Synthesis of a new heterobinuclear iron-ruthenium complex, [cyclic] (CO)3Fe(.mu.-.eta.4-C(O)C(Ph):C:CH2)Ru(CO)Cp, and its reactions to give trinuclear metal clusters

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oxidation potentials, $E_{1/2}$, observed for substituted ferrocenes clearly reflect the electron-donating or -accepting properties of the substituents,[27] it is interesting to point out the drastic effect due to pentacoordination at silicon (Table II). In the case of **6**, the shift ($\Delta E_{1/2} = -0.47$ V) is similar to that observed for 1,1′-bis(dimethylamino)ferrocene (**7**; $\Delta E_{1/2} = -0.54$ V).[26,27] Strong electron-withdrawing substituents show an effect of the same magnitude, but in the opposite sense ($\Delta E_{1/2} = 0.48$ V for 1,1′-diacetylferrocene (**8**)[25]). In contrast, the groups $Si(OMe)_3$ ($\Delta E_{1/2} = 0.15$ V) in **1**, $SiMe_3$ ($\Delta E_{1/2} = 0.09$ V) in 1,1′-bis(trimethylsilyl)ferrocene (**9**),[28] and SiH_3 ($\Delta E_{1/2} = 0.21$ V) in 1,1′-disilylferrocene (**2**) behave as weakly electron-attracting species.

In conclusion, we have reported the very easy synthesis of molecules containing two hypervalent silicon species. These hypervalent anionic and neutral silicon moieties behave as electron donors, in contrast to the electron-withdrawing effect of the $Si(OMe)_3$ groups, although in both cases silicon is surrounded by oxygen atoms.

At the present time, the interpretation is not obvious since very little is known about the electronic effect of hypervalent silicon substituents. However, ab initio calculations[29] performed on pentacoordinated silicon compounds have shown that the electron density is spread on the surrounding ligands. The silicon atom behaves as an electron donor and thus becomes positively charged. This explanation could account for the lower redox potentials observed. In the case of the silatranes a strong transmission of electron density from nitrogen to iron via silicon, due to the bis-apical positions in the trigonal bipyramid, could be suggested.

Further work is in progress for the preparation of other models in order to understand better the behavior of silicon in hypervalent species.

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Synthesis of a New Heterobinuclear Iron–Ruthenium Complex, $(CO)_3\overline{Fe(\mu\text{-}\eta^4\text{-}C(O)C(Ph){=}C{=}CH_2)Ru}(CO)Cp$, and Its Reactions To Give Trinuclear Metal Clusters

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Summary: The reaction of the new ruthenium–propargyl complex $PhC{\equiv}CCH_2Ru(CO)_2Cp$ (**1**) with $Fe_2(CO)_9$ in THF at 0 °C or in diethyl ether at reflux temperature affords a novel heterobinuclear metal–(allenylcarbonyl) complex, $(CO)_3\overline{Fe(\mu\text{-}\eta^4\text{-}C(O)C(Ph){=}C{=}CH_2)Ru}(CO)Cp$ (**2**), as the major product. In contrast, reaction between $PhC{\equiv}CCH_2Fe(CO)_2Cp$ and $Fe_2(CO)_9$ yields $(CO)_3Fe[\eta^4\text{-}C(O)C(Ph){=}C(Fe(CO)_2Cp){=}CH_2]$ (**4**). A mechanism for the formation of **2** and **4** is proposed which is somewhat analogous to that for [3 + 2] cycloaddition reactions of metal–propargyl complexes with neutral electrophiles. **2** reacts with $Fe_2(CO)_9$ to give the trinuclear Fe_2Ru clusters $Fe_2(CO)_6RuCp(\mu_2\text{-}CO)_2(\mu_3\text{-}\eta^1\text{-}CCH{=}CHPh)$ (**3**) and $Fe_2(CO)_6Ru(CO)Cp(\mu_3\text{-}\eta^3\text{-}C(Ph){=}C{=}CH_2)$ (**5**) as the major products and with $Pt(PPh_3)_2(C_2H_4)$ to afford two FeRuPt complexes. The structures of **2**, **4**, and **5** were determined by X-ray crystallography.

The chemistry of transition-metal–propargyl complexes $RC{\equiv}CCH_2ML_n$ is highlighted by the reactions with protic acids to give the metal–allene cations $[(\eta^2\text{-}CH_2{=}C{=}CHR)ML_n]^+$ and with various uncharged electrophiles E═Nu (e.g., SO_2, $(CN)_2C{=}C(CN)_2$ (TCNE), and $ClSO_2NCO$, inter alia) to afford the [3 + 2] cycloadducts $\overline{CH_2NuEC(R){=}C}ML_n$ (E = electrophilic part and Nu = nucleophilic part of E═Nu).[1,2] A more recent development is the use of propargyl complexes in conjunction with metal carbonyls in the synthesis of heterobinuclear and -trinuclear metal compounds containing bridging alkyne and allenyl ligands.[3-5] In this communication we report (i) an extension of the latter reactions to the synthesis of other types of binuclear metal compounds, (ii) the apparent mechanistic relationship among these diverse reactions of metal–propargyl complexes, and (iii) the use of a new FeRu complex in the preparation of trinuclear metal clusters.

