The reaction mixture was stirred at 50–60 °C for 4 h. The homogeneous dark yellow brown solution was filtered through a Celite layer and the volatiles were removed in vacuo. The residue was redissolved at 50–60 °C in ca. 50 mL of toluene. Hexane was added until a beginning cloudiness remained, and the solution was slowly cooled, first to room temperature and then to 5 °C. The dark yellow crystals formed were isolated by Schlenk filtration, washed with hexane, dried in vacuo, and kept under argon.

Yield: 14.8 g (~90%). Anal. Calcd for $C_{31}H_{42}OP_2Ni$: C, 67.53; H, 7.68. Found: C, 67.7; H, 7.5. ESCA: BE ($Ni2p_{3/2}$) 853.5 eV. Mass spectrum: $m/e$ 550 ($M^+$ for $^{58}Ni$), 507 (M − Pr), 376 (M − $Pr_3PCH_2$), 318 ($Ph_3PCHCMeO$), 174 ($Pr_3PCH_2$), 77 (Ph). $^1H$ NMR ($C_6D_6$, TMS internal): intact ylide ligand $i$-$Pr_3PCH_2$, $\delta$ +0.53 (dd, $^2J(P,H)$ = 13.1 Hz, $^3J(P,H)$ = 5.4 Hz, $CH_2$), +0.91 (dd, $^3J(P,H)$ = 14.4 Hz, $^3J(H,H)$ = 7.0 Hz, 6 $CH_3$), +1.88 (approx d-sept, $^2J(P,H)$ = 12 Hz, $^3J(H,H)$ = 7 Hz, 3 H); rearranged ylide, $\delta$ +2.10 (s, $CH_3$), +4.38 (d, $^2J(P,H)$ = 0.6 Hz, CH), +6.84 to +7.77 (m, 3 $C_6H_5$). $^{13}C$ NMR ($C_6D_6$, TMS internal) data are given in Table III. For $^{31}P$ NMR data, see eq 1 in the text.

**Crystallographic Structure Determination for Complex 1a.** A yellow crystal of **1a** (0.15 × 0.175 × 0.225 mm$^3$) was mounted on an Enraf-Nonius CAD4 diffractometer, equipped with graphite-monochromated Cu K$\alpha$ radiation ($\lambda$ = 1.540 56 Å). Cell parameters were determined by a least-square refinement of angular coordinates of 22 reflections. Data were collected at room temperature by the $\theta$–$2\theta$ scan technique. A total of 4366 independent reflections was measured in the range 10° < $\theta$ < 60° ($\pm h,+k,+l$) of which 2688 with $I \geq 3\sigma(I)$ were used in the subsequent refinements. Data were corrected for absorption[18] (transmission factors: 0.998 max, 0.947 min) and Lorentz–polarization effects. Calculations were performed on a Micro VAX computer using the Enraf-Nonius structure determination package.[19] Crystal data are found in Table IV. The structure was solved by a combination of direct methods and Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms isotropically. Fractional atomic coordinates of non-hydrogen atoms are given in Table V.

**Registry No.** **1a**, 89743-12-4; $i$-$Pr_3PCH_2$, 29218-76-6; $Ni(COD)_2$, 1295-35-8; $Ph_3PCHCMeO$, 1439-36-7.

**Supplementary Material Available:** Tables of crystal structure data, atomic coordinates, thermal parameters, bond lengths, bond angles, dihedral angles, and least-squares planes and a figure showing a unit cell and packing diagram (12 pages). Ordering information is given on any current masthead page.

OM910761Y

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# Cluster Building on a Bicarbide Fragment: Synthesis and Structure of $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$

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*Summary:* Thermal reaction of the ethynediyl complex $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C{\equiv}C)]$ (**1**) with diiron nonacarbonyl occurs with formation of $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ (**2**), a cluster containing a bicarbide ligand. A structural study has shown that one of the ruthenium atoms migrates from a position where it is $\sigma$-bonded to a single ethynediyl carbon to become $\eta^2$-bonded to the ethynediyl unit. Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with $a$ = 9.579 (5) Å, $b$ = 24.789 (4) Å, $c$ = 10.621 (5) Å, $\beta$ = 115.02°, $Z$ = 4, $V$ = 2285 (2) Å$^3$, 2679 reflections with $I \geq 3\sigma(I)$, $R$ = 0.049, $R_w$ = 0.056.

