plexes,[11,12] no silylene rotation was observed,[29] rotation of the germylene moiety in analogous germanium complexes has been observed and quantitatively analyzed. This difference reflects both the greater stability of $M = ER_2$ when E is Ge as opposed to Si[6,30] and the weaker nature of the Ge–O as compared with the Si–O bond.

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**Registry No.** 1, 32054-63-0; 2, 137364-17-1; 3, 137364-18-2; 4, 137364-19-3; 5, 137364-20-6; 6, 137364-21-7; $[Cp(CO)_2FeGeMe_2GeMe_2Cl]$, 137364-22-8; $[Cp'(CO)_2FeGeMe_2GeMe_2Cl]$, 137364-23-9; $ClGeMe_3$, 1529-47-1; $Na[FeCp(CO)_2]$, 12152-20-4; $ClMe_2GeGeMe_3$, 22640-93-3; $ClMe_2GeGeMe_2Cl$, 22702-77-8; $Na[FeCp'(CO)_2]$, 52409-74-2.

**Supplementary Material Available:** Figures of $^1H$ NMR spectra of 6 and 4 (2 pages). Ordering information is given on any current masthead page.

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# New Pathways for Reactions of Transition-Metal–Propargyl Complexes with $Fe_2(CO)_9$. Characterization of Products Derived from Iron and Chromium Propargyls

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Reactions of the isoelectronic metal–propargyl complexes $Cp(CO)_2FeCH_2C\equiv CPh$ (**1**) and $Cp(NO)_2CrCH_2C\equiv CPh$ (**2**) with $Fe_2(CO)_9$ were investigated. In pentane at room temperature **1** affords a binuclear metal–$\eta^4$-allylcarbonyl product, $(CO)_3Fe[\eta^4\text{-}C(O)C(Ph)\cdots C(Fe(CO)_2Cp)\cdots CH_2]$ (**3**), whereas in hexane, also at room temperature, **2** surprisingly yields a homobinuclear metal–$\mu$-$\eta^2,\eta^3$-allenyl product, $(CO)_3Fe(\mu\text{-}\eta^2,\eta^3\text{-}PhC{=}C{=}CH_2)Fe(CO)_2(NO)$ (**4**), and known $CpCr(CO)_2(NO)$. A mechanism for the formation of **3** is proposed which is similar to that for the cycloaddition reactions of metal–propargyl complexes with neutral electrophiles. Complex **4** arises by an unprecedented complete transfer of the propargyl group as the corresponding allenyl ligand from the parent transition metal (Cr) to the substrate metal (Fe). The diyne $(PhC\equiv CCH_2)_2$ (**5**), which forms in the preparation of **1** and **2**, reacts with $Fe_2(CO)_9$ to give a new bicyclic ferrole complex, $(CO)_6Fe_2[PhC{=}C(C_2H_4)C{=}CPh]$ (**6**). Complexes **3**, **4**, and **6** were characterized by a combination of elemental analysis, mass spectrometry, and IR and $^1H$ and $^{13}C$ NMR spectroscopy; the structures of **3** and **6** were determined by single-crystal X-ray analysis. Crystallographic parameters: **3** $P\bar{1}$, $a = 8.967$ (2) Å, $b = 9.304$ (3) Å, $c = 12.533$ (4) Å, $\alpha = 98.02$ (3)°, $\beta = 104.84$ (2)°, $\gamma = 105.48$ (3)°, $Z = 2$, $R = 0.032$, $R_w = 0.032$ for 4121 independent reflections with $I > 3\sigma(I)$; **6** $P\bar{1}$, $a = 7.895$ (1) Å, $b = 9.056$ (1) Å, $c = 15.722$ (2) Å, $\alpha = 78.27$ (1)°, $\beta = 79.84$ (1)°, $\gamma = 77.12$ (1)°, $Z = 2$, $R = 0.028$, $R_w = 0.028$ for 3784 independent reflections with $I > 3\sigma(I)$.

## Introduction

The reactions of transition-metal–propargyl complexes $L_nMCH_2C\equiv CR$ ($L_nM = Cp(CO)_3Mo$ and -W, $Cp(CO)_2Ru$) with metal carbonyls have recently been used for the convenient synthesis of heterobinuclear and -trinuclear metal compounds with a variety of bridging hydrocarbyl ligands,[1-4] especially allenyls.[2,3,5] In particular, diverse products have been obtained with $Fe_2(CO)_9$ which depend on the identity of $L_nM$. To further elucidate the effect of $L_nM$ on these reactions, the behavior of the isoelectronic (formally $d^6$) transition-metal–propargyl compounds $Cp(CO)_2FeCH_2C\equiv CPh$ (**1**) and $Cp(NO)_2CrCH_2C\equiv CPh$ (**2**) toward $Fe_2(CO)_9$ was investigated. Portions of this work have been previously communicated.[3]

## Experimental Section

**General Procedures and Measurements.** All reactions and manipulations of air-sensitive compounds were conducted under

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an atmosphere of Ar according to standard procedures.[6] Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Melting points were measured in capillary tubes and are uncorrected. Infrared (IR) spectra were collected on a Perkin-Elmer Model 337 spectrophotometer and were calibrated with polystyrene. $^1H$ NMR spectra were recorded on a Bruker AM-250 spectrometer. $^{13}C$ NMR spectra were also recorded on the Bruker AM 250 instrument, some by Mr. Carl Engelman. Electron impact (EI) mass spectra were obtained on a VG70-250S spectrometer by Mr. C. R. Weisenberger.

**Materials.** All solvents were purified by distillation under an atmosphere of Ar. Pentane and hexane were distilled from Na/K alloy ($NaK_{2.8}$), THF and diethyl ether were distilled from Na/K and benzophenone, and dichloromethane was distilled from $P_4O_{10}$.

Reagents were obtained from various commercial sources and used as received, except as noted below. $Fe_2(CO)_9$ was synthesized according to the literature.[7] The diyne $(PhC{\equiv}CCH_2)_2$ (**5**) was prepared by a close adaptation of the literature procedure.[8] The propargyl complex $Cp(CO)_2FeCH_2C{\equiv}CPh$ (**1**) was prepared by the literature method,[9] and $Cp(NO)_2CrCH_2C{\equiv}CPh$ (**2**) was prepared by close adaption of the literature procedure[10] using the reaction of $PhC{\equiv}CCH_2MgCl$ (freshly prepared in a "continuous Grignard apparatus"[11]) with $Cp(NO)_2CrCl$.

**Reaction of $Cp(CO)_2FeCH_2C{\equiv}CPh$ (1) with $Fe_2(CO)_9$.** To a stirred, room-temperature solution of **1** (0.85 g, 2.9 mmol) in pentane (300 mL) was added $Fe_2(CO)_9$ (1.1 g, 2.9 mmol) as a solid. The resulting suspension was stirred for 40 h, during which time the reaction mixture turned dark green and then orange. Stirring was discontinued at that point, and the mixture was allowed to settle. The orange solution was decanted by cannula from a brown precipitate and set aside for future workup.