The first known ruthenium–propargyl complex, $PhC{\equiv}CCH_2Ru(CO)_2Cp$ (**1**), was obtained by reduction of $[Ru(CO)_2Cp]_2$ with $NaK_{2.8}$ in THF followed by addition of $PhC{\equiv}CCH_2Cl$ at −78 °C. Warming to room temperature, removing the solvent, and crystallizing from hexane afforded a light yellow solid in 70% yield.[6-8] **1** undergoes

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(6) Selected spectroscopic data for **1**: IR (THF) ν(CO) 2014 (s), 1959 (s), ν(C≡C) 2182 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.33 (s, Cp), 2.17 (s, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 200.7 (CO), 101.2, 81.6 (C≡C), −26.4 (CH_2).

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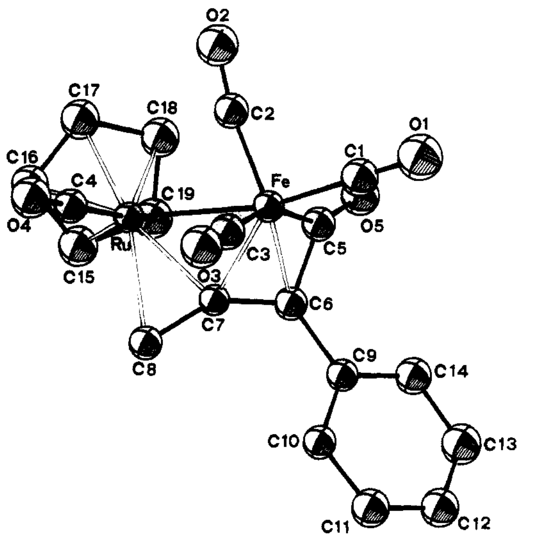
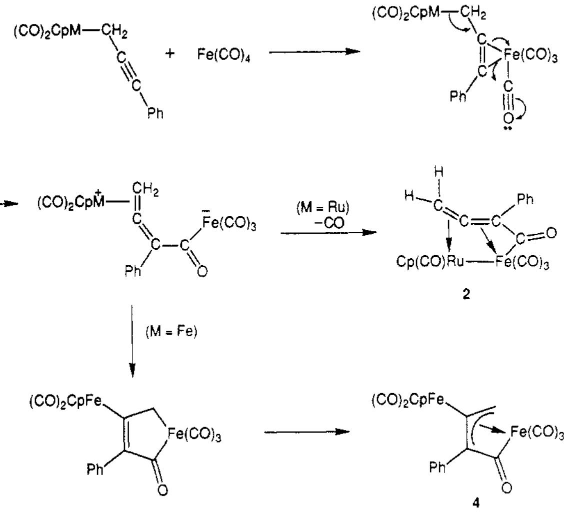


Figure 1. ORTEP drawing of molecule A of 2. Selected bond distances (Å) and angles (deg): Fe–Ru, 2.748 (2); Fe–C(5), 1.91 (1); Fe–C(6), 2.14 (1); Fe–C(7), 2.02 (1); Ru–C(7), 2.08 (1); Ru–C(8), 2.22 (1); C(5)–C(6), 1.46 (2); C(6)–C(7), 1.37 (2); C(7)–C(8), 1.40 (2); O(5)–C(5), 1.20 (2); C(6)–C(7)–C(8), 146 (1).

Scheme I



typical reactions of metal–propargyl complexes with electrophilic reagents; e.g., it is rapidly converted to $[\eta^2\text{-}CH_2{=}C{=}CHPh)Ru(CO)_2Cp]^{+}$[8] by the action of $HBF_4\cdot OEt_2$ in diethyl ether, and it cycloadds TCNE to furnish $CH_2C(CN)_2C(CN)_2C(Ph){=}CRu(CO)_2Cp$,[8] both reactions being essentially quantitative.

