molecules of the

Chart I



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type $M_3(CO)_{10}(\mu_3$-η^2-$\|$-RC≡CR), in which the alkyne triple bond lies parallel to one edge of the M_3 triangle.[7]

Terminal alkynes (HC≡CR) undergo oxidative addition with $M_3(CO)_{12}$ (M = Ru, Os), affording the now classical hydrido acetylides (μ-H)$M_3(CO)_9(\mu_3$-η^2-C≡CR).[8] Strangely enough, such acetylides are not obtained in the direct reactions of terminal alkynes with $Fe_3(CO)_{12}$ and the few trinuclear iron compounds of this type that have been characterized were synthesized indirectly from alkoxyalkyne[9] and ketenylidene[10] clusters or via oxidative cleavage of C–H and P–C bonds in precoordinated terminal alkynes or phosphinoalkynes.[11,12]

In the Wade–Mingos PSEPT formalism[13] homonuclear molecules $Fe_3(CO)_9(\eta_3$-η^2-$\perp$-RC≡CR) and heteronuclear molecules (η^5-C_5H_5)$NiFe_2(CO)_6(\mu_3$-η^2-C≡CR) have six-electron-pair five-vertex closo trigonal-bipyramidal structures when the alkyne (two CR units) and the acetylide (C and CR) are considered as contributing two skeletal atoms and six or five electrons to the polyhedron (A and B, Chart I). With the alkynes as four-electron ligands the EAN electron count for $Fe_3(CO)_9(\mu_3$-η^2-$\perp$-RC≡CR) molecules is only 46 electrons, implying, at least formally, electronic unsaturation. In practice these $\perp$-acetylene clusters are prone to electrochemical two-electron reduction,[14] to addition of CO[15] or further alkyne,[4] and to exchange of metal fragments.[14] All of these reactions result in reorientation of the alkyne on the M_3 face, generating nido octahedral structures with μ_3-η^2-$\|$-alkyne coordination. With phosphines, however, simple substitution of CO gives $M_3(CO)_8(\mu_3$-η^2-$\perp$-RC≡CR)(L) complexes.[11]

Clearly there should be significant structural and electronic similarities between the $Fe_3(CO)_9(\mu_3$-η^2-$\perp$-RC≡CR) clusters and the corresponding isoelectronic acetylides. In this paper we describe the molecular structures of two new heteronuclear clusters of the latter class, namely (η^5-C_5H_5)$NiFe_2(CO)_5(L)(\mu_3$-η^2-C≡CR) (L = CO, R = Pr^i; L = PPh_3, R = Bu^t), and examine in detail the structural consequences of replacing a CR (alkyne) fragment by a C (acetylide) unit. We focus particularly on the suggestion[16] that these acetylides may be described as "alkylidyne–carbides" and draw comparisons with the related class of tetranuclear cluster carbides[17] (C and D, Chart I).

Experimental Section

The complex (η^5-C_5H_5)$NiFe_2(CO)_6(\mu_3$-η^2-C≡CPr^i) (1) was obtained in a two-step reaction. The nickel dimer [(η^5-C_5H_5)Ni(CO)]$_2$ (0.2 g) in *n*-heptane (100 mL) was reacted with the phosphinoalkyne Ph_2PC≡CPr^i [18] (~3-fold excess) under reflux until the initially dark red solution turned dark brown and IR spectroscopy indicated complete consumption of starting material. A heptane suspension (50 mL) of $Fe_2(CO)_9$ (0.3 g) or $Fe_3(CO)_{12}$ (0.4 g) was then added to the hot solution under nitrogen and the mixture refluxed for a further 20 min. The dark brown suspension obtained was filtered under nitrogen and the insoluble fraction discarded. The filtrate was evaporated under reduced pressure to a few milliliters and chromatographed on preparative TLC plates (Merck, Kieselgel) with use of a diethyl ether–light petroleum ether mixture (1:9) for development. Small amounts of [(η^5-C_5H_5)Ni(CO)]$_2$ and $Fe_3(CO)_{12}$ were detected together with the following compounds in order of development: complex 1 (10%); (η^5-C_5H_5)$_2Ni_2Fe_2(CO)_6(\mu_4$-η^2-HC≡CPr^i) (10%); (η^5-C_5H_5)$_2Ni_2Fe_2(CO)_5(\mu_4$-η^2-C≡CPr^i)(μ-PPh_2) (5%); (η^5-C_5H_5)-$NiFe_3(CO)_7(\mu_4$-η^2-HC_2Pr^i)(μ-PPh_2) (25%); trace amounts of two other unidentified clusters.[19]

Table I. Experimental Data for the X-ray Diffraction Studies of (η^5-C_5H_5)$NiFe_2(CO)_6(\mu_3$-η^2-C≡CPr^i) (1) and (η^5-C_5H_5)$NiFe_2(CO)_5(PPh_3)(\mu_3$-$\eta^2$-C≡CBu^t) (2)

	1	2
mol formula	$C_{16}H_{12}Fe_2NiO_6$	$C_{35}H_{29}Fe_2NiO_5P\cdot{}^1/_2C_7H_{16}$
mol wt	470.67	781.10
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	14.769 (7)	10.058 (3)
b, Å	14.824 (6)	13.225 (6)
c, Å	8.708 (4)	26.906 (8)
α, deg	91.77 (2)	
β, deg	96.45 (2)	96.08 (2)
γ, deg	109.27 (2)	
V, Å^3	1784 (1)	3559 (2)
Z	4	4
D_{calcd}, g cm^{-3}	1.753	1.458
$F(000)$	944	1612
cryst dimens, mm	0.16 × 0.18 × 0.24	0.24 × 0.28 × 0.31
μ(Mo Kα), cm^{-1}	26.83	14.13
diffractometer	Siemens AED	Syntex P2$_1$
scan type	$\theta/2\theta$	$\theta/2\theta$
2θ range, deg	6–54	3.2–45
rflns measd	$\pm h,\pm k,l$	$h,k,\pm l$
total no. of unique data	7672	4676
no. of unique obsd data	5143 ($I > 2\sigma(I)$)	3289 ($I > 3\sigma(I)$)
R	0.048	0.056
R_w	0.054	0.066

Analytical and Spectroscopic Data for 1. Anal. Calcd for $C_{16}H_{12}O_6NiFe_2$: C, 40.83; H, 2.57. Found: C, 41.0; H, 2.8. IR (ν(CO), C_7H_{16}): 2067 vs, 2021 vs, 1994 vs, 1987 w, sh, 1973 m cm^{-1}. ^{1}H NMR (CDCl$_3$, 293 K): δ 4.90 s (5 H, C_5H_5), 3.73 m (1 H, C*H*Me$_2$), 1.45 d, 1.31 d (6 H, CH(CH_3)$_2$).