The brown precipitate was dissolved in THF (50 mL), and the solution was filtered through a Florisil plug (2 × 5 cm) on a sintered glass frit (D porosity). The filtrate was concentrated to 5 mL, and the precipitated solid was recrystallized from hexane (10 mL) at room temperature to give yellow crystals (0.150 g, 11% yield) of $(CO)_3Fe[\eta^4\text{-}C(O)C(Ph)\overline{\cdots}C(Fe(CO)_2Cp)\overline{\cdots}CH_2]$ (**3**).

The orange solution was evaporated to dryness under vacuum to afford a brown residue, which was dissolved in $CH_2Cl_2$ (4 mL) and introduced onto a 2 × 10 cm column of Florisil (60–100 mesh) packed in hexane. Elution with 15:1 hexane/THF gave a purple band, which was collected and evaporated to dryness to afford $[Cp(CO)_2Fe]_2$ (0.104 g, 10%), identified by comparison of its IR and $^1H$ NMR spectra with the literature values.[12] Elution with 3:1 hexane/THF gave an orange band, which was collected and freed of the solvent to yield additional **3** (0.255 g, 19%; combined yield of **3**, 0.405 g, 30%): mp 81 °C dec; IR (cyclohexane, $cm^{-1}$) $\nu(CO)$ 2055 (s), 2023 (m), 1992 (vs), 1983 (sh), 1780 (m); $^1H$ NMR ($CDCl_3$) $\delta$ 7.50–7.34 (m, 5 H, Ph), 4.64 (s, 5 H, Cp), 2.75, 2.00 (2 d, $^2J$ = 3.0 Hz, 2 H, $=CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 233.2 (C=O), 215.6, 215.3 ($Fe(CO)_2Cp$), 210.0 ($Fe(CO)_3$), 140.2 (CFe), 134.9 (ipso C of Ph), 131.1, 128.6, 128.2 (*o*-, *m*-, and *p*-C's of Ph), 86.8 (Cp), 73.2 (CPh), 54.7 ($CH_2$); EI MS *m/z* (relative intensity) 460 ($M^+$, 2), 432 ($M^+ - CO$, 2), 404 ($M^+ - 2CO$, 5). Anal. Calcd for $C_{20}H_{12}Fe_2O_6$: C, 52.22; H, 2.63. Found: C, 52.06; H, 2.60.

**Reaction of $Cp(NO)_2CrCH_2C{\equiv}CPh$ (2) with $Fe_2(CO)_9$.** To a stirred, room-temperature solution of **2** (0.20 g, 0.69 mmol) in hexane (45 mL) was added $Fe_2(CO)_9$ (0.50 g, 1.4 mmol) as a solid. The ensuing reaction was complete after 1 h, as determined by the disappearance of the IR $\nu(NO)$ absorptions at 1789 and 1688 $cm^{-1}$ of **2**. The resulting red-brown solution was freed of the solvent under vacuum to give a red tar. This residue was dissolved in $CH_2Cl_2$ (0.5 mL), and the solution was introduced onto a 2 × 75 cm column of silica gel (TLC grade) packed in hexane. Slow elution with hexane gave a large red band, which was collected and concentrated to give $(CO)_3Fe(\mu\text{-}\eta^2,\eta^3\text{-}PhC{=}C{=}CH_2)Fe(CO)_2(NO)$ (**4**) as a red oil (0.095 g, 35% yield). Complex **4** sublimes onto a coldfinger at ca. −78 °C under reduced pressure (ca. 0.1 torr): IR (cyclohexane, $cm^{-1}$) $\nu(CO)$ 2065 (s), 2031 (vs), 2009 (vs), 1931 (w), $\nu(NO)$ 1778 (vs); $^1H$ NMR ($CD_2Cl_2$) $\delta$ 7.57, 7.52, 7.33, 7.32 (4 s, 5 H, Ph), 4.58, 4.29 (2 d, $^2J$ = 0.7 Hz, 2 H, $=CH_2$); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 211.4, 210.4 ($Fe(CO)_2NO$), 209.6 (br, $Fe(CO)_3$), 138.1, 130.6, 129.3, 128.6 (Ph), 111.8 (=C=), 80.5 (=CPh), 70.5 ($=CH_2$); $^{13}C$ NMR ($CD_2Cl_2$) $\delta$ 70.5 (t, $^1J_{C-H}$ = 169 Hz, $=CH_2$); EI MS *m/z* (relative intensity) 396.900 (exact $M^+$, 4.4; calcd for $C_{14}H_7Fe_2NO_6$ 396.897), 369 ($M^+ - CO$, 46), 341 ($M^+ - 2CO$, 40), 313 ($M^+ - 3CO$, 41), 283 ($M^+ - 3CO - NO$, 17), 227 ($M^+ - 5CO - NO$, 36), 115 ($C_3H_2Ph^+$, 100).

Continued elution with hexane gave an orange band, which was collected and evaporated to dryness to afford known $CpCr(CO)_2(NO)$[13] as an orange solid (0.032 g, 23% yield).

**Reaction of $(PhC{\equiv}CCH_2)_2$ (5) with $Fe_2(CO)_9$.** A suspension of $Fe_2(CO)_9$ (1.1 g, 3.0 mmol) in a hexane solution (30 mL) of **5** (0.71 g, 3.1 mmol) was heated at reflux for 15 min. The reaction mixture was cooled to room temperature and filtered, and the filtrate was concentrated under vacuum to a red oil. Crystallization of the oil from 1:1 pentane/$CH_2Cl_2$ provided $(CO)_6Fe_2[PhC{=}C(C_2H_4)C{=}CPh]$ (**6**) as light yellow air-stable crystals (1.4 g, 89% yield): mp 162 °C; IR (cyclohexane, $cm^{-1}$) $\nu(CO)$ 2062 (m), 2029 (s), 1994 (s), 1939 (w); $^1H$ NMR ($CDCl_3$) $\delta$ 7.29 (s, br, 10 H, 2 Ph), 3.32, 2.76 (2 m, $^2J$ = 10.9 Hz, 4 H, $C_2H_4$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 214.0, 211.4, 206.3 (CO's), 163.6 (*C*(Fe)Ph's), 145.4 ($=CCH_2$'s), 134.0 (ipso C of Ph's), 132.1, 128.2, 127.4 (*o*-, *m*-, and *p*-C's of Ph's), 28.2 ($CH_2$'s); EI MS *m/z* (relative intensity) 510 ($M^+$, 2), 482 ($M^+ - CO$, 1), 454 ($M^+ - 2CO$, 3), 426 ($M^+ - 3CO$, 5), 398 ($M^+ - 4CO$, 5), 342 ($M^+ - 6CO$, 11), 286 ($M^+ - Fe - 6CO$, 5), 230 ($M^+ - 2Fe - 6CO$, 25), 115 ($C_3H_2Ph^+$, 100). Anal. Calcd for $C_{24}H_{14}Fe_2O_6$: C, 56.52; H, 2.77. Found: C, 55.91; H, 2.71.

When $Cp(CO)_2FeCH_2C{\equiv}CPh$ (**1**) containing an impurity of **5** was reacted with $Fe_2(CO)_9$ in pentane (for reaction conditions, vide supra), complex **6** was eluted off the Florisil column ahead of $[Cp(CO)_2Fe]_2$ as a yellow band during workup.