Alkynes have long been known to react with metal carbonyls, particularly $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$, to give an enormous variety of interesting complexes.[1,2] Extension of this methodology to metal alkynyls (acetylides, $L_nM{-}C{\equiv}CR$) gave complexes in which the carbon–carbon triple bond is coordinated to Fe or Co, sometimes with the concomitant formation of direct M—Fe or M—Co bonds.[3-11]

Ethynediyl complexes ($L_nM{-}C{\equiv}C{-}ML_n$) comprise a relatively small but rapidly expanding group of compounds whose reactivity is little studied.[12-30] Our recent report

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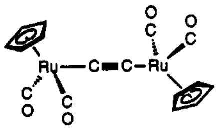
of the preparation of [{Ru(CO)$_2$($\eta$-C$_5$H$_5$)}$_2$($\mu$-C$\equiv$C)] (1)[12] by alkyne metathesis provided a suitable starting point for the investigation of the chemistry of ethynediyl complexes.



1

## Experimental Section

The reaction was carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques, but the workup was performed in air. Thin-layer chromatography was done on Whatman silica gel 60A plates, 20 × 20 cm, 500-$\mu$m layer. Solvents were purified and dried under nitrogen by standard techniques and transferred to reaction vessels by cannula or syringe. Microanalysis was performed by the Canadian Microanalytical Service, Delta, British Columbia. The infrared spectrum was recorded in CH$_2$Cl$_2$ on a Perkin-Elmer 1710 FT-IR spectrometer using NaCl optics. The $^1$H spectrum was acquired on a Varian Gemini 200 spectrometer and was referenced internally to residual CHCl$_3$.

**Synthesis of [Fe$_2$Ru$_2$($\mu_4$-C$\equiv$C)($\mu$-CO)(CO)$_8$($\eta$-C$_5$H$_5$)$_2$] (2).** [{Ru(CO)$_2$($\eta$-C$_5$H$_5$)}$_2$($\mu$-C$\equiv$C)] (40 mg, 0.085 mmol) and [Fe$_2$(CO)$_9$] (50 mg, 0.14 mmol) were dissolved in THF (30 mL) in a Schlenk flask, and the solution was stirred for 3 h at room temperature. The solvent was removed in vacuo, and the residue was redissolved in a minimum of CH$_2$Cl$_2$. Separation by TLC on silica gel using CH$_2$Cl$_2$/hexane (3/7) as eluant developed six bands: (in order of decreasing $R_f$) red, yellow-green, yellow, brown, yellow, dark green. The major component, yellow-green band 2, was extracted with CH$_2$Cl$_2$ and crystallized from CH$_2$Cl$_2$/hexane at −20 °C to give 21 mg (34%) of 2 as green-black, pyramidal crystals, mp > 150 °C. Anal. Calcd for C$_{21}$H$_{10}$Fe$_2$O$_9$Ru$_2$: C, 35.03; H, 1.40. Found: C, 34.53; 1.47. IR (CH$_2$Cl$_2$, $\nu$(CO)): 2062 (m), 2043 (m), 2012 (s), 2000 (sh), 1979 (m), 1946 (w), 1858 (w). $^1$H NMR (200 MHz, CDCl$_3$): 5.51 (s, 5 H, C$_5$H$_5$), 5.17, (s, 5 H, C$_5$H$_5$).

**X-ray Structure Determination of Complex 2.** Crystal structure calculations were performed on an IBM 3090 computer system, using the direct methods-difference Fourier program DIRDIF,[31] local version of Ibers' NUCLS least-squares program (based on the Busing–Levy ORFLS), Zalkin's FORDAP Fourier program, the Busing–Levy ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program.[32] Anomalous dispersion corrections were included for the scattering of Ru, P, and F atoms.

Crystals of 2 suitable for X-ray diffraction were obtained from CH$_2$Cl$_2$/hexane at −20 °C. The crystal was coated with epoxy and mounted on a glass fiber, nearly aligned along the long axis of the crystal. Crystal properties and details of X-ray data collection, solution, and refinement are listed in Table I.

The ruthenium atoms were located by using the Patterson function in DIRDIF. The iron atoms and 19 carbon or oxygen atoms were located by using DIRDIF. The remaining non-hydrogen atoms were found by using difference Fourier methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Cyclopentadienyl hydrogen atoms were placed in calculated positions and were assigned isotropic thermal parameters equal to $B$(attached carbon) + 1.0. An empirical absorption correction was made by using DIFABS.[33] No corrections for decay or extinction were applied to the data.