The phosphine-substituted complex (η^5-C_5H_5)$NiFe_2(CO)_5$-(PPh_3)(μ_3-η^2-C≡CBu^t) was obtained as previously described[11] and recrystallized from *n*-heptane.

IR spectra were measured on a Perkin-Elmer 580 B spectrometer and NMR spectra on a JEOL JNM GX 270 FT instrument. Microanalyses were carried out by Pascher Microanalytical Laboratories, Remagen, Germany.

X-ray Data Collection, Structure Determination, and Refinement for 1 and 2. Dark brown crystals of 1 and 2 were grown from *n*-heptane; those of the latter also contained heptane molecules of solvation. The crystallographic data for both compounds are summarized in Table I. Unit cell parameters were determined from the θ values of 25 (1) and 15 (2) carefully centered reflections chosen from different regions of reciprocal space. Data were collected at room temperature on a Siemens AED diffractometer (1) using niobium-filtered Mo Kα radiation and on a Syntex P2$_1$ diffractometer (2) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The reflections were collected with a variable scan speed of 3–12° min^{-1} and a scan width from (θ − 0.6)° to (θ + 0.6 + 0.346 tan θ)° for 1 and with a variable scan speed of 2.93–29.3° min^{-1} and a scan width of 0.75° below Kα_1 to 0.75° above Kα_2 for 2. One standard reflection was monitored every 50 measurements for 1, and two standard reflections were

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Table II. Fractional Atomic Coordinates (×10⁴) with Esd's in Parentheses for the Non-Hydrogen Atoms of 1

	x/a	*y/b*	*z/c*
Ni(11)	−3130 (1)	1748 (1)	7372 (1)
Fe(11)	−3180 (1)	2947 (1)	9423 (1)
Fe(21)	−1707 (1)	2371 (1)	9206 (1)
O(11)	−4828 (3)	3416 (4)	7997 (6)
O(21)	−2256 (4)	4649 (3)	11512 (5)
O(31)	−4157 (3)	1629 (3)	11599 (5)
O(41)	−2353 (3)	1055 (3)	11577 (5)
O(51)	−188 (3)	3893 (4)	11127 (6)
O(61)	−434 (3)	1458 (3)	8025 (6)
C(11)	−4192 (4)	3231 (4)	8565 (7)
C(21)	−2629 (4)	3979 (4)	10719 (6)
C(31)	−3772 (4)	2152 (4)	10773 (6)
C(41)	−2110 (4)	1584 (4)	10680 (6)
C(51)	−777 (4)	3300 (4)	10384 (6)
C(61)	−928 (4)	1791 (4)	8510 (6)
C(71)	−2401 (3)	3112 (3)	7906 (5)
C(81)	−1902 (3)	2814 (3)	7035 (5)
C(91)	−1342 (4)	3008 (4)	5719 (6)
C(101)	−385 (4)	3822 (6)	6207 (9)
C(111)	−1931 (6)	3250 (6)	4366 (7)
C(121)	−3480 (5)	286 (4)	6794 (8)
C(131)	−4125 (4)	443 (4)	7706 (8)
C(141)	−4617 (4)	1000 (4)	6962 (8)
C(151)	−4253 (5)	1195 (4)	5533 (7)
C(161)	−3555 (5)	759 (4)	5446 (7)
Ni(12)	2649 (1)	3258 (1)	3697 (1)
Fe(12)	3564 (1)	2711 (1)	1827 (1)
Fe(22)	1695 (1)	2016 (1)	1829 (1)
O(12)	5512 (3)	3375 (4)	3511 (7)
O(22)	3792 (3)	1261 (3)	−245 (5)
O(32)	3810 (3)	4264 (3)	−238 (6)
O(42)	1535 (3)	3210 (3)	−705 (5)
O(52)	1166 (4)	230 (3)	−114 (5)
O(62)	−160 (3)	1809 (4)	2867 (6)
C(12)	4755 (4)	3129 (4)	2836 (7)
C(22)	3712 (3)	1839 (4)	536 (6)
C(32)	3718 (4)	3654 (4)	544 (7)
C(42)	1624 (4)	2745 (4)	292 (6)
C(52)	1358 (4)	916 (4)	666 (6)
C(62)	552 (3)	1881 (4)	2406 (6)
C(72)	2878 (3)	2049 (3)	3257 (5)
C(82)	2171 (3)	1845 (3)	4062 (5)
C(92)	1738 (4)	1345 (4)	5379 (6)
C(102)	1319 (6)	276 (5)	4987 (9)
C(112)	2514 (6)	1581 (8)	6781 (7)
C(122)	2704 (6)	4625 (4)	3249 (9)
C(132)	3561 (5)	4680 (4)	4136 (9)
C(142)	3321 (6)	4292 (5)	5533 (8)
C(152)	2319 (6)	4018 (5)	5475 (8)
C(162)	1938 (6)	4218 (4)	4064 (9)

monitored every 100 measurements for **2**; no significant decay was noticed over the time of data collection. Lorentz and polarization corrections were applied to the data and the intensitites reduced to structure factors in the normal way. No absorption corrections were deemed necessary.