**Crystallographic Analyses of $(CO)_3Fe[\eta^4\text{-}C(O)C(Ph)\overline{\cdots}C(Fe(CO)_2Cp)\overline{\cdots}CH_2]$ (3) and $(CO)_6Fe_2[PhC{=}C(C_2H_4)C{=}CPh]$ (6).** Crystals of **3** were grown from 1:1 $CH_2Cl_2$/pentane at 10 °C whereas crystals of **6** were obtained from 1:1 $CHCl_3$/pentane at 10 °C. They were mounted on an Enraf-Nonius CAD4 diffractometer, and lattice parameters were obtained by a least-squares refinement of 25 accurately centered reflections. A summary of the crystal data and the details of the intensity data collection and refinement for **3** and **6** are provided in Table I. No significant change in intensities, due to crystal decay, was observed over the course of all data collections. The structures were solved by Patterson and Fourier methods. Hydrogen atoms were entered in ideally calculated positions, in good agreement with the difference Fourier maps. Final full-matrix least-squares refinement of the structures, with the fixed contribution of H atoms ($B = 1.3B_{eq}$ Å$^2$), converged to $R$ = 0.032 and $R_w$ = 0.032 and $R$ = 0.028 and $R_w$ = 0.028 for **3** and **6**, respectively. All the non-hydrogen atoms had anisotropic temperature factors. Scattering factors, anomalous dispersion terms, and programs were taken from the Enraf-Nonius SDP library.[14] Final positional and equivalent thermal parameters are given for **3** and **6** in Tables II and III, respectively. Lists of anisotropic thermal parameters, hydrogen atom coordinates, and structure factors are available as supplementary material.[15]

## Results and Discussion

**Reaction of $Cp(CO)_2FeCH_2C{\equiv}CPh$ (1) with $Fe_2(CO)_9$.** The allylcarbonyl (more precisely, $\eta^3$-allyl-$\eta^1$-carbonyl) complex $(CO)_3Fe[\eta^4\text{-}C(O)C(Ph)\overline{\cdots}C(Fe(CO)_2Cp)\overline{\cdots}CH_2]$ (**3**) was isolated as a slightly air-sensitive

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[15] See paragraph at end of paper regarding supplementary material.

**Table I. Crystal Data and Data Collection and Refinement of 3 and 6**

| | 3 | 6 |
|---|---|---|
| | Crystal Data | |
| molecular formula | $Fe_2C_{20}H_{12}O_6$ | $Fe_2C_{24}H_{14}O_6$ |
| fw | 754.1 | 510.1 |
| cryst syst | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| *a*, Å | 8.967 (2) | 7.895 (1) |
| *b*, Å | 9.304 (3) | 9.056 (1) |
| *c*, Å | 12.533 (4) | 15.722 (2) |
| α, deg | 98.02 (3) | 78.27 (1) |
| β, deg | 104.84 (2) | 79.84 (1) |
| γ, deg | 105.48 (3) | 77.12 (1) |
| *V*, $Å^3$ | 949.6 (5) | 1062.7 (2) |
| *Z* | 2 | 2 |
| $D_{calcd}$, g $cm^{-1}$ | 1.609 | 1.594 |
| *F*(000), e | 464 | 516 |
| μ(Mo Kα), $cm^{-1}$ | 15.6 | 14.0 |
| cryst size, mm | 0.15 × 0.24 × 0.50 | 0.20 × 0.35 × 0.60 |
| | Data Collection and Refinement | |
| diffractometer | Enraf-Nonius CAD4 | |
| temp, K | 294 ± 1 | |
| radiation | Mo Kα, graphite monochromated (λ = 0.71069 Å) | |
| scan type | ω/2θ | |
| scan speed, deg $min^{-1}$ | 0.82–16.5 | 0.3–5.5 |
| scan angle[a] | 1.0 + 0.35 tan θ | 0.6 + 0.35 tan θ |
| aperture width, mm | 1.0 + tan θ | |
| 2θ range, deg | 6–60 | 6–56 |
| no. of refls measd | ±*h*,±*k*,+*l* | |
| no. of orientation monitors[b] | 3 | 3 |
| no. of intensity monitors[c] | 3 | 3 |
| total no. of measd data | 5754 | 5328 |
| no. of unique data ($I > 3\sigma(I)$)[d] | 4121 | 3784 |
| transm factors | 0.796–0.998 | 0.863–0.999 |
| no. of variables | 254 | 290 |
| minimized function | $\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2$ | |
| *w* | 1 | 1 |
| *R* ($\sum\Delta/\sum\lvert F_o\rvert$)[e] | 0.032 | 0.028 |
| $R_w$ ($[\sum w\Delta^2/\sum wF_o^2]^{1/2}$)[e] | 0.032 | 0.028 |
| goodness of fit | 0.65 | 0.622 |
| residuals in final map, e $Å^{-3}$ | +0.33, −0.45 | −0.26, +0.29 |

[a] Extended by 25% on both sides for background measurements. [b] Measured after each 1000 reflections for 3 and 400 reflections for 6; new orientation matrix if angular change >0.20 for 3 and >0.11 for 6. [c] Measured after each 4000 and 3600 s for 3 and 6, respectively. [d] Standard deviation from counting statistics. [e] $\Delta = \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert$.

**Table II. Positional and Equivalent Thermal Parameters for 3**

| atom | *x* | *y* | *z* | *B*,[a] $Å^2$ |
|---|---|---|---|---|
| Fe(1) | 0.03197 (3) | 0.06907 (4) | 0.25614 (3) | 2.478 (6) |
| Fe(2) | −0.24767 (4) | 0.32405 (4) | 0.22727 (3) | 2.725 (6) |
| O(1) | 0.2632 (3) | 0.3420 (3) | 0.2381 (2) | 6.77 (7) |
| O(2) | 0.0419 (3) | 0.1969 (3) | 0.4836 (2) | 5.35 (6) |
| O(3) | 0.0752 (3) | 0.5260 (3) | 0.3813 (2) | 6.04 (6) |
| O(4) | −0.3359 (3) | 0.5168 (2) | 0.0739 (2) | 6.25 (6) |
| O(5) | −0.4060 (3) | 0.3854 (3) | 0.3979 (2) | 6.65 (6) |
| O(6) | −0.5715 (2) | 0.1117 (2) | 0.0825 (2) | 3.69 (4) |
| C(1) | 0.1712 (3) | 0.2365 (3) | 0.2460 (3) | 3.94 (6) |
| C(2) | 0.0349 (3) | 0.1458 (3) | 0.3933 (2) | 3.53 (5) |
| C(3) | −0.0458 (3) | 0.4448 (3) | 0.3230 (2) | 3.75 (6) |
| C(4) | −0.2981 (3) | 0.4483 (3) | 0.1386 (2) | 3.89 (6) |
| C(5) | −0.3452 (3) | 0.3618 (3) | 0.3314 (2) | 4.14 (6) |
| C(6) | −0.0703 (3) | −0.1657 (3) | 0.2450 (2) | 3.39 (5) |
| C(7) | 0.0980 (3) | −0.1192 (3) | 0.3038 (2) | 3.51 (5) |
| C(8) | 0.1843 (3) | −0.0621 (3) | 0.2320 (2) | 3.77 (5) |
| C(9) | 0.0678 (3) | −0.0747 (3) | 0.1266 (2) | 3.90 (5) |
| C(10) | −0.0877 (3) | −0.1390 (3) | 0.1349 (2) | 3.57 (5) |
| C(11) | −0.1545 (3) | 0.2327 (3) | 0.1048 (2) | 2.89 (4) |
| C(12) | −0.1592 (2) | 0.1329 (2) | 0.1821 (2) | 2.38 (4) |
| C(13) | −0.3162 (2) | 0.0805 (2) | 0.1944 (2) | 2.39 (4) |
| C(14) | −0.3789 (2) | −0.0380 (2) | 0.2544 (2) | 2.55 (4) |
| C(15) | −0.4681 (3) | −0.1833 (3) | 0.1889 (2) | 3.31 (5) |
| C(16) | −0.5338 (3) | −0.3001 (3) | 0.2373 (2) | 4.17 (6) |
| C(17) | −0.5117 (3) | −0.2713 (3) | 0.3523 (2) | 4.26 (6) |
| C(18) | −0.4254 (3) | −0.1276 (3) | 0.4178 (2) | 4.10 (6) |
| C(19) | −0.3595 (3) | −0.0096 (3) | 0.3701 (2) | 3.30 (5) |
| C(20) | −0.4308 (3) | 0.1537 (3) | 0.1386 (2) | 2.67 (4) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

