cleophilic additions to alkyl ketones.[18]

**Acknowledgment.** We are grateful to the National Institutes of Health, the Harris Corporation, and the National Science Foundation San Diego Supercomputer Center for financial support of this research.

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## Synthesis and Structure of a Diiron Divinylidene Complex Formed by Oxidative Carbon-Carbon Coupling

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Transition-metal vinylidene complexes and higher metallacumulenes[1] are carbon-rich species which model reactive intermediates formed from surface carbides in heterogeneously catalyzed CO reduction and acetylene conversion reactions.[2] Of particular interest are reactions in which carbon-carbon bonds are formed, modeling hydrocarbon chain growth or graphite layer formation. We report here an oxidatively induced coupling of iron vinylidene complexes.

On the basis of Gladysz's conversion of methylene to formaldehyde on rhenium,[3] we anticipated that reactions of cationic iron vinylidene complexes[4] $[Fe(C{=}CR_2)(PR_3)_2(Cp)]^+$ with oxygen atom donors would lead to ketene complexes $[Fe(O{=}C{=}CR_2)(PR_3)_2(Cp)]^+$. However, $[Fe(C{=}CMe_2)(dppe)(Cp)]^+$ does not react with either trimethylamine *N*-oxide or iodosobenzene, and $[Fe(C{=}CHMe)(dppe)(Cp)]^+$ (**1**) is simply deprotonated by $Me_3NO$.[4] The reaction of $[Fe(C{=}CHMe)(dppe)(Cp)][BF_4]$ (**1**, 0.39 g, 0.60 mmol) with iodosobenzene[6] (1.2 g, 5.45 mmol) in acetonitrile (20 mL) under nitrogen at room temperature for 4 h, followed by evaporation and recrystallization of the residue from dichloromethane/ethyl ether, gave deep red-purple crystals of $[Fe_2(\mu\text{-}C_4Me_2)(dppe)_2(Cp)_2][BF_4]_2$ (**2**, 0.30 g, 77%).[7] The most striking feature of the X-ray crystal structure[8] of **2** (Figure 1) is that the $C_\beta$–H bonds of 2 equiv of **1** have been replaced by a carbon-carbon bond. A 2,3-dimethyl-1,3-butadien-1,4-diylidene ligand bridges the two iron atoms. The configuration at the C3–C4 single bond is s-trans (the C1–C3–C4–C2 torsional angle is −150.7°). The predicted dihedral angle between the symmetry plane of a $[FeL_2(Cp)]$ group and an attached vinylidene ligand is 90°.[1,9,10] The (CP0–Fe–C1)[11] to (C1–C3–C4–C5) dihedral angle in **2** is exactly 90.0°, whereas the (CP10–Fe–C2)[11] to (C2–C4–C3–C6) dihedral angle of 117.2° deviates considerably. This may be due to steric crowding, since there are close (3.5–3.8 Å) intramolecular contacts between methyl groups (C5 and C6) and the aromatic rings of the dppe ligands. The 27° twisting of the vinylidene ligand on Fe2 may account for the lengthening of Fe2–C2 relative to Fe1–C1, due to less effective orbital overlap.

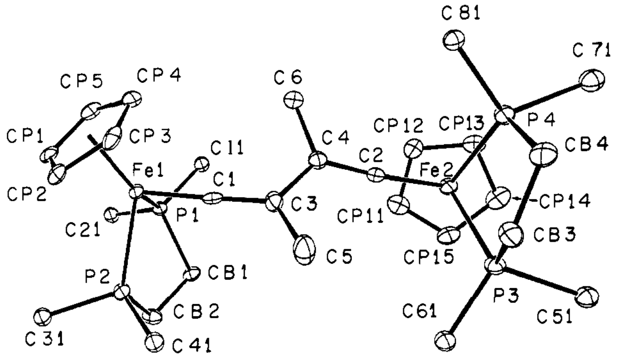

**Figure 1.** ORTEP[20] plot of the central portion of the cation in $[Fe_2(\mu\text{-}C_4Me_2)(dppe)_2(Cp)_2][BF_4]_2$ showing 50% probability ellipsoids. Phenyl groups are abbreviated for clarity. Important distances (Å) and angles: Fe1–C1 1.746 (9), Fe1–P1 2.222 (3), Fe1–P2 2.223 (3), Fe2–C2 1.766 (9), Fe2–P3 2.207 (3), Fe2–P4 2.201 (3), C1–C3 1.33 (1), C3–C4 1.50 (1), C3–C5 1.54 (1), C2–C4 1.32 (1), C4–C6 1.52 (1); C1–Fe1–P1 88.6 (3)°, C1–Fe1–P2 92.6 (3)°, C2–Fe2–P3 96.8 (3)°, C2–Fe2–P4 88.7 (3)°, Fe1–C1–C3 174.9 (7)°, C1–C3–C4 120.4 (9)°, C1–C3–C5 121.0 (9)°, C4–C3–C5 118.4 (8)°, Fe2–C2–C4 170.0 (8)°, C2–C4–C3 123.7 (8)°, C2–C4–C6 118.3 (8)°, C3–C4–C6 118.0 (8)°.