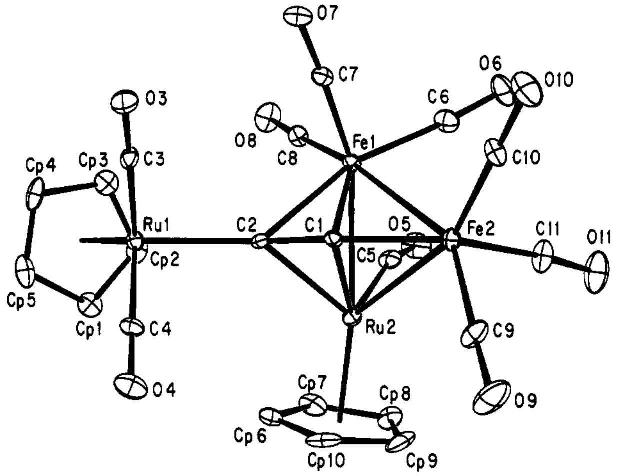


**Figure 1.** Perspective drawing of the molecular structure of [Fe$_2$Ru$_2$($\mu_4$-C$\equiv$C)($\mu$-CO)(CO)$_8$($\eta$-C$_5$H$_5$)$_2$] (2). The ellipsoids correspond to 50% probability contours of atomic displacement. The hydrogen atoms have been omitted for the sake of clarity.

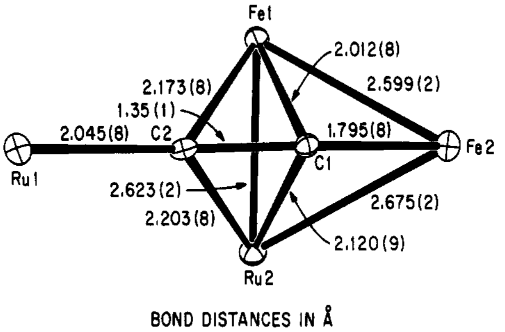
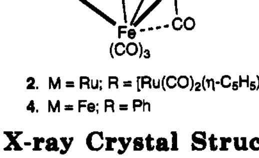


**Figure 2.** Perspective drawing of the core of [Fe$_2$Ru$_2$($\mu_4$-C$\equiv$C)($\mu$-CO)(CO)$_8$($\eta$-C$_5$H$_5$)$_2$] (2).

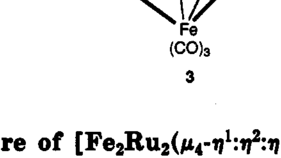
## Results

Reaction of 1 with [Fe$_2$(CO)$_9$] affords [Fe$_2$Ru$_2$($\mu_4$-C$\equiv$C)($\mu$-CO)(CO)$_8$($\eta$-C$_5$H$_5$)$_2$] (2) as the major product after thin-layer chromatographic separation of the mixture obtained. Purification was achieved by crystallization from dichloromethane/hexane. A $^1$H NMR spectrum of the tetranuclear cluster 2 showed the presence of two distinct cyclopentadienyl ligands. The solution infrared spectrum of 2 displayed six terminal and one bridging (1858 cm$^{-1}$) $\nu$(CO) bands. Microanalytical data in conjunction with this spectroscopic data proved insufficient to unambiguously characterize complex 2.



**2.** M = Ru; R = [Ru(CO)$_2$($\eta$-C$_5$H$_5$)]

**4.** M = Fe; R = Ph



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**X-ray Crystal Structure of [Fe$_2$Ru$_2$($\mu_4$-$\eta^1$:$\eta^2$:$\eta^1$:$\eta^2$-C$\equiv$C)($\mu$-CO)(CO)$_8$($\eta$-C$_5$H$_5$)$_2$] (2).** Crystals suitable for the X-ray structure determination were obtained from dichloromethane/hexane at −30 °C. Experimental details

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**Table I. Summary of the Crystal Data and Details of Intensity Collection and Refinement for $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ (2)**

| | |
|---|---|
| color and form | green-black, truncated pyramid |
| formula | $C_{21}H_{10}Fe_2O_9Ru_2$ |
| fw | 720.136 |
| space group | $P2_1/c$ (No. 14) |
| $a$, Å | 9.579 (5) |
| $b$, Å | 24.789 (4) |
| $c$, Å | 10.621 (5) |
| $\beta$, deg | 115.02 (2) |
| vol, Å$^3$ | 2285 (2) |
| temp, K | 297 (1) |
| $Z$ | 4 |
| imposed symmetry | none |
| density (calcd), g·cm$^{-3}$ | 2.102 |
| $F(000)$ | 1392 |
| $F(000)$ corrected | 1383.222 |
| cryst dimens, mm | 0.3 × 0.5 × 0.5 |
| diffractometer | Enraf-Nonius CAD-4 |
| λ(Mo Kα radiation), Å | 0.7107 |
| monochromator | graphite |
| sets of setting angles refined | 25 |
| $\theta$ range for cell, deg | 10.0–14.2 |
| $\theta$ limits for data, deg | 2–25 |
| $h,k,l$ ranges | 0–11, 0–29, −12 to +12 |
| max counting time, s | 90 |
| scan type | $\omega$ |
| scan range, deg | 1.10 + 0.35 tan $\theta$ |
| X-ray exposure time, h | 74.4 |
| no. of stds | 3 |
| % max variation | 4.7 (random) |
| no. of unique data | 3985 |
| no. of data with $I \geq 3\sigma(I)$ | 2679 |
| abs corr | empirical (DIFABS) |
| $\mu$, cm$^{-1}$ | 25.771 |
| min corr factors on $F$ | 0.569 |
| max corr factors on $F$ | 1.515 |
| av corr factors on $F$ | 1.012 |
| final no. of variables | 307 |
| p factor | 0.02 |
| $(\Delta/\sigma)_{max}$ | 0.03 ($\beta_{22}$ of Ru1) |
| $R$,[a] % | 4.9 |
| $R_w$,[a] % | 5.6 |
| GOF[b] | 2.7243 |
| $\Delta(\rho)_{max}$, e·Å$^{-3}$ | 0.070 |