The reaction of 1 with $Fe_2(CO)_9$ was studied under a variety of conditions to optimize yields of the different products. The initial product $(CO)_3Fe(\mu\text{-}\eta^4\text{-}C(O)C(Ph){=}C{=}CH_2)Ru(CO)Cp$ (**2**; see Scheme I) was obtained in highest yield by stirring a suspension of $Fe_2(CO)_9$ (1.0 g, 3.0 mmol) in a THF solution (150 mL) of 1 (0.50 g, 1.5 mmol) under Ar at 0 °C for 20 h. A ^1H NMR spectrum showed that the reaction was only ca. 75% complete; however, other products were beginning to form in substantial amounts at this point. The mixture was concentrated and chromatographed on alumina; elution with 3:1 hexane–diethyl ether removed the major yellow-orange band, from which the orange solid 2 was isolated (0.22 g) in 31% yield. Other, smaller chromatographic bands were observed as well.[9] When this reaction was conducted in diethyl ether at reflux for 20 min, only one other major product was obtained but the yield of 2 was not as high. Chromatography as above afforded yellow-orange and brown-orange bands; they yielded, respectively, 2 (20%) and dark brown $Fe_2(CO)_6RuCp(\mu_2\text{-}CO)_2(\mu_3\text{-}\eta^1\text{-}CCH{=}CHPh)$ (3; vide infra) (15%).

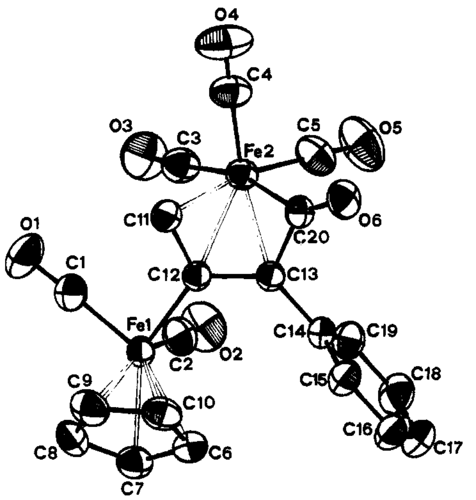


Figure 2. ORTEP drawing of 4. Selected bond distances (Å) and angles (deg): Fe(2)–C(11), 2.110 (3); Fe(2)–C(12), 2.194 (3); Fe(2)–C(13), 2.133 (3); Fe(2)–C(20), 1.905 (2); C(11)–C(12), 1.434 (3); C(12)–C(13), 1.417 (3); C(13)–C(20), 1.489 (3); O(6)–C(20), 1.203 (2); Fe(2)–C(11)–C(12), 78.3 (1); C(11)–C(12)–C(13), 111.5 (2); C(12)–C(13)–C(20), 114.4 (2).

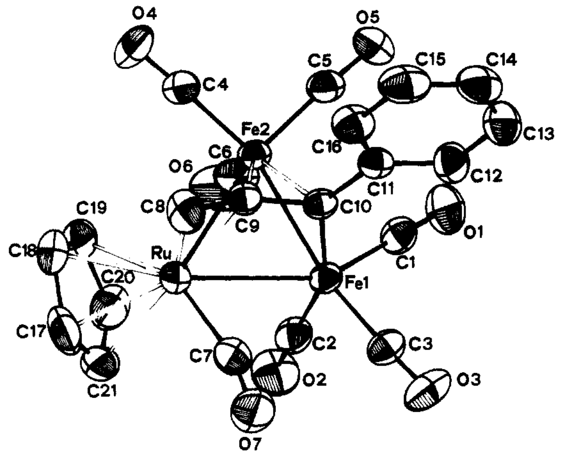


Figure 3. ORTEP drawing of 5. Selected bond distances (Å) and angles (deg): Ru–Fe(1), 2.7803 (8); Ru–Fe(2), 2.6869 (8); Fe(1)–Fe(2), 2.496 (4); C(8)–C(9), 1.409 (8); C(9)–C(10), 1.372 (7); C(8)–C(9)–C(10), 148.4 (5).

The structure of 2 was elucidated by X-ray crystallography[8,10] (Figure 1). The molecules consist of the $Fe(CO)_3$

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[7] However, the corresponding reaction of $[Ru(CO)_2Cp]^-$ with $HC{\equiv}CCH_2Cl$ affords (70%) the allenyl complex $CH_2{=}C{=}CHRu(CO)_2Cp$.

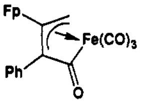
[8] Analytical, (additional) spectroscopic, and, in some cases, (additional) X-ray crystallographic data for new compounds are provided in the supplementary material. This information will be published in our full paper.

[9] Some of the bands were those of the trinuclear Fe_2Ru clusters reported in this communication and of $[Ru(CO)_2Cp]_2$.

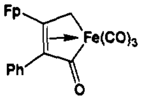
[10] Crystal data for 2: space group $P2_1/c$ with $a = 7.037$ (5) Å, $b = 17.20$ (1) Å, $c = 29.69$ (2) Å, $\alpha = 90°$, $\beta = 95.58$ (5)°, $\gamma = 90°$, $V = 3577$ (4) Å^3, $Z = 8$, and $D_{calcd} = 1.773$ g cm^{-3}; data collected at 294 ± 1 K with Mo Kα radiation, $\lambda(K\alpha) = 0.71069$ Å, $\mu = 16.7$ cm^{-1}, 2θ limits 6–54°, 3979 unique reflections