The formation of **2** is evidently due to one-electron oxidation of vinylidene complex **1**, which can also be effected by using copper(II) acetate in methanol. $[Fe(C{=}CHPh)(dppe)(Cp)][PF_6]$ is also oxidatively coupled in this way, but $[Fe(C{=}CH_2)(dppe)(Cp)][PF_6]$ gives a mixture of products. One-electron oxidation of $[FeXL_2(Cp)]$ (X = halide, Me, $SnMe_3$, etc.; L = CO, phosphine, phosphite, isonitrile) complexes leading to low-spin iron(III) complexes has been studied by several groups.[13-16] In

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(8) Crystal data for **2**: crystal dimensions 0.4 × 0.4 × 0.5 mm; Enraf-Nonius CAD4 diffractometer; Mo K$\alpha$ radiation; 8088 reflections collected, 4716 with $(F_o)^2 \geq 3\sigma(F_o)^2$ used; space group $P2_1/n$; $Z = 4$; $a = 11.763$ (5) Å, $b = 28.05$ (1) Å, $c = 18.739$ (6) Å, $\beta = 102.33$ (3)°, $V = 6040.9$ Å$^3$, $\rho_{calcd} = 1.419$ g·cm$^{-3}$, $\mu = 6.70$ cm$^{-1}$. The structure was solved by using MULTAN 77 and difference Fourier methods. Least-squares refinement with isotropic phenyl carbons, fixed hydrogens, and all other atoms anisotropic led to $R$ = 7.6% and $R_w$ = 9.0%.

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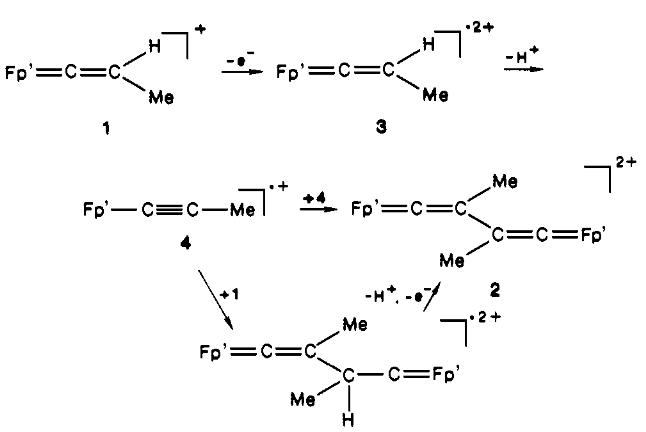
**Scheme I**



a few cases oxidation apparently occurs at a bound ligand, leading to C–C[14a] or S–S[13c,d] bond formation. Complex **2** may form by one-electron oxidation of **1** to a radical dication **3**, followed by deprotonation to **4** and subsequent coupling according to Scheme I. Other mechanistic possibilities including hydrogen *atom* abstraction from **1** to give **4** cannot be ruled out at this time. Attempts to oxidize alkynyl complex $[Fe(C{\equiv}CMe)(dppe)(Cp)]$ directly to **2** by using copper(II), silver(I), and anodic oxidation were unsuccessful, suggesting that acidic protons are required for the formation of **2**.

The oxidative coupling of vinylidene ligands is significant in several contexts. Potential oxidants $C_7H_7^+$, $PhN_2^+$, and halogens act as electrophiles rather than oxidants toward $[Ru(C{\equiv}CPh)(PR_3)_2(Cp)]$,[17] and aerial oxidation of ruthenium vinylidene complexes leads to oxidative *cleavage* of the vinylidene C=C bond.[1,17d] Oxidative coupling to form **2** may represent a significant difference between the iron and ruthenium systems. However, the anionic vinylidene complex $Li[Mo(C{=}CHCMe_3)\{P(OMe)_3\}_2(Cp)]$ is oxidatively coupled to a bis(alkylidyne) complex *without* hydrogen loss.[18] The vinylidene coupling reaction may provide useful insights into the oxidative coupling of terminal alkynes using copper(II),[19] as well as chain-growth reactions of putative vinylidene fragments on heterogeneous catalysts.[2]

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**Supplementary Material Available:** Listings of bond distances and angles (Table I), positional and thermal atomic parameters (Table III), parameters for fixed atoms (Table IV), and anisotropic thermal parameters (Table V) (10 pages); observed and calculated structure factors (Table II) (34 pages). Ordering information is given on any current masthead page.

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# *anti*-Tricyclo[4.2.1.1$^{2,5}$]deca-3,7-diene-9,10-diyl Dication: A Sandwiched Bishomoaromatic System[1a]

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Schahab Keyanian,[1b] George A. Olah,*[1b]
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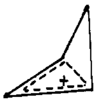
The homoaromaticity concept was first advanced by Winstein almost 30 years ago.[2] Since then it has been of great interest to experimental and theoretical chemists alike.[3,4] The question of homoaromatic overlap has been studied in six-π-electron as well as two-π-electron Hückeloid systems. The simplest two-π-electron monohomoaromatic cation is homocyclopropenium ion **1**.[5] The parent bishomoaromatic 4-cyclopentenyl cation **2** is still elusive, although the bishomoaromaticity in ethano- and etheno-bridged analogues (i.e., 7-norbornenyl and 7-norbornadienyl cations **3** and **4**) is well established.[6,7] Even several trishomoaromatic systems such as **5**, **6**, and **7** have been prepared and characterized.[8]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3


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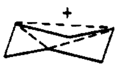
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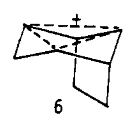
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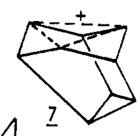
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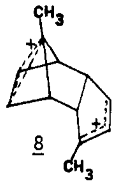

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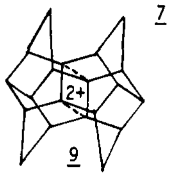

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We reported recently the generation and observation of *endo*-3,10-dimethyltricyclo[5.2.1.0$^{2,6}$]deca-4,8-diene-3,10-diyl cation

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