The structures were solved by Patterson and Fourier methods and refined first by full-matrix least squares with isotropic thermal parameters and then by blocked (**1**) and full (**2**) matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms of **1** were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. A disordered heptane molecule was found in **2**, and the heptane carbon atoms were refined with isotropic thermal parameters and an occupancy factor of 0.5. The hydrogen atoms of **2** were not included in the refinement. The final cycles of refinement were carried out on the basis of 476 (**1**) and 417 (**2**) variables; after the last cycles, no parameters shifted by more than 1.23 (**1**) and 0.85 (**2**) esd. The largest remaining peaks in the final difference maps were equivalent to about 0.9 (**1**) and 0.7 (**2**) e/Å³. The function minimized in the least-squares refinements was $\sum w|F_o - F_c|^2$. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used for **1**; at convergence the K value was 1.000 and the g value 0.0048. For **2** the weighting scheme was $w^{-1} = 1.98 - 0.0185|F_o| + 0.00013|F_o|^2$.

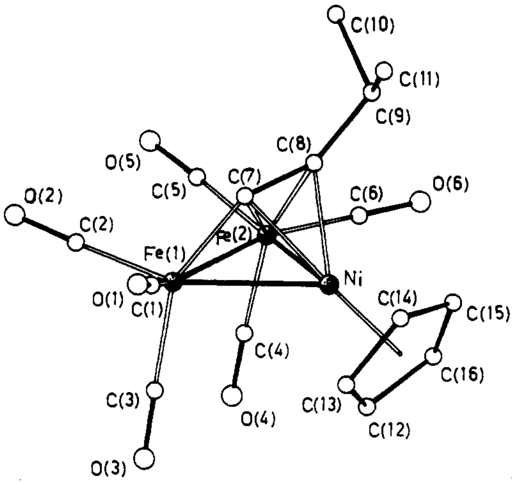

Figure 1. View of the molecular structure of the complex (η^5-C_5H_5)NiFe_2(CO)$_6$(μ_3-η^2-⊥-C≡CPr^i) (**1**) together with the atomic numbering scheme.

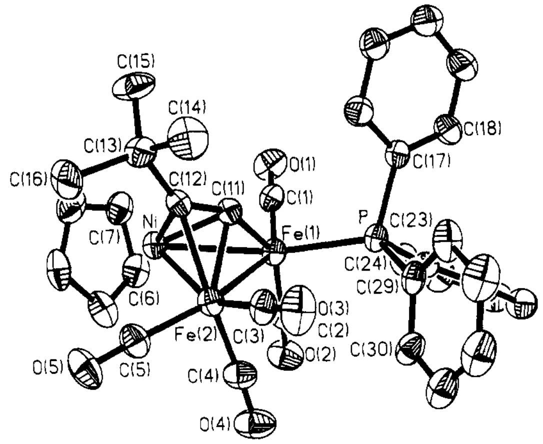

Figure 2. View of the molecular structure of the complex (η^5-C_5H_5)NiFe_2(CO)$_5$(PPh_3)(μ_3-η^2-⊥-C≡CBu^t) (**2**) together with the atomic numbering scheme.

The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 20. All calculations for **1** were carried out on the Cray X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) using the SHELX-76 system of crystallographic computer programs[21] and all of those for **2** on IBM 4341 computers at the University of Waterloo, Department of Computing Services using computer programs described elsewhere.[22] The final atomic coordinates for the non-hydrogen atoms are given in Tables II (**1**) and III (**2**). The atomic coordinates of the hydrogen atoms are given in Table SI (**1**; supplementary material) and the thermal parameters in Tables SII and SIII (**1** and **2**, respectively; supplementary material).

Results and Discussion

Comparison of the Structures of 1 and 2. The molecular structures of the compounds **1** and **2** are depicted in Figures 1 and 2, respectively, together with the atomic labeling schemes. In the crystals of **1** two crystallographically independent, but practically identical, molecules are present. Important bond distances and angles

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Table III. Fractional Atomic Coordinates (×10^4) with Esd's in Parentheses for 2

atom	x	y	z
Ni	4183 (1)	1905 (1)	2570 (1)
Fe(1)	3393 (1)	1587 (1)	1653 (1)
Fe(2)	2008 (1)	2568 (1)	2288 (1)
P	2066 (2)	1025 (2)	1008 (1)
O(1)	5440 (7)	89 (6)	1554 (3)
O(2)	4694 (8)	3204 (6)	1140 (3)
O(3)	-879 (6)	2398 (7)	2033 (3)
O(4)	2459 (8)	4277 (6)	1635 (3)
O(5)	1851 (8)	3883 (6)	3156 (3)
C(1)	4623 (9)	683 (7)	1594 (3)
C(2)	4161 (9)	2562 (7)	1334 (4)
C(3)	265 (9)	2467 (8)	2123 (3)
C(4)	2318 (10)	3570 (8)	1874 (4)
C(5)	1918 (9)	3357 (8)	2823 (4)
C(6)	6118 (8)	2363 (9)	2453 (4)
C(7)	6227 (9)	1409 (9)	2705 (4)
C(8)	5694 (10)	1568 (10)	3168 (4)
C(9)	5282 (10)	2616 (10)	3187 (4)
C(10)	5532 (9)	3094 (9)	2762 (4)
C(11)	2663 (8)	1156 (6)	2211 (3)
C(12)	2416 (8)	1234 (6)	2664 (3)
C(13)	1929 (10)	661 (7)	3101 (3)
C(14)	430 (11)	399 (10)	2946 (4)
C(15)	2772 (13)	-315 (8)	3176 (4)
C(16)	2055 (13)	1302 (9)	3581 (4)
C(17)	1809 (8)	-333 (7)	1027 (3)
C(18)	1890 (10)	-947 (8)	605 (4)
C(19)	1721 (11)	-2000 (8)	640 (4)
C(20)	1447 (10)	-2449 (9)	1093 (4)
C(21)	1365 (10)	-1830 (8)	1516 (4)
C(22)	1554 (9)	-784 (8)	1488 (4)
C(23)	2618 (9)	1226 (7)	386 (3)
C(24)	3982 (10)	1177 (8)	338 (3)
C(25)	4429 (11)	1286 (9)	-139 (4)
C(26)	3505 (13)	1454 (9)	-551 (4)
C(27)	2128 (12)	1498 (8)	-513 (4)
C(28)	1695 (10)	1384 (8)	-29 (3)
C(29)	376 (9)	1554 (8)	927 (3)
C(30)	264 (10)	2605 (8)	846 (3)
C(31)	-1006 (11)	3053 (10)	770 (4)
C(32)	-2158 (12)	2439 (11)	787 (4)
C(33)	-2034 (11)	1405 (11)	872 (4)
C(34)	-766 (9)	944 (9)	943 (4)
C(35)[a]	121 (4)	-19 (3)	535 (1)
C(36)[a]	278 (4)	13 (3)	523 (1)
C(37)[a]	306 (3)	88 (3)	497 (1)
C(38)[a]	404 (4)	76 (3)	492 (1)
C(39)[a]	453 (3)	-98 (2)	526 (1)
C(40)[a]	530 (4)	-68 (3)	527 (1)
C(41)[a]	615 (3)	78 (2)	462 (1)