[a] $R = (\sum||F_o| - |F_c||/\sum|F_o|)$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = 4I/(\sigma^2(I) + 0.02I^2)$. [b] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

**Table II. Positional Parameters and Equivalent $B$ Values for the Atoms of $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ (2)**

| atom | $x$ | $y$ | $z$ | $B_{eq}$,[a] Å$^2$ |
|---|---|---|---|---|
| Ru1 | 0.24265 (8) | 0.12193 (3) | 0.04448 (8) | 3.68 (2) |
| Ru2 | 0.54839 (9) | 0.13458 (3) | 0.43169 (7) | 3.88 (3) |
| Fe1 | 0.6711 (2) | 0.08720 (5) | 0.2813 (1) | 3.29 (4) |
| Fe2 | 0.7731 (2) | 0.18215 (6) | 0.3850 (1) | 3.43 (4) |
| C1 | 0.585 (1) | 0.1627 (3) | 0.2595 (9) | 2.9 (3) |
| C2 | 0.456 (1) | 0.1323 (3) | 0.2034 (8) | 2.9 (3) |
| C3 | 0.321 (1) | 0.1432 (4) | −0.080 (1) | 3.9 (3) |
| C4 | 0.201 (1) | 0.1935 (4) | 0.070 (1) | 4.0 (4) |
| C5 | 0.660 (1) | 0.0722 (5) | 0.497 (1) | 4.9 (4) |
| C6 | 0.869 (1) | 0.0728 (5) | 0.377 (1) | 5.4 (4) |
| C7 | 0.687 (1) | 0.0926 (4) | 0.124 (1) | 3.9 (4) |
| C8 | 0.593 (1) | 0.0206 (5) | 0.245 (1) | 4.7 (4) |
| C9 | 0.737 (1) | 0.2489 (5) | 0.424 (1) | 5.6 (4) |
| C10 | 0.893 (1) | 0.1980 (5) | 0.303 (1) | 4.9 (4) |
| C11 | 0.914 (1) | 0.1672 (4) | 0.553 (1) | 5.6 (4) |
| Cp1 | 0.069 (1) | 0.0806 (6) | 0.105 (1) | 6.2 (5) |
| Cp2 | 0.193 (2) | 0.0460 (6) | 0.135 (1) | 6.4 (5) |
| Cp3 | 0.200 (1) | 0.0340 (5) | 0.011 (2) | 6.2 (5) |
| Cp4 | 0.079 (2) | 0.0614 (6) | −0.099 (1) | 6.9 (5) |
| Cp5 | 0.000 (1) | 0.0909 (6) | −0.042 (2) | 6.8 (5) |
| Cp6 | 0.320 (1) | 0.1526 (7) | 0.433 (1) | 6.6 (5) |
| Cp7 | 0.392 (2) | 0.1166 (6) | 0.536 (1) | 6.7 (6) |
| Cp8 | 0.528 (2) | 0.1394 (7) | 0.633 (1) | 6.7 (5) |
| Cp9 | 0.535 (2) | 0.1908 (7) | 0.589 (2) | 7.9 (7) |
| Cp10 | 0.411 (2) | 0.1996 (6) | 0.464 (2) | 7.4 (7) |
| O3 | 0.368 (1) | 0.1567 (4) | −0.1571 (8) | 6.4 (3) |
| O4 | 0.177 (1) | 0.2376 (4) | 0.086 (1) | 6.9 (4) |
| O5 | 0.722 (1) | 0.0360 (4) | 0.5710 (9) | 8.2 (4) |
| O6 | 0.995 (1) | 0.0601 (4) | 0.433 (1) | 8.3 (4) |
| O7 | 0.690 (1) | 0.0964 (3) | 0.0175 (9) | 5.7 (3) |
| O8 | 0.548 (1) | −0.0221 (3) | 0.219 (1) | 8.1 (4) |
| O9 | 0.718 (1) | 0.2922 (4) | 0.446 (1) | 9.7 (5) |
| O10 | 0.970 (1) | 0.2088 (4) | 0.250 (1) | 7.8 (4) |
| O11 | 0.997 (1) | 0.1583 (4) | 0.666 (1) | 9.7 (4) |