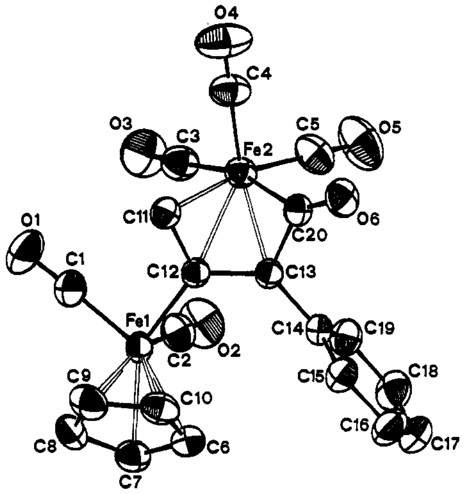
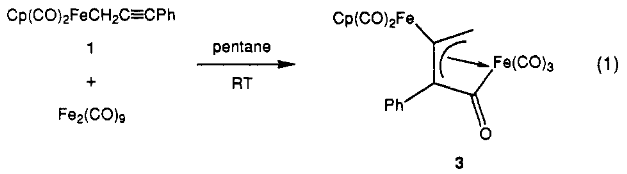


**Figure 1.** ORTEP plot of 3 showing atom-numbering scheme. Non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms are omitted.

rust-colored solid from the reaction of 1 with $Fe_2(CO)_9$ (eq 1) under a variety of conditions. The reaction is optimally carried out over 24 h at room temperature in pentane; under these conditions 3 is isolated in 30% yield, although the yield before workup is considerably higher (≥60%) as ascertained spectroscopically. The absence of products containing metal–metal bonding is surprising, since the reactions of $Fe_2(CO)_9$ with $Cp(CO)_3MCH_2C{\equiv}CR$ (M = Mo, W; R = Ph, Me)[2] and $Cp(CO)_2RuCH_2C{\equiv}CPh$,[3] the ruthenium congener of 1, all gave heteronuclear metal–metal-bonded compounds.



A combination of elemental analysis, mass spectrometry, and IR and $^1H$ and $^{13}C$ NMR spectroscopies was used in the characterization of 3. These methods were also employed in the characterization of the other new products discussed later.

The IR spectrum of 3 reveals ν(CO) absorptions of terminal CO ligands attached to two different Fe atoms. On the basis of intensity and position,[16] the bands at 2023 and 1983 $cm^{-1}$ are assigned to $CpFe(CO)_2$; the remaining bands at 2055 and 1992 $cm^{-1}$ belong to $Fe(CO)_3$. In addition, there is an acyl ν(CO) absorption at 1780 $cm^{-1}$. The presence of an acyl group in 3 accords with a single resonance (δ 233.2) in the diagnostic region of the $^{13}C$ NMR spectrum.[17] The resonances of the allylic carbons are observed at δ 140.2 (CFe), 73.2 (CPh), and 54.7 ($CH_2$), again consistent with an $\eta^3$-allyl structure.[18,19] The as-

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(16) Johnson, M. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 4, Chapter 31.2, p 345.

(17) (a) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089. (b) Farnell, L. F.; Randall, E. W.; Rosenberg, E. *Chem. Commun.* **1971**, 1078.

**Table III. Positional and Equivalent Thermal Parameters for 6**

| atom | *x* | *y* | *z* | $B^a$ Å$^2$ |
|---|---|---|---|---|
| Fe(1) | 0.0323 (4) | 0.59316 (4) | 0.79241 (2) | 2.816 (6) |
| Fe(2) | −0.19447 (4) | 0.78080 (4) | 0.71349 (2) | 2.718 (6) |
| O(1) | 0.3238 (3) | 0.6534 (3) | 0.8593 (2) | 6.41 (6) |
| O(2) | −0.0976 (3) | 0.3845 (2) | 0.9475 (1) | 5.79 (5) |
| O(3) | 0.2255 (3) | 0.3216 (2) | 0.7176 (1) | 5.47 (5) |
| O(4) | −0.2351 (3) | 0.8379 (3) | 0.5284 (1) | 5.23 (5) |
| O(5) | −0.5511 (3) | 0.9502 (3) | 0.7528 (1) | 5.79 (6) |
| O(6) | −0.3017 (3) | 0.4836 (2) | 0.7478 (1) | 4.90 (5) |
| C(1) | 0.2104 (3) | 0.6272 (3) | 0.8339 (2) | 3.91 (6) |
| C(2) | −0.0514 (3) | 0.4674 (3) | 0.8885 (2) | 3.65 (5) |
| C(3) | 0.1468 (3) | 0.4278 (3) | 0.7441 (2) | 3.71 (5) |
| C(4) | −0.2183 (3) | 0.8157 (3) | 0.6004 (2) | 3.45 (5) |
| C(5) | −0.4128 (3) | 0.8827 (3) | 0.7400 (2) | 3.67 (5) |
| C(6) | −0.2388 (3) | 0.5889 (3) | 0.7400 (2) | 3.48 (5) |
| C(7) | 0.0797 (3) | 0.7403 (3) | 0.6789 (1) | 2.86 (4) |
| C(8) | 0.0244 (3) | 0.8918 (3) | 0.6948 (2) | 3.07 (5) |
| C(9) | 0.0099 (4) | 1.0662 (3) | 0.6608 (2) | 4.20 (6) |
| C(10) | −0.1045 (4) | 1.0916 (3) | 0.7512 (2) | 4.43 (6) |
| C(11) | −0.0783 (3) | 0.9152 (3) | 0.7755 (1) | 3.09 (5) |
| C(12) | −0.1186 (3) | 0.7859 (3) | 0.8344 (1) | 2.81 (4) |
| C(13) | −0.2242 (3) | 0.7996 (3) | 0.9212 (1) | 2.98 (5) |
| C(14) | −0.3549 (3) | 0.7153 (3) | 0.9561 (2) | 3.78 (6) |
| C(15) | −0.4485 (4) | 0.7300 (4) | 1.0392 (2) | 4.77 (7) |
| C(16) | −0.4100 (4) | 0.8258 (4) | 1.0873 (2) | 5.18 (7) |
| C(17) | −0.2820 (4) | 0.9100 (4) | 1.0537 (2) | 5.02 (7) |
| C(18) | −0.1891 (4) | 0.8982 (3) | 0.9706 (2) | 3.92 (6) |
| C(19) | 0.1842 (3) | 0.7076 (3) | 0.5945 (1) | 2.98 (5) |
| C(20) | 0.3138 (3) | 0.7915 (3) | 0.5546 (2) | 3.71 (5) |
| C(21) | 0.4097 (3) | 0.7661 (4) | 0.4737 (2) | 4.38 (6) |
| C(22) | 0.3777 (4) | 0.6577 (4) | 0.4321 (2) | 4.50 (7) |
| C(23) | 0.2521 (4) | 0.5722 (3) | 0.4710 (2) | 4.27 (6) |
| C(24) | 0.1564 (3) | 0.5965 (3) | 0.5517 (2) | 3.64 (5) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3))]$.