[a] Disordered heptane of solvation, occupancy 0.5.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 1

	molecule A	molecule B
Fe(1)–Fe(2)	2.608 (2)	2.608 (2)
Ni–Fe(1)	2.504 (1)	2.504 (1)
Ni–Fe(2)	2.386 (1)	2.368 (1)
Fe(1)–C(1)	1.776 (7)	1.775 (5)
Fe(1)–C(2)	1.773 (5)	1.770 (6)
Fe(1)–C(3)	1.782 (5)	1.789 (6)
Fe(1)–C(7)	1.818 (5)	1.800 (4)
Fe(2)–C(4)	1.781 (6)	1.761 (6)
Fe(2)–C(5)	1.783 (5)	1.783 (5)
Fe(2)–C(6)	1.791 (6)	1.766 (5)
Fe(2)–C(7)	2.024 (5)	2.012 (5)
Fe(2)–C(8)	2.041 (5)	2.045 (4)
Ni–C(7)	1.964 (4)	1.963 (5)
Ni–C(8)	2.031 (4)	2.025 (5)
Ni–C(12)	2.087 (6)	2.053 (6)
Ni–C(13)	2.061 (6)	2.089 (5)
Ni–C(14)	2.092 (5)	2.093 (6)
Ni–C(15)	2.100 (6)	2.081 (8)
Ni–C(16)	2.088 (6)	2.066 (9)
C(7)–C(8)	1.278 (7)	1.281 (7)
C(8)–C(9)	1.469 (7)	1.476 (7)
C(9)–C(10)	1.531 (8)	1.511 (9)
C(9)–C(11)	1.508 (9)	1.523 (9)
C(12)–C(13)	1.377 (10)	1.383 (11)
C(13)–C(14)	1.398 (10)	1.394 (10)
C(14)–C(15)	1.411 (10)	1.394 (12)
C(15)–C(16)	1.392 (11)	1.375 (11)
C(12)–C(16)	1.399 (9)	1.380 (11)
C(1)–O(1)	1.130 (9)	1.139 (7)
C(2)–O(2)	1.130 (7)	1.123 (7)
C(3)–O(3)	1.130 (7)	1.130 (8)
C(4)–O(4)	1.126 (7)	1.147 (7)
C(5)–O(5)	1.133 (6)	1.141 (7)
C(6)–O(6)	1.118 (8)	1.141 (7)
Ni–Fe(1)–Fe(2)	55.60 (6)	55.16 (6)
Ni–Fe(2)–Fe(1)	60.00 (6)	60.20 (6)
Fe(1)–Ni–Fe(2)	64.40 (6)	64.65 (6)
Fe(2)–Fe(1)–C(2)	100.5 (2)	99.5 (2)
Fe(2)–Fe(1)–C(3)	99.9 (2)	103.7 (2)
Ni–Fe(1)–C(1)	99.4 (2)	101.4 (2)
Ni–Fe(1)–C(3)	99.6 (2)	98.8 (2)
C(1)–Fe(1)–C(2)	99.0 (3)	98.1 (3)
C(1)–Fe(1)–C(3)	98.1 (3)	97.1 (3)
C(2)–Fe(1)–C(3)	98.0 (3)	98.1 (3)
Fe(1)–Fe(2)–C(4)	87.9 (2)	85.9 (2)
Fe(1)–Fe(2)–C(5)	100.3 (2)	103.1 (2)
Ni–Fe(2)–C(4)	97.3 (2)	97.2 (2)
Ni–Fe(2)–C(6)	102.1 (2)	98.2 (2)
C(4)–Fe(2)–C(5)	98.2 (3)	96.5 (3)
C(4)–Fe(2)–C(6)	96.8 (3)	97.2 (3)
C(5)–Fe(2)–C(6)	96.2 (3)	97.8 (3)
Fe(1)–C(7)–C(8)	151.6 (4)	152.6 (4)
C(7)–C(8)–C(9)	146.1 (5)	147.2 (5)
Fe(1)–C(1)–O(1)	178.8 (6)	178.0 (5)
Fe(1)–C(2)–O(2)	177.7 (6)	177.9 (5)
Fe(1)–C(3)–O(3)	178.2 (5)	178.2 (6)
Fe(2)–C(4)–O(4)	176.8 (5)	177.0 (6)
Fe(2)–C(5)–O(5)	179.6 (5)	177.4 (5)
Fe(2)–C(6)–O(6)	176.8 (5)	176.0 (5)

for 1 and 2 are given in Tables IV and V, respectively.

The core of both molecules 1 and 2 consists of an asymmetric triangle of two Fe and one Ni atom with an acetylide σ-bound to the Fe(1) atom and π-bonded to the Fe(2) and Ni atoms in such a way that the acetylenic triple bond lies almost perpendicular to the Ni–Fe(2) edge. This is the classical μ_3-η^2-$\perp$-bonding mode first documented for $Fe_3(CO)_9(PhC{\equiv}CPh)$ by Dahl, Hübel, and co-workers.[2b] It is interesting that in these heterometallic clusters the metal atoms adopt an unsymmetrical arrangement with the alkynyl group σ-bound to one iron atom, rather than the alternative, symmetrical arrangement with the RC≡C group σ-bonded to the unique Ni atom. The latter arrangement might also be expected on electronic grounds, since all three metal atoms would achieve the presumably favored 18-electron configuration, whereas in the unsymmetrical arrangement Fe(1) is a 17-electron center and the Ni atom has 19 electrons. The position of the nickel atom in both structures was unequivocally confirmed by different refinements carried out by placing the nickel atom in the other two possible positions of the metal triangle. In both cases the effect of switching positions for Fe and Ni was to increase significantly the *R* factors and to adversely affect the thermal parameters of the atoms.