[a] The equivalent displacement parameter is defined as (4/3)Tr(**B**·**G**), where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

**Table III. Bond Distances (Å) with Esd's for the Structure of $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ (2)**

| | | | |
|---|---|---|---|
| Ru1–C4 | 1.853 (11) | Fe2–C10 | 1.748 (13) |
| Ru1–C3 | 1.855 (11) | Fe2–C11 | 1.766 (9) |
| Ru1–C2 | 2.045 (8) | Fe2–C9 | 1.769 (13) |
| Ru1–Cp3 | 2.210 (11) | Fe2–C1 | 1.795 (8) |
| Ru1–Cp4 | 2.233 (11) | C1–C2 | 1.349 (11) |
| Ru1–Cp5 | 2.240 (12) | C3–O3 | 1.130 (11) |
| Ru1–Cp2 | 2.245 (11) | C4–O4 | 1.141 (12) |
| Ru1–Cp1 | 2.258 (11) | C5–O5 | 1.171 (12) |
| Ru1–Cp01[a] | 1.898 | C6–O6 | 1.138 (12) |
| Ru2–C5 | 1.836 (12) | C7–O7 | 1.153 (12) |
| Ru2–C1 | 2.120 (9) | C8–O8 | 1.130 (12) |
| Ru2–Cp10 | 2.196 (12) | C9–O9 | 1.124 (13) |
| Ru2–C2 | 2.203 (8) | C10–O10 | 1.131 (13) |
| Ru2–Cp9 | 2.215 (12) | C11–O11 | 1.145 (11) |
| Ru2–Cp8 | 2.227 (11) | Cp1–Cp2 | 1.385 (18) |
| Ru2–Cp6 | 2.234 (12) | Cp1–Cp5 | 1.431 (18) |
| Ru2–Cp7 | 2.245 (13) | Cp2–Cp3 | 1.376 (19) |
| Ru2–Cp02[b] | 1.893 | Cp3–Cp4 | 1.421 (17) |
| Ru2–Fe1 | 2.623 (2) | Cp4–Cp5 | 1.362 (20) |
| Ru2–Fe2 | 2.675 (2) | Cp6–Cp7 | 1.348 (17) |
| Fe1–C7 | 1.742 (12) | Cp6–Cp10 | 1.400 (19) |
| Fe1–C6 | 1.771 (11) | Cp7–Cp8 | 1.392 (18) |
| Fe1–C8 | 1.778 (12) | Cp8–Cp9 | 1.363 (19) |
| Fe1–C1 | 2.012 (8) | Cp9–Cp10 | 1.375 (19) |
| Fe1–C2 | 2.173 (8) | | |
| Fe1–C5 | 2.371 (10) | | |
| Fe1–Fe2 | 2.599 (2) | | |

[a] Cp01 is the centroid of the Cp1–Cp5 cyclopentadienyl ring. [b] Cp02 is the centroid of the Cp6–Cp10 cyclopentadienyl ring.

are given in Table I, positional and thermal parameters in Table II, and selected bond distances and angles in Tables III and IV. An ORTEP[32] plot of the entire molecule is shown in Figure 1. One ruthenium, two irons, and two carbon atoms adopt the closed, trigonal-bipyramidal arrangement illustrated in Figure 2. The Fe1–Fe2 bond of 2 (2.599 (2) Å) is significantly longer than the 2.503 (3) Å alkynyl-bridged Fe—Fe bond in $[Fe_2W(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}C{\equiv}CPh)(CO)_8(\eta\text{-}C_5H_5)]$[34] (3) but about the same length as the unbridged Fe—Fe bonds in $[Fe_3(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$ (4)[6] (average 2.636 (5) Å). A search of the Cambridge Structural Database[35,36] located 44 structures containing iron–ruthenium bonds. The mean of 55 Fe—Ru bond lengths found in 26 of these structures not rejected on the basis of disorder or other problems is 2.696 Å, with a range 2.451–2.940 Å. The Fe—Ru bonds in 2 are slightly shorter than the mean, with the Fe1—Ru2 bond (2.623 (2) Å) which is spanned by a semibridging carbonyl being slightly shorter than the unbridged Fe2—Ru2 bond (2.675 (2) Å). The second ruthenium atom (Ru1) is contained in a discrete $[Ru(CO)_2(\eta\text{-}C_5H_5)]$ substituent on the