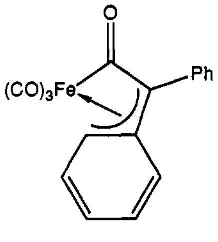
**Table IV. Selected Bond Distances (Å) and Angles (deg) for 3**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Fe(1)–C(1) | 1.761 (3) | O(1)–C(1) | 1.136 (4) |
| Fe(1)–C(2) | 1.758 (3) | O(2)–C(2) | 1.144 (3) |
| Fe(1)–C(12) | 2.009 (2) | O(3)–C(3) | 1.134 (3) |
| Fe(2)–C(3) | 1.845 (2) | O(4)–C(4) | 1.139 (4) |
| Fe(2)–C(4) | 1.776 (3) | O(5)–C(5) | 1.134 (4) |
| Fe(2)–C(5) | 1.792 (3) | O(6)–C(20) | 1.203 (2) |
| Fe(2)–C(11) | 2.110 (3) | C(11)–C(12) | 1.434 (3) |
| Fe(2)–C(12) | 2.194 (3) | C(12)–C(13) | 1.417 (3) |
| Fe(2)–C(13) | 2.133 (3) | C(13)–C(14) | 1.489 (3) |
| Fe(2)–C(20) | 1.905 (2) | C(13)–C(20) | 1.465 (3) |
| Bond Angles | | | |
| Fe(1)–C(1)–O(1) | 178.1 (3) | C(11)–C(12)–C(13) | 111.5 (2) |
| Fe(1)–C(2)–O(2) | 177.9 (2) | C(12)–C(13)–C(14) | 128.9 (2) |
| Fe(2)–C(3)–O(3) | 176.1 (3) | C(12)–C(13)–C(20) | 114.4 (2) |
| Fe(2)–C(4)–O(4) | 173.9 (2) | C(14)–C(13)–C(20) | 116.7 (2) |
| Fe(2)–C(5)–O(5) | 179.5 (3) | Fe(2)–C(20)–O(6) | 145.9 (2) |
| Fe(2)–C(11)–C(12) | 73.8 (1) | Fe(2)–C(20)–C(13) | 77.3 (1) |
| Fe(1)–C(12)–C(11) | 123.3 (2) | O(6)–C(20)–C(13) | 135.8 (2) |
| Fe(1)–C(12)–C(13) | 125.2 (2) | | |

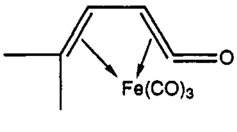
signment of the first two signals conforms to the general pattern of the central allylic carbon resonating at a lower field vis-à-vis terminal allylic carbons. The relative downfield position of the methylene carbon signal implies that there is more π than σ character in the Fe–$CH_2$ bond. In the $^1H$ NMR spectrum, the methylene protons appear as two doublets (δ 2.75, 2.00) with a geminal coupling constant (3.0 Hz) indicative of $sp^2$ hybridization.[20]

Unequivocal confirmation of the structure of **3** was obtained by X-ray diffraction analysis. The molecular structure and atom-numbering scheme appear in Figure 1. Selected bond distances and angles are provided in Table IV.

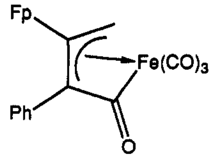
The molecular structure confirms the absence of Fe–Fe bonding in **3** as evidenced by a distinct separation of the metal atoms (Fe(1)···Fe(2) 3.8726 (6) Å). The iron atoms are bridged by an $\eta^4$-allylcarbonyl ligand that is σ-bonded to Fe(1) (Fe(1)–C(12) 2.009 (2) Å) and σ- and π-bonded to Fe(2) (Fe(2)–C(20) 1.905 (2) Å, Fe(2)–C(13) 2.133 (3) Å, Fe(2)–C(12) 2.194 (3) Å, Fe(2)–C(11) 2.110 (3) Å). These bond distances closely agree with those of related iron–$\eta^4$-allylcarbonyl complexes,[21] such as I[22] and II.[23] The four-atom fragment C(11)C(12)C(13)C(20) is planar within 0.074 Å (C(11) +0.021 (2) Å, C(12) −0.037 (2) Å, C(13) +0.037 (2) Å, C(20) −0.021 (2) Å), and the atoms Fe(1), Fe(2), and O(6) are displaced out of this plane by −0.117 (0), −1.547 (0), and +0.554 (2) Å, respectively. The bond distances involving the carbon atoms (C(13)–C(20) 1.465 (3) Å, C(12)–C(13) 1.417 (3) Å, C(11)–C(12) 1.434 (3) Å) and the carbonyl group (O(6)–C(20) 1.203 (2) Å) as well as the bond angle O(6)–C(20)–C(13) (135.8 (2)°) of the $\eta^4$-allylcarbonyl ligand all compare extremely well with the corresponding values reported for analogous compounds.[21-23] Some of these compounds (e.g., II[23]) have been alternatively formulated in terms of a vinylketene bonding description (cf. allylcarbonyl III vs vinylketene IV; Fp ≡ $Cp(CO)_2Fe$). We prefer formulation III over IV for complex **3**, mainly because the carbon atoms C(11), C(12), and C(13) form a typical $\eta^3$-allyl skeleton found in iron tricarbonyl complexes[24] (C(20) and O(6) are displaced −0.175 and +0.314 Å out of this plane) and the bond distance C(13)–C(20) is distinctly longer than the bond distances C(11)–C(12) and C(12)–C(13). The significant displacement of the oxygen atom O(6) out of the plane of the carbon atoms is also shown by the torsion angle C(12)–C(13)–C(20)–O(6) of 137.8°, which means a twisting of the



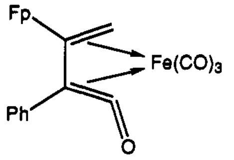
**I**



**II**



**III**



**IV**

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(18) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135.

(19) Gregg, M. R.; Powell, J.; Sawyer, J. F. *J. Organomet. Chem.* **1988**, *352*, 357.

(20) Jackman, L. M. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: New York, 1969; Chapter 4-1.