In attempting to rationalize these facts, we can make the following remarks. (i) In both structures the Fe(1)–C$_\alpha$ (Fe(1)–C(7) = 1.814 (5) Å in 1; Fe(1)–C(11) = 1.831 (8) Å in 2) bonds are rather short. Indeed, these distances approach the iron–carbonyl bond lengths to the same atom (Fe(1)–CO$_{av}$ = 1.777 (6) Å in 1; Fe(1)–CO$_{av}$ = 1.755 (9) Å in 2) and are much shorter than any of the remaining metal–carbon distances to the unsaturated hydrocarbyl. Churchill and Chang[23a] have previously tabulated Fe–C$_{sp^3}$,

Table V. Selected Bond Lengths (Å) and Angles (deg) for 2

(A) Bond Lengths			
Ni–Fe(1)	2.546 (2)	Ni–Fe(2)	2.404 (2)
Ni–C(6)	2.094 (9)	Ni–C(7)	2.152 (10)
Ni–C(8)	2.138 (11)	Ni–C(9)	2.114 (11)
Ni–C(10)	2.089 (11)	Ni–C(11)	1.985 (8)
Ni–C(12)	2.026 (8)	Fe(1)–Fe(2)	2.655 (2)
Fe(1)–P	2.205 (2)	Fe(1)–C(1)	1.740 (9)
Fe(1)–C(2)	1.771 (10)	Fe(1)–C(11)	1.831 (8)
Fe(2)–C(3)	1.768 (9)	Fe(2)–C(4)	1.780 (10)
Fe(2)–C(5)	1.788 (10)	Fe(2)–C(11)	1.998 (9)
Fe(2)–C(12)	2.054 (8)	P–C(17)	1.816 (9)
P–C(23)	1.836 (9)	P–C(29)	1.830 (9)
C(1)–O(1)	1.15 (1)	C(2)–O(2)	1.16 (1)
C(3)–O(3)	1.15 (1)	C(4)–O(4)	1.15 (1)
C(5)–O(5)	1.14 (1)	C(6)–C(7)	1.43 (2)
C(7)–C(8)	1.42 (1)	C(8)–C(9)	1.45 (2)
C(9)–C(10)	1.44 (2)	C(10)–C(6)	1.38 (1)
C(11)–C(12)	1.28 (1)	C(12)–C(13)	1.52 (1)
C(13)–C(14)	1.56 (1)	C(13)–C(15)	1.55 (2)
C(13)–C(16)	1.54 (1)		
(B) Bond Angles			
Fe(1)–Ni–Fe(2)	64.78 (4)	Fe(1)–Ni–C(6)	95.8 (3)
Fe(1)–Ni–C(7)	107.9 (3)	Fe(1)–Ni–C(8)	144.9 (3)
Fe(1)–Ni–C(9)	156.6 (3)	Fe(1)–Ni–C(10)	116.6 (3)
Fe(1)–Ni–C(11)	45.6 (2)	Fe(1)–Ni–C(12)	82.0 (2)
Fe(2)–Ni–C(6)	132.5 (3)	Fe(2)–Ni–C(7)	170.2 (3)
Fe(2)–Ni–C(8)	149.8 (3)	Fe(2)–Ni–C(9)	117.9 (3)
Fe(2)–Ni–C(10)	109.8 (3)	Fe(2)–Ni–C(11)	53.1 (2)
Fe(2)–Ni–C(12)	54.4 (2)		
Ni–Fe(1)–Fe(2)	55.02 (3)	Ni–Fe(1)–P	156.93 (6)
Ni–Fe(1)–C(1)	92.9 (3)	Ni–Fe(1)–C(2)	104.0 (3)
Ni–Fe(1)–C(11)	50.8 (2)	Fe(2)–Fe(1)–P	110.87 (6)
Fe(2)–Fe(1)–C(1)	145.2 (3)	Fe(2)–Fe(1)–C(2)	104.0 (3)
Fe(2)–Fe(1)–C(11)	48.8 (2)	P–Fe(1)–C(1)	94.2 (3)
P–Fe(1)–C(2)	97.1 (3)	P–Fe(1)–C(11)	106.2 (3)
C(1)–Fe(1)–C(2)	96.1 (4)	C(1)–Fe(1)–C(11)	102.2 (4)
C(2)–Fe(1)–C(11)	149.0 (4)	Ni–Fe(2)–Fe(1)	60.20 (3)
Ni–Fe(2)–C(3)	153.8 (3)	Ni–Fe(2)–C(4)	104.8 (3)
Ni–Fe(2)–C(5)	94.6 (3)	Ni–Fe(2)–C(11)	52.6 (2)
Ni–Fe(2)–C(12)	53.4 (2)	Fe(1)–Fe(2)–C(3)	112.1 (3)
Fe(1)–Fe(2)–C(4)	79.9 (3)	Fe(1)–Fe(2)–C(5)	151.4 (3)
Fe(1)–Fe(2)–C(11)	43.6 (2)	Fe(1)–Fe(2)–C(12)	78.8 (2)
C(3)–Fe(2)–C(4)	97.7 (4)	C(3)–Fe(2)–C(5)	96.5 (4)
C(3)–Fe(2)–C(11)	103.4 (4)	C(3)–Fe(2)–C(12)	101.5 (4)
C(4)–Fe(2)–C(5)	95.5 (4)	C(4)–Fe(2)–C(11)	123.4 (4)
C(4)–Fe(2)–C(12)	155.4 (4)	C(5)–Fe(2)–C(11)	132.4 (4)
C(5)–Fe(2)–C(12)	97.4 (4)	C(11)–Fe(2)–C(12)	36.6 (3)
Fe(1)–P–C(17)	112.8 (3)	Fe(1)–P–C(23)	116.9 (3)
Fe(1)–P–C(29)	116.3 (3)	C(17)–P–C(23)	103.0 (4)
C(17)–P–C(29)	104.4 (4)	C(23)–P–C(29)	101.8 (4)
Fe(1)–C(1)–O(1)	179.7 (4)	Fe(1)–C(2)–O(2)	177.7 (4)
Fe(2)–C(3)–O(3)	177.6 (4)	Fe(2)–C(4)–O(4)	173.6 (4)
Fe(2)–C(5)–O(5)	178.1 (4)		
Ni–C(11)–Fe(1)	83.6 (2)	Ni–C(11)–Fe(2)	74.3 (2)
Ni–C(11)–C(12)	73.3 (4)	Fe(1)–C(11)–Fe(2)	87.7 (2)
Fe(1)–C(11)–C(12)	153.6 (4)	Fe(2)–C(11)–C(12)	74.1 (4)
Ni–C(12)–Fe(2)	72.2 (2)	Ni–C(12)–C(11)	69.8 (4)
Ni–C(12)–C(13)	132.3 (4)	Fe(2)–C(12)–C(11)	69.3 (4)
Fe(2)–C(12)–C(13)	138.1 (4)	C(11)–C(12)–C(13)	144.1 (5)
C(12)–C(13)–C(14)	106.6 (5)	C(12)–C(13)–C(15)	107.4 (5)