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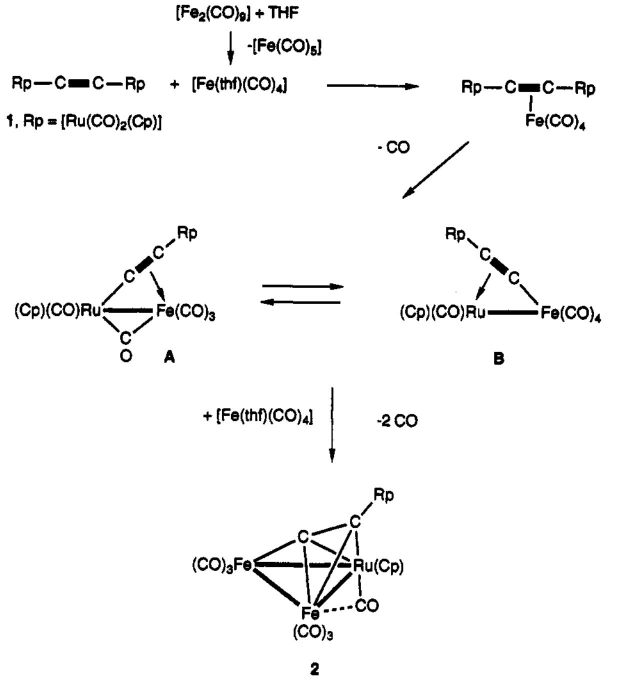
**Table IV. Selected Bond Angles (deg) with Esd's for the Structure of $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ (2)**

| | | | |
|---|---|---|---|
| C4–Ru1–C3 | 90.5 (5) | C10–Fe2–C11 | 99.8 (5) |
| C4–Ru1–C2 | 87.8 (4) | C10–Fe2–C9 | 98.1 (6) |
| C3–Ru1–C2 | 89.3 (4) | C10–Fe2–C1 | 110.7 (5) |
| C4–Ru1–Cp01[a] | 125.4 | C10–Fe2–Fe1 | 101.6 (4) |
| C3–Ru1–Cp01[a] | 126.0 | C10–Fe2–Ru2 | 159.6 (4) |
| Cp01[a]–Ru1–C2 | 126.1 | C11–Fe2–C9 | 95.5 (5) |
| C5–Ru2–C1 | 108.8 (4) | C11–Fe2–C1 | 142.5 (5) |
| C5–Ru2–C2 | 107.2 (4) | C11–Fe2–Fe1 | 103.3 (4) |
| C5–Ru2–Fe1 | 61.3 (3) | C11–Fe2–Ru2 | 92.9 (4) |
| C5–Ru2–Fe2 | 93.1 (4) | C9–Fe2–C1 | 101.0 (5) |
| C1–Ru2–C2 | 36.3 (3) | C9–Fe2–Fe1 | 149.8 (4) |
| C1–Ru2–Fe1 | 48.8 (2) | C9–Fe2–Ru2 | 96.5 (5) |
| C1–Ru2–Fe2 | 42.0 (2) | C1–Fe2–Fe1 | 50.6 (3) |
| C2–Ru2–Fe1 | 52.6 (2) | C1–Fe2–Ru2 | 52.2 (3) |
| C2–Ru2–Fe2 | 77.7 (2) | Fe1–Fe2–Ru2 | 59.6 (0) |
| Fe1–Ru2–Fe2 | 58.7 (0) | C2–C1–Fe2 | 157.0 (7) |
| C5–Ru2–Cp02[b] | 116.0 | C2–C1–Fe1 | 77.8 (5) |
| Cp02[b]–Ru2–C1 | 135.2 | C2–C1–Ru2 | 75.2 (6) |
| Cp02[b]–Ru2–C2 | 124.3 | Fe2–C1–Fe1 | 85.9 (3) |
| Cp02[b]–Ru2–Fe1 | 171.0 | Fe2–C1–Ru2 | 85.8 (3) |
| Cp02[b]–Ru2–Fe2 | 130.1 | Fe1–C1–Ru2 | 78.8 (3) |
| C7–Fe1–C6 | 93.2 (5) | C1–C2–Ru1 | 147.6 (7) |
| C7–Fe1–C8 | 93.6 (5) | C1–C2–Fe1 | 64.8 (5) |
| C7–Fe1–C1 | 90.9 (4) | C1–C2–Ru2 | 68.5 (5) |
| C7–Fe1–C2 | 92.7 (4) | Ru1–C2–Fe1 | 134.9 (4) |
| C7–Fe1–Fe2 | 99.6 (3) | Ru1–C2–Ru2 | 135.1 (5) |
| C7–Fe1–Ru2 | 142.2 (3) | Fe1–C2–Ru2 | 73.6 (2) |
| C6–Fe1–C8 | 100.8 (5) | O3–C3–Ru1 | 179.0 (10) |
| C6–Fe1–C1 | 122.7 (4) | O4–C4–Ru1 | 179.4 (10) |
| C6–Fe1–C2 | 159.3 (4) | O5–C5–Ru2 | 160.7 (10) |
| C6–Fe1–Fe2 | 79.6 (4) | O5–C5–Fe1 | 123.3 (9) |
| C6–Fe1–Ru2 | 113.0 (4) | Ru2–C5–Fe1 | 76.0 (4) |
| C8–Fe1–C1 | 135.9 (4) | O6–C6–Fe1 | 175.2 (12) |
| C8–Fe1–C2 | 98.6 (4) | O7–C7–Fe1 | 177.0 (10) |
| C8–Fe1–Fe2 | 166.7 (4) | O8–C8–Fe1 | 176.6 (13) |
| C8–Fe1–Ru2 | 106.8 (4) | O9–C9–Fe2 | 176.7 (14) |
| C1–Fe1–C2 | 37.4 (3) | O10–C10–Fe2 | 179.3 (12) |
| C1–Fe1–Fe2 | 43.6 (2) | O11–C11–Fe2 | 174.8 (13) |
| C1–Fe1–Ru2 | 52.4 (3) | | |
| C2–Fe1–Fe2 | 79.9 (2) | | |
| C2–Fe1–Ru2 | 53.7 (2) | | |
| Fe2–Fe1–Ru2 | 61.6 (1) | | |