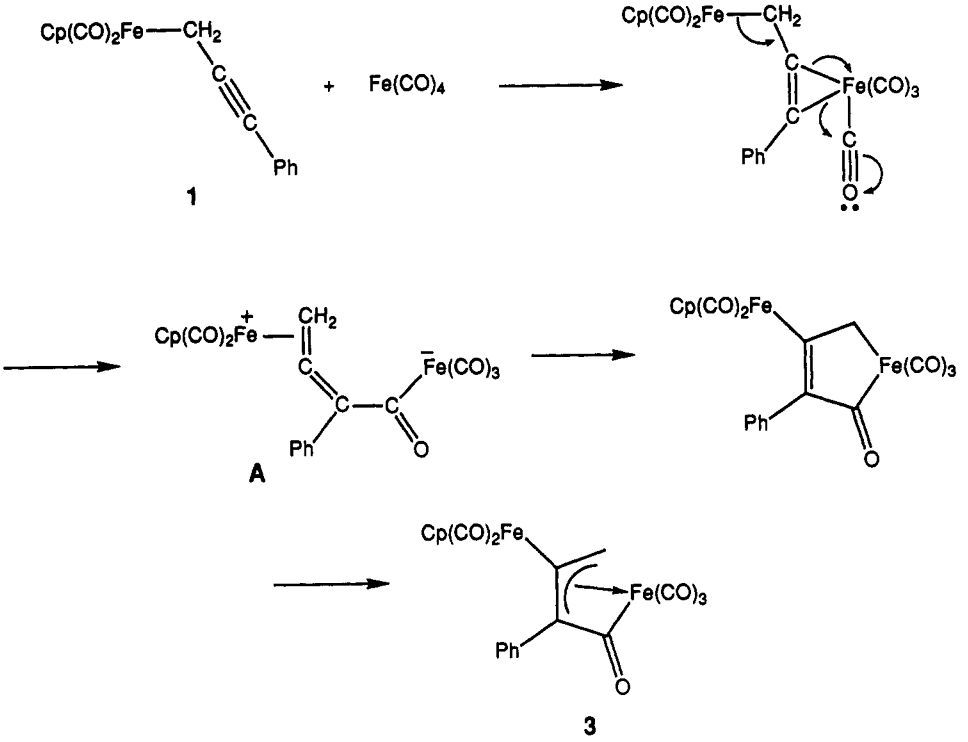
(21) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 4, Chapter 31.3, pp 457–458.

(22) Bkouche-Waksman, I.; Ricci, J. S., Jr.; Koetzle, T. F.; Weichmann, J.; Herrmann, W. A. *Inorg. Chem.* **1985**, *24*, 1492.

(23) Binger, C. P.; Četinkaya, B.; Krüger, C. *J. Organomet. Chem.* **1978**, *159*, 63.

(24) Reference 21, pp 399–425.

Scheme I

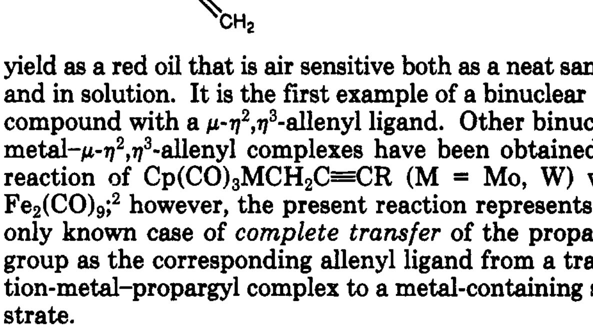


$C(20)-O(6)$ bond with respect to the $C(13)-C(20)$ bond by 42.2° away from a planar arrangement. These data are more consistent with an allylcarbonyl (III) than a vinylketene (IV) structure. Nevertheless, representation IV can also be accommodated by the spectroscopic and structural results and undoubtedly contributes substantially to the bonding description of 3.

The question of a possible mechanism of this interesting conversion of 1 to 3 by $Fe_2(CO)_9$ has been addressed elsewhere[25] and will receive only a brief mention herein. A suggested mechanism, based on that given for the reactions of metal–propargyl complexes with various neutral electrophiles,[26,27] is set out in Scheme I. It is proposed that the reaction proceeds by ligation of the propargylic $C\equiv C$ to a coordinatively unsaturated $Fe(CO)_4$ species to give a binuclear iron–acetylene complex. This complex rearranges to a dipolar metal–$\eta^2$-allene compound bearing an $Fe(CO)_3$ group as the negative terminus. The latter intermediate then collapses by attack of $Fe(CO)_3$ at the coordinated allene.

**Reaction of $Cp(NO)_2CrCH_2C\equiv CPh$ (2) with $Fe_2(CO)_9$.** The title reaction was investigated to further explore the effect of varying the metal of a transition-metal–propargyl compound on the latter's interaction with $Fe_2(CO)_9$. We thought that complexes 1 and 2 might undergo similar reactions, since they are isoelectronic and almost certainly adopt very similar piano-stool structures, with the two nitrosyl ligands in 2 replacing the two carbonyl ligands in 1. Moreover, since both Fe and Cr are first-row transition metals, 1 and 2 were considered relatively unlikely to exhibit a different course of reaction toward $Fe_2(CO)_9$, as do 1 and its Ru congener $Cp(CO)_2RuCH_2C\equiv CPh$.[3]

Reaction of 2 with $Fe_2(CO)_9$ in hexane at room temperature is complete within 1 h and affords after workup $(CO)_3Fe(\mu-\eta^2,\eta^3-PhC=C=CH_2)Fe(CO)_2(NO)$ (4) and $CpCr(CO)_2(NO)$ (eq 2). Complex 4 was isolated in 35% yield as a red oil that is air sensitive both as a neat sample and in solution. It is the first example of a binuclear iron compound with a $\mu-\eta^2,\eta^3$-allenyl ligand. Other binuclear metal–$\mu-\eta^2,\eta^3$-allenyl complexes have been obtained by reaction of $Cp(CO)_3MCH_2C\equiv CR$ (M = Mo, W) with $Fe_2(CO)_9$;[2] however, the present reaction represents the only known case of *complete transfer* of the propargyl group as the corresponding allenyl ligand from a transition-metal–propargyl complex to a metal-containing substrate.



(2)

The characterization of 4 is facilitated by the similarity of its $^1H$ and $^{13}C$ NMR spectra to those of the previously synthesized and, in one case, structurally elucidated, by X-ray diffraction, heteronuclear metal–$\mu-\eta^2,\eta^3$-allenyl complexes.[2] The chemical shifts of the resonances assigned to the allenyl carbons ($\delta$ 111.8 (=C=), 80.5 (=CPh), 70.5 (=$CH_2$)) and protons ($\delta$ 4.58, 4.29) correspond closely with previously reported values for the analogous carbons and protons of $Cp(CO)_2M(\mu-\eta^2,\eta^3-RC=C=CH_2)Fe(CO)_3$ (M = Mo, W).[2] The values of the coupling constants of the $CH_2$ group ($^2J$ = 0.7 Hz, $^1J_{C-H}$ = 169 Hz) are indicative of $sp^2$ hybridization at this carbon.[20,28] The presence of the NO

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[25] Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35.