Fe–C_{sp^2}, and Fe–Cp_{sp} bond lengths in a variety of organoiron compounds. It would appear from this tabulation that a normal single-bond length for an Fe–C_{sp^3} linkage (i.e. in the absence of multiple-bond character) should be ~ 2.09 Å. The observed Fe–C_{sp} bond length in (η^5-C_5H_5)-$Fe(CO)_2(C{\equiv}CPh)$, where a component of π-bonding may be already present, is 1.920 (6) Å.[23b] We can conclude that there must be substantial multiple-bond character in the Fe–C_α interaction in 1 and 2. This result contrasts sharply with the situation observed in $Fe_3(CO)_9(\mu_3$-η^2-⊥-$RC{\equiv}CR)$ compounds, where the Fe–C_α (Fe–C_α being considered as the equatorial carbon atom in the trigonal bipyramid) bond lengths are much longer, averaging 2.07 Å.[2e] We will return to this point in a general context later in the discussion. (ii) When we take into account the slight contraction in the covalent radius of the metal from Fe to Ni, the metal–acetylide η^2 interactions are not significantly different in 2 ($\Delta(M–C_\alpha)$ = 0.013 Å; $\Delta(M–C_\beta)$ = 0.028 Å) and the acetylide is only slightly more strongly bound to Ni in 1 ($\Delta(M–C_\alpha)$ = 0.055 Å; $\Delta(M–C_\beta)$ = 0.015 Å). Thus, it is unlikely that the metal–acetylide π-bonding dictates the adoption of the unsymmetrical structure. (iii) Calculations on closo heterometallic acetylene complexes $M_2M'(\mu_3$-η^2-⊥-$RC{\equiv}CR)L_n$ suggests that unsymmetrical isomers of this type are more stable by 1–4 kcal mol^{-1}, although there does not appear to be a single explanation for this in molecular orbital terms.[3b]

The principal difference between 1 and 2 is the substitution of an equatorial CO by a PPh_3 ligand at the iron atom σ-bonded to the acetylide. The phosphine is approximately trans to the Ni–Fe(1) bond (Ni–Fe(1)-P = 156.9 (1)°) possibly to minimize steric contacts with the η^5-C_5H_5 ring on nickel. Carbonyl substitution in acetylide clusters most frequently occurs at the σ-bound metal atom,[24] and for heterometallic systems with (η^5-C_5H_5)Ni fragments the disposition of the phosphine in an equatorial site trans to an (η^5-C_5H_5)Ni–M bond is common.[25] More interesting is the effect on the dimensions of the cluster core. Recent results on an extensive series of substituted triruthenium carbonyls suggest only small changes in intracluster distances following phosphine substitution.[26] For 1 and 2, however, the effect is quite distinct. The Fe(1)–Fe(2) bond length in 2 (2.655 (2) Å) is significantly elongated in comparison to that in 1 (2.608 (2) Å) or to the Fe–Fe bond length in $CpNiFe_2(CO)_6(\mu_3$-η^2-$C{\equiv}CBu^t)$ (2.610 (3) Å) (Table VI). Thus, it seems that phosphine substitution at the metal atom σ-bound to the acetylide effects a lengthening of the cis homonuclear metal–metal bond. The situation is less clear for the trans heteronuclear Fe(1)–Ni bond, which for 2 (2.546 (2) Å) is intermediate in length between the values for 1 (2.504 (1) Å) and the *tert*-butylacetylide analogue (2.564 (3) Å). The effect of phosphine substitution on the third distant heterometallic bond Fe(2)–Ni is to cause a slight but significant lengthening (Fe(2)–Ni = 2.378 (1) (1), 2.404 (2) Å (2)).

Structural Comparison of Trinuclear μ_3-η^2-Acetylide and μ_3-η^2-Acetylene Clusters with Closo Trigonal-Bipyramidal M_3C_2 Skeletons. Despite the characterization of $Fe_3(CO)_9(\mu_3$-η^2-⊥-$PhC{\equiv}CPh)$ in 1966[2a] relatively few molecules with this type of structure have been subjected to X-ray analysis. Other examples are as follows: homonuclear $Fe_3(CO)_9(\mu_3$-η^2-⊥-$EtC{\equiv}CEt)$[2e] and heteronuclear $FeRu_2(CO)_9(\mu_3$-η^2-⊥-$PhC{\equiv}CPh)$,[2d] (η^5-$C_5H_5)_2M_2Fe(CO)_6(\mu_3$-$\eta^2$-⊥-$RC{\equiv}CR)$ (M = Mo, W; R = *p*-tolyl),[27] and (η^5-$C_5H_5)_2W_2Fe(CO)_5(O)(\mu_3$-$\eta^2$-⊥-$RC{\equiv}CR)$ (R = *p*-tolyl).[28] Structurally characterized acetylides in-