[a] Cp01 is the centroid of the Cp1–Cp5 cyclopentadienyl ring. [b] Cp02 is the centroid of the Cp6–Cp10 cyclopentadienyl ring.

ethynediyl bridge. This $[Ru(CO)_2(\eta\text{-}C_5H_5)]$ unit does not interact with the other metals in the cluster. The Ru1—C2 bond length of 2.045 (8) Å is unchanged from the Ru—alkynyl bond lengths in 1 (2.05 (1) Å, 2.04 (1) Å), being slightly shorter than the average Ru—C bond length of 2.09 Å in five related structures.[12,37–40] Other features of the $[Ru(CO)_2(\eta\text{-}C_5H_5)]$ unit closely resemble those in the related compounds.

**Scheme I**



Comparing the geometry about the bicarbide fragment in 2 to that of the phenylethynyl fragment in 4 reveals few differences. Both are 1σ–2π ligands and the Fe–C and C–C distances are similar in length (Fe2–C1 1.795 (8), C1–C2 1.35 (1) Å in 2; cf. Fe1–C8 1.829 (6), C8–C9 1.30 (1) Å in 4). The Fe–C–C angles are identical within experimental error (157.0 (7), 152.9 (5)° in 2 and 4, respectively). All except one CO ligand are linear in 2. Carbonyl C5O5 spans the Ru2–Fe1 bond in a semibridging bonding mode.[41–44] The C5–O5 distance is longer than the terminal CO groups in the complex and the Ru2–C5–O5 geometry is bent (160.7 (10)°).

A formal electron count shows that the $[(\eta\text{-}C_5H_5)Ru(CO)_2(C{\equiv}C)]$ unit functions as a five-electron donor in the electron precise (48 cluster valence electrons) cluster, giving rise to a closo, trigonal-bipyramidal, six skeletal electron pair structure. The formal count for each metal atom amounts to 17, 19, and 18 valence electrons at Fe2, Ru2, and Fe1, respectively.

## Discussion

The most striking feature of the structure of 2 is the disruption of the linear Ru—C≡C—Ru bonding pattern. Whereas Ru2 interacted with the $C_2$ fragment in an $\eta^1$ mode in the starting material 1, Ru2 bonds to the $C_2$ fragment in an $\eta^2$ mode in the cluster 2. It is ambiguous from the structure of 4 whether the reaction of $[Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)]$ (5) with $[Fe_2(CO)_9]$ proceeds with rearrangement of the metal cluster framework or migration of a cyclopentadienyl ring from one iron to another. The positions of the ruthenium atoms in structure 2 imply that a metal cluster framework rearrangement occurs during the formation of 4. A possible mechanism for the formation of complex 2 is depicted in Scheme I. Lightly stabilized $[Fe(CO)_4(thf)]$, from $[Fe_2(CO)_9]$ in thf,[45] would be expected to react with the unsaturated CC fragment to give an initial $\eta^2$ complex. Metal–metal bond formation probably occurs with expulsion of CO to give putative intermediate A which could rearrange to B. This type of fluxional process or "windshield-wiper" oscillation has been firmly established for binuclear[16] and polynuclear[46–48] complexes containing μ-alkynyl ligands. Similarly, the reaction of 5 with $[Re(CO)_5(FBF_3)]$ resulted in the migation of the σ-alkynyl ligand from the Fe to the Re atom,[49]