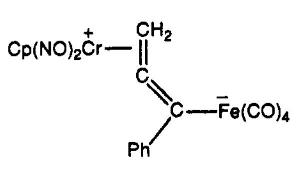
[26] Wojcicki, A. In *Fundamental Research in Organometallic Chemistry*; Tsutsui, M., Ishii, Y., Huang, Y., Eds.; Van Nostrand-Reinhold: New York, 1982; pp 569–597.

[27] Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122.

[28] Cooper, J. W. *Spectroscopic Techniques for Organic Chemists*; Wiley-Interscience: New York, 1980; p 87.

ligand was confirmed by a strong absorption (1778 $cm^{-1}$) in the diagnostic region of the IR spectrum.[29]

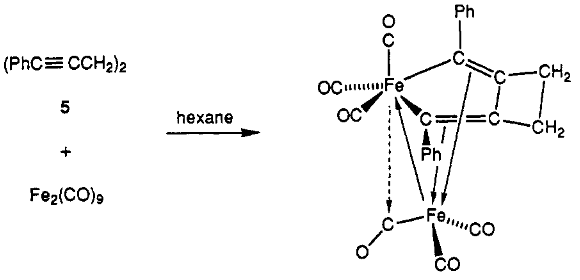
Although detailed speculation on the mechanism of this reaction seem inappropriate, some thoughts on the observed complete transfer of the propargyl ligand are in order. If we assume that the reaction proceeds similarly to that between 1 and $Fe_2(CO)_9$, it would lead to the formation of a CrFe complex strictly analogous to the dipolar binuclear metal–$\eta^2$-allene-$\eta^1$-carbonyl intermediate (A) in Scheme I or, without the CO insertion, to the corresponding binuclear metal–$\eta^2$-allene-$\eta^1$-yl species (V). Such a complex might be expected to display low stability with respect to chromium–$\eta^2$-allene bond dissociation, since $[CpCr(NO)_2]^+$ has been shown to behave as a hard acid toward 2-electron donor ligands.[30] Dissociation of this bond would then trigger reactions leading to the observed formation of 4 and $CpCr(CO)_2(NO)$.



V

**Synthesis of $(CO)_6Fe_2[PhC{=}C(C_2H_4)C{=}CPh]$ (6).** Preliminary investigations of the reactions of 1 and 2 with $Fe_2(CO)_9$ showed that in each case there was another, very minor product. This product, isolated as a yellow solid (6), does not contain a Cp ligand, as revealed by its $^1H$ NMR spectrum. An inspection of the $^1H$ NMR spectra of 1 and 2 used in these reactions showed the presence of a small amount of extraneous material with a resonance at $\delta$ 2.75. This signal matches that of the $CH_2$ protons of $(PhC{\equiv}CCH_2)_2$ (5), a byproduct formed from coupling of the phenylpropargyl groups in the syntheses of 1 and 2. Careful purification of 1 (by crystallization) and 2 (by chromatography) removed the impurity of 5, and when the reactions of the two metal propargyls with $Fe_2(CO)_9$ were repeated, 6 was no longer isolated.

In order to determine the identity of 6, reaction of 5 with $Fe_2(CO)_9$ in hexane was examined at various temperatures. It was found that 6, later identified as the ferrole[31] $(CO)_6Fe_2[PhC{=}C(C_2H_4)C{=}CPh]$, is indeed produced; it is obtained nearly quantitatively in 15 min at reflux temperature (eq 3).



6

(3)

The IR spectrum of 6 contains $\nu(CO)$ absorptions at 2062 (m), 2029 (s), 1994 (s), and 1939 (w) $cm^{-1}$, indicative of the molecule's high degree of symmetry. The weak band at 1939 $cm^{-1}$ is assigned to a semibridging carbonyl ligand.[32] Semibridging carbonyls occur in ferrole complexes of the so-called "nonsawhorse" configuration, presumably to reaccept some of the electronic charge which is accumulated on the ring iron atom by the formal dative Fe→Fe bond.[33] In the $^{13}C\{^1H\}$ NMR spectrum of 6, the ferrole-ring carbon atoms show the chemical shifts that are very similar to those reported for $(CO)_6Fe_2[PhC{=}C(Ph)C(Ph){=}CPh]$.[34] The salient features of the $^1H$ NMR spectrum of 6 are two multiplets, comprising an AA′BB′ spectrum, at $\delta$ 3.32 and 2.76; they are assigned to the $C_2H_4$ protons of the four-membered ring.

**Table V. Selected Bond Distances (Å) and Angles (deg) for 6**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Fe(1)–Fe(2) | 2.4798 (4) | O(1)–C(1) | 1.129 (4) |
| Fe(1)–C(1) | 1.775 (3) | O(2)–C(2) | 1.130 (3) |
| Fe(1)–C(2) | 1.811 (2) | O(3)–C(3) | 1.135 (3) |
| Fe(1)–C(3) | 1.808 (3) | O(4)–C(4) | 1.135 (3) |
| Fe(1)–C(6) | 2.421 (3) | O(5)–C(5) | 1.132 (3) |
| Fe(1)–C(7) | 2.033 (2) | O(6)–C(6) | 1.146 (4) |
| Fe(1)–C(12) | 2.035 (2) | C(7)–C(8) | 1.404 (3) |
| Fe(2)–C(4) | 1.778 (3) | C(7)–C(19) | 1.481 (3) |
| Fe(2)–C(5) | 1.786 (2) | C(8)–C(9) | 1.546 (3) |
| Fe(2)–C(6) | 1.800 (3) | C(8)–C(11) | 1.408 (3) |
| Fe(2)–C(7) | 2.104 (2) | C(9)–C(10) | 1.574 (4) |
| Fe(2)–C(8) | 2.136 (3) | C(10)–C(11) | 1.541 (3) |
| Fe(2)–C(11) | 2.137 (3) | C(11)–C(12) | 1.397 (3) |
| Fe(2)–C(12) | 2.103 (2) | C(12)–C(13) | 1.481 (3) |
| Bond Angles | | | |
| C(1)–Fe(1)–C(2) | 97.8 (1) | C(4)–Fe(2)–C(5) | 91.2 (1) |
| C(1)–Fe(1)–C(3) | 97.0 (1) | C(4)–Fe(2)–C(6) | 97.6 (1) |
| C(1)–Fe(1)–C(6) | 170.6 (1) | C(4)–Fe(2)–C(7) | 89.3 (1) |
| C(1)–Fe(1)–C(7) | 91.4 (1) | C(4)–Fe(2)–C(12) | 163.4 (1) |
| C(1)–Fe(1)–C(12) | 88.8 (1) | C(5)–Fe(2)–C(6) | 98.1 (1) |
| C(2)–Fe(1)–C(3) | 90.1 (1) | C(5)–Fe(2)–C(7) | 159.4 (1) |
| C(2)–Fe(1)–C(6) | 84.5 (1) | C(5)–Fe(2)–C(12) | 94.0 (1) |
| C(2)–Fe(1)–C(7) | 170.1 (1) | Fe(1)–C(1)–O(1) | 177.9 (2) |
| C(2)–Fe(1)–C(12) | 93.0 (1) | Fe(1)–C(2)–O(2) | 177.4 (2) |
| C(3)–Fe(1)–C(6) | 92.1 (1) | Fe(1)–C(3)–O(3) | 176.1 (3) |
| C(3)–Fe(1)–C(7) | 92.2 (1) | Fe(2)–C(4)–O(4) | 179.4 (2) |
| C(3)–Fe(1)–C(12) | 173.0 (1) | Fe(2)–C(5)–O(5) | 176.8 (2) |
| C(6)–Fe(1)–C(7) | 85.81 (9) | Fe(1)–C(6)–Fe(2) | 70.2 (1) |
| C(6)–Fe(1)–C(12) | 81.89 (9) | Fe(1)–C(6)–O(6) | 126.0 (2) |
| C(7)–Fe(1)–C(12) | 83.72 (8) | Fe(2)–C(6)–O(6) | 163.8 (2) |
| Fe(1)–C(7)–Fe(2) | 73.64 (7) | Fe(2)–C(11)–C(8) | 70.7 (2) |
| Fe(1)–C(7)–C(8) | 108.9 (2) | Fe(2)–C(11)–C(12) | 69.5 (2) |
| Fe(1)–C(7)–C(19) | 129.4 (2) | C(8)–C(11)–C(10) | 93.3 (2) |
| C(8)–C(7)–C(19) | 120.8 (2) | C(8)–C(11)–C(12) | 117.8 (2) |
| Fe(2)–C(8)–C(7) | 69.5 (1) | C(10)–C(11)–C(12) | 148.7 (2) |
| Fe(2)–C(8)–C(11) | 70.8 (2) | Fe(1)–C(12)–Fe(2) | 73.60 (8) |
| C(7)–C(8)–C(11) | 117.9 (2) | Fe(1)–C(12)–C(11) | 109.2 (1) |
| C(8)–C(9)–C(10) | 86.9 (2) | Fe(1)–C(12)–C(13) | 128.1 (2) |
| C(9)–C(10)–C(11) | 86.9 (2) | C(11)–C(12)–C(13) | 121.4 (2) |