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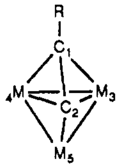
Table VI. Structural Parameters for μ_3-η^2-⊥-Acetylene and μ_3-η^2-Acetylide Clusters of Iron[a]

	structural params								
	3–5	4–5	3–4[b]	2–5[c]	2–3 2–4[d]	1–3 1–4[e]	1–2	1–2–5	ref
$(Cp)Fe_3(CO)_7(C_2Ph)$	2.632 (1)	2.639 (1)	2.524 (1)	1.829 (6)	2.040 (4) 2.006 (5)	2.031 (5) 2.031 (5)	1.299 (9)	152.9 (5)	29
$[Fe_3(CO)_9(CCOC(O)Me)]^-$	2.626 (1)	2.646 (1)	2.494 (1)	1.809 (6)	2.033 (5) 2.044 (5)	2.047 (5) 2.011 (5)	1.314 (8)	150.6 (4)	10
$(Cp)WFe_2(CO)_8(C_2R)$[f]	2.897 (2)[g]	2.874 (3)[g]	2.503 (3)	1.999 (15)	2.025 (11) 2.011 (11)	2.091 (13) 2.086 (12)	1.30 (2)	163	28
$(Cp)NiFe_2(CO)_6(C_2Bu^t)$	2.610 (3)	2.564 (3)[g]	2.378 (3)[g]	1.813 (10)	2.010 (10) 1.929 (10)	2.060 (10) 2.034 (10)	1.284 (14)	155.8 (9)	32
$(Cp)NiFe_2(CO)_6(C_2Pr^i)$[h]	2.608 (2)	2.504 (1)[g]	2.386 (1)[g]	1.818 (5)	2.024 (5) 1.964 (4)	2.034 (5) 2.031 (4)	1.278 (5)	151.6 (4)	this work
	2.608 (2)	2.504 (1)[g]	2.368 (1)[g]	1.800 (4)	2.012 (5) 1.963 (5)	2.045 (4) 2.025 (5)	1.281 (7)	152.6 (4)	this work this work
$(Cp)NiFe_2(CO)_5(PPh_3)(C_2Bu^t)$	2.655 (2)	2.546 (2)[g]	2.404 (2)[g]	1.831 (8)	1.998 (9) 1.985 (8)	2.054 (8) 2.026 (8)	1.273 (11)	153.6 (4)	this work
$(Cp)_2Mo_2Fe(CO)_6(C_2R_2)$[f]	2.764 (1)	2.761 (1)[g]	2.732 (1)[g]	2.297 (3)	2.299 (3) 2.016 (2)	2.070 (3) 2.049 (3)	1.399 (4)	131.1 (2)	33
$(Cp)_2W_2Fe(CO)_6(C_2R_2)$[f]	2.747 (1)	2.745 (1)[g]	2.731 (1)[g]	2.264 (7)	2.289 (5) 2.011 (5)	2.040 (6) 2.052 (5)	1.399 (9)	130.7 (4)	27
$(Cp)_2(O)W_2Fe(CO)_5(C_2R_2)$[f]	2.848 (1)	2.677 (1)[g]	2.747 (2)[g]	2.259 (8)	2.480 (10) 2.027 (9)	2.046 (10) 2.017 (9)	1.441 (11)	124.2 (6)	27
$Fe_3(CO)_9(C_2Ph_2)$	2.501 (9)	2.480 (10)	2.579 (11)	2.048 (16)	2.043 (15) 2.098 (15)	1.945 (15) 1.947 (16)	1.409 (22)	126.9 (10)	2b
$Fe_3(CO)_9(C_2Et_2)$	2.4749 (5)	2.4734 (5)	2.5666 (5)	2.063 (3)	2.070 (3)	1.947 (3)	1.391 (4)	126.3 (1)	2e
$Fe_2Ru(CO)_9(C_2Ph_2)$	2.564 (2)[g]	2.582 (3)[g]	2.588 (3)	2.198 (17)	2.088 (12) 2.052 (13)	1.941 (16) 1.961 (12)	1.413 (20)	126.6	2d

[a] Bond distances are in Å and angles in deg. Structural key:



[b] Bridged M–M. [c] M_σ–C_α. [d] M_π–C_α. [e] M_π–C_β. [f] R = C_6H_4-Me-4 (*p*-tolyl). [g] Heterometallic edge. [h] Two independent molecules.

Table VII. Summary of Pertinent Intraskeletal Bond Lengths for Iron Acetylene (A) and Acetylide (B) Clusters[a]

	type A	type B
$M\sigma$—$C\alpha$, Å	2.05–2.30	1.80–1.83
$M\pi$—$C\alpha$ (mean), Å	2.06–2.25	1.97–2.02
$M\pi$—$C\beta$ (mean), Å	1.95–2.05	2.03–2.88
C≡C, Å	1.39–1.44	1.28–1.31
$M\sigma$—$C\alpha$—$C\beta$, deg	90–130	150–165

[a] For A and B structural types see Chart I.

clude the following: homonuclear $(\eta^5\text{-}C_5H_5)Fe_3(CO)_7(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)$,[29] the anion $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}COC(O)Me)]$,[10] and heteronuclear $(\eta^5\text{-}C_5H_5)WFe_2(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)$ (R = *p*-tolyl), as well as the new molecules 1 and 2. To facilitate comparisons, we have listed important structural parameters for these clusters in Table VI together with the skeletal key shown. Table VII provides a short summary of the range for iron complexes only of metal–carbon and carbon–carbon distances as well as the angles at C_α and C_β of the hydrocarbyls which indicate the distortion of the M_σ—C_α≡C_β—C fragments from linearity. Several remarkable points arise from these comparisons. (i) Even through Table VII makes no allowance for differences in the π-bound metals, for iron clusters the Fe–C_α distances all lie within the narrow range of 1.80–1.83 Å for the acetylides and in a quite separate, much higher range of 2.05–2.30 Å for the μ_3-η^2-⊥-acetylene complexes. (ii) There are major differences in the stereochemistry at the C_α atom in the two series, with the intrapolyhedral Fe–C_α–C_β angle (150–165°) being much larger in the acetylide clusters than in the acetylenes (126–130°). (iii) Although the –C≡C– bond length is not always a sensitive probe of the perturbation of an acetylene or acetylide upon coordination, there are again two distinct ranges in Table VII, with the triple bonds being more elongated in the μ_3-η^2-⊥-acetylenes. (iv) In general, metal π-interactions are stronger to C_α in the acetylides and to C_β in the acetylenes.