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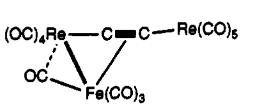
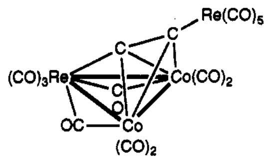
presumably through an intermediate similar to **A** or **B**. Carty and co-workers[50,51] have reported the isolation of binuclear complexes similar to the postulated intermediates **A** and **B** from the reaction of phosphinoalkynes and $[Fe_2(CO)_9]$.

The reaction of $[\{Re(CO)_5\}_2(\mu\text{-}C{\equiv}C)]$ (**6**) with a number of metal substrates[52] was reported while this manuscript was in preparation. It is noteworthy that the reaction of **6** with $[Fe_2(CO)_9]$ incorporates only one Fe atom giving $[FeRe_2(\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}C{\equiv}C)(CO)_{13}]$ (**7**) in which the integrity of the Re—C≡C—Re unit in **5** is maintained. The $[Fe(CO)_4]$ unit in **7** interacts with the bicarbide ligand and one Re atom without the formation of a metal triangle, unlike the reaction of **6** with $[Co_2(CO)_8]$ which gives $[Co_2Re_2(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C{\equiv}C)(\mu\text{-}CO)_2(CO)_{12}]$ (**8**), structurally analogous to **4**.



**7**



**8**

## Conclusion

The reaction of a metal ethynediyl complex with a metal carbonyl is a useful method for the synthesis of mixed-metal bicarbide complexes. Substantial skeletal rearrangement can occur during the formation of the bicarbide complexes. The positions of the metal atoms in the frameworks of the bicarbide products may reflect the relative propensities of the metal centers to form σ- or π-bonds with the $C_2$ ligand. In $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ (**2**), the cluster ruthenium atom Ru2 has migrated from a σ-bonding position in precursor **1** to a π-bonding position, while Fe2 has moved into the σ-bonding position.

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**Supplementary Material Available:** Tables of anisotropic displacement parameters, complete bond angles, hydrogen atom parameters, least-squares planes, and torsion angles for **2** (5 pages). Ordering information is given on any current masthead page.

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# Highly Selective Synthesis of Chlorosilanes from Hydrosilanes

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*Summary:* A highly selective synthesis of chlorosilanes from hydrosilanes is reported. The reactions of $PhMe_2SiH$, $Ph_2MeSiH$, and $Bu_2MeSiH$ with 2 equiv of $CuCl_2$ and a catalytic amount of CuI in $Et_2O$ afforded the respective triorganochlorosilanes. Similar reactions of polyhydrosilanes such as $Et_2SiH_2$, $PhMeSiH_2$, $PhSiH_3$, $HEt_2SiSiEt_2H$, and HMePhSiSiPhMeH with 2 equiv of the $CuCl_2$(CuI) reagent gave the corresponding monochlorinated hydrosilanes selectively, while treatment with 4 equiv of the reagent afforded dichlorosilanes as the sole product. Similar treatment of $t$-$BuMe_2SiH$ with 2 equiv of the reagent in a mixed $Et_2O$ and THF solvent afforded $t$-$BuMe_2SiCl$.

Chlorosilanes are useful starting materials in synthetic organosilicon chemistry. In an attempt to prepare desired silicon compounds, sometimes we have been confronted with the problem of preparing chlorosilanes from hydrosilanes. To date, several methods are available for the preparation of chlorosilanes from hydrosilanes.[1-6] These methods give the chlorosilanes in good yields. However, it is difficult to prepare selectively silicon compounds which contain both Si–Cl and Si–H bonds from polyhydrosilanes. In an effort to develop a method for the preparation of chlorohydrosilanes such as monosubstituted chlorosilanes, $RSiH_2Cl$, disubstituted chlorosilanes, $R_2SiHCl$, and 1-chloro-2-hydrodisilanes, $ClR_2SiSiR_2H$, we have found that the reaction of the H of the hydrosilanes with $CuCl_2$ in the presence of a catalytic amount of CuI is a convenient method for the synthesis of such chlorosilanes.

## Results and Discussion

Triorganosilanes do not react with copper(II) chloride by themselves. For example, treatment of dimethylphenylsilane (**1a**)[7] with 2 molar equiv of $CuCl_2$ in diethyl ether or in THF afforded no chlorodimethylphenylsilane.

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