Product 6 was unequivocally shown by an X-ray diffraction analysis to adopt a unique bicyclic ferrole framework (Figure 2). Selected bond distances and angles are listed in Table V.

The molecule has approximate $C_s$ symmetry defined by a mirror plane that passes through Fe(1), Fe(2), and the C(1)O(1) and C(6)O(6) carbonyl groups and bisects the bridging hydrocarbyl ligand and the C(2)–Fe(1)–C(3) and C(4)–Fe(2)–C(5) bond angles. The metal–metal bond (Fe(1)–Fe(2) 2.4798 (4) Å) is somewhat shorter than that reported for the ferrole complexes $(CO)_6Fe_2[CH{=}CHCH{=}CH]$ (2.515 (1) Å)[35] and $(CO)_6Fe_2[PhC{=}C(Ph)C$-

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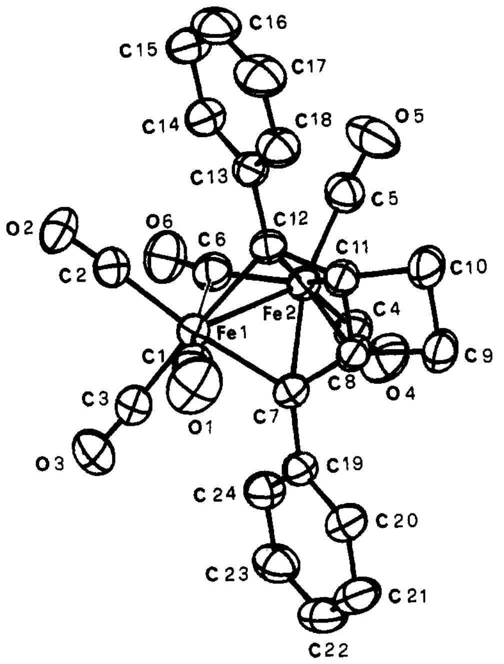

**Figure 2.** ORTEP plot of **6** showing atom-numbering scheme. Non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms are omitted.

(Ph)=CPh] (2.505 (1) Å).[36] The presence of a semibridging CO ligand, indicated by the IR spectrum, was confirmed. Although the carbonyl group C(6)O(6) is essentially bonded to Fe(2) (Fe(2)–C(6) 1.800 (3) Å), the elongation of the C(6)–O(6) bond (1.146 (4) Å vs 1.132 (3) Å (average) for the other carbonyls) and the bending of the Fe(2)–C(6)–O(6) fragment (163.8 (2)° vs 177.5 (2)° (average) for the other carbonyls) both point to a weak interaction between C(6) and Fe(1) (Fe(1)–C(6) 2.421 (3) Å). The foregoing values as well as the angles Fe(1)–C(6)–O(6) and Fe(1)–C(6)–Fe(2) of 126.0 (2) and 70.2 (1)°, respectively, are in accord with the corresponding data reported for semibridging CO groups.[37]

The most notable feature of the structure of **6** is the presence of a strained four-membered ring, the first such bicyclic arrangement in ferrole complexes. This ring is planar (within ±0.001 Å) and nearly coplanar (within 0.047 Å) with the two adjacent carbon atoms C(7) and C(12) and the ipso carbon atoms C(13) and C(19) of the phenyl groups. The sp$^2$ hybridization of the ferrole carbons C(8) and C(11) contributes severe strain to the four-membered ring (C(8)–C(9)–C(10)–C(11) torsion angle −0.12°), which accounts for the long bonds C(8)–C(9), C(9)–C(10) ($C_{sp^2}$–$C_{sp^3}$ 1.546 (3) Å (average)), and C(10)–C(11) ($C_{sp^3}$–$C_{sp^3}$ 1.574 (4) Å (average)). These bond lengths compare well with those reported for some strained bicyclic benzocyclobutenes.[38] All bond distances and angles not associated with the $C_4$ ring of **6** show good agreement with the corresponding distances and angles of $(CO)_6Fe_2[CH{=}CH{-}CH{=}CH]$[35] and $(CO)_6Fe_2[PhC{=}C(Ph)C(Ph){=}CPh]$.[36]

## Conclusion

The reactions of **1** and **2** with $Fe_2(CO)_9$ illustrate the dependency of the products on the identity of the metal of the transition-metal–propargyl complexes. They further suggest that propargyl complexes of the first-row transition metals might not be suitable reagents if formation of metal–metal-bonded binuclear and/or polynuclear complexes is endeavored. By way of contrast, propargyl complexes of the second- and third-row transition metals, viz. $Cp(CO)_3MCH_2C{\equiv}CR$ (M = Mo, W) and $Cp(CO)_2RuCH_2C{\equiv}CPh$, have yielded stable hydrocarbyl-bridged metal–metal-bonded products[2,3] and, on the basis of results to date, appear to be most promising synthons for such compounds.

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**Registry No.** **1**, 33114-75-9; **2**, 76498-84-5; **3**, 128803-66-7; **4**, 137465-55-5; **5**, 49769-16-6; **6**, 137465-56-6; $Fe_2(CO)_9$, 15321-51-4.

**Supplementary Material Available:** For **3** and **6**, figures of the hydrogen labeling schemes and listings of anisotropic thermal parameters and hydrogen atom coordinates (8 pages); tables of structure factors for complexes **3** and **6** (33 pages). Ordering information is given on any current masthead page.

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