The net consequence of these distinctive features is that the C_α–R fragment in the μ_3-η^2-⊥-acetylene clusters approximates much more closely to an equatorial skeletal component of a trigonal bipyramid than the "bare" C_α in the acetylides. Indeed, the Fe_3 acetylides show a closer resemblance to the Fe_4 cluster carbides such as $[Fe(CO)_{12}C]^{2-}$ and $[Fe_4(CO)_{13}C]$,[14,30] if a wingtip metal atom of the latter class is replaced by C_β–R of the acetylide as illustrated in B and D (Chart I). In the tetrairon carbides

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$[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$, $[HFe_4(CO)_{12}(\mu_4\text{-}C)]$, $[Fe_4(CO)_{12}(\mu_4\text{-}CO)]$, $[HFe_4(CO)_{12}(\mu_4\text{-}CH)]$, and $[HFe_4(CO)_{12}(\mu_4\text{-}COCH_3)]$, the μ_4 carbon atom is semiencapsulated and almost collinear with the wingtip atoms (Fe–(μ_4-C)–Fe angles lie in the range 170–177°). These angles are somewhat larger than the corresponding Fe–C_α–C_β angles (150–165°) in the acetylides, but the latter lie closer to the Fe_4 carbides than the μ_3-η^2-$\perp$-acetylenes. The analogy can be taken a step further by recognizing that the formal attachment of a non-cluster-bound substitutent R^+ (R = COOMe) on the μ_4-carbide atom of $[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$ gives $[Fe_4(CO)_{12}(\mu_4\text{-}COCOOMe)]^-$, an anion in which the wingtip–(μ_4-C)–wingtip angle is 148°.[31] In the Fe_3–acetylide M_4–carbide analogy this anion corresponds to the $Fe_3(\mu_3\text{-}\eta^2\text{-}RC{\equiv}CR)$ structures. It will be interesting to see whether these structural analogies translate into patterns of chemical reactivity for the $M_3(\mu_3\text{-}\eta^2\text{-acetylides})$ similar to those of the butterfly carbides.

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Supplementary Material Available: Positional coordinates and isotropic thermal parameters for the hydrogen atoms of 1 (Table SI) and anisotropic thermal parameters for the non-hydrogen atoms of 1 and 2 (Tables SII and SIII, respectively) (3 pages); observed and calculated structure factors from the final cycle of least-squares refinement for 1 and 2 (Tables SIV and SV, respectively) (47 pages). Ordering information is given on any current masthead page.

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Formation of Diaziridines by Reaction of $(CO)_5W{=}C(OMe)Ph$ with Electron-Deficient Azo Compounds

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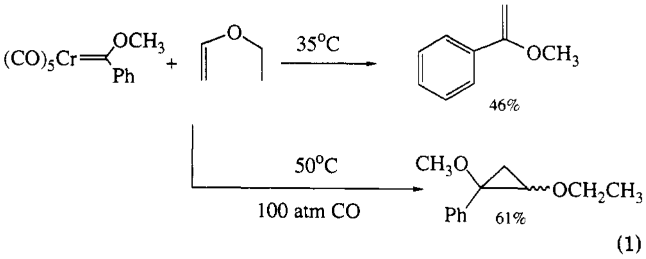
The reaction between $(CO)_5W{=}C(OMe)Ph$ (**7**) and 4-methyl-1,2,4-triazoline-3,5-dione in acetonitrile results in the formation of two isomeric diaziridines **8a** and **8b** in a 2:1 ratio. The related azo compound diethyl azodicarboxylate also reacts with **7** to produce a diaziridine product. This reactivity of electron-poor azo compounds is analogous to the cyclopropanation of olefins and contrasts with the previously reported metathesis reaction of tungsten carbenes with *cis*-azobenzene.

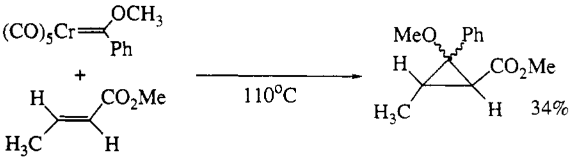
Introduction

We previously reported the isolation of zwitterionic intermediate **4** in the azo metathesis reaction between $(CO)_5W{=}C(OCH_3)CH_3$ (**1**) and *cis*-azobenzene (**2**).[1] The proposed mechanism involves initial nucleophilic attack of *cis*-azobenzene on the carbene complex to give **3**, which then rearranges to give the observed zwitterionic species **4** (Scheme I). Cleavage of zwitterion **4** yields imino ether **5** and products derived from the low-valent nitrene complex **6**.

The current work addresses the question of how the reaction manifold is altered when less nucleophilic azo compounds are reacted with Fischer carbenes. Olefins react with carbene complexes to produce mixtures of metathesis and cyclopropanation products,[2] depending on the reaction conditions and the nature of the olefin substrate. For example, the chromium carbene $(CO)_5Cr{=}C(OCH_3)Ph$ undergoes metathesis with ethyl vinyl ether under mild conditions, but under a high pressure of CO, the metathesis pathway is shut down and only cyclopropanation occurs (eq 1).[3] When the electron-poor methyl crotonate is used, the reaction pathway is cyclopropanation and no metathesis products are observed (eq 2).[4] The reaction between **1** and *cis*-azobenzene gives only the azo metathesis product. We now have observed the equivalent of the cyclopropanation pathway for azo compounds. Reactions of $(CO)_5W{=}C(OMe)Ph$ (**7**) with the more electron-deficient azo substrates 4-methyl-1,2,4-tri-



(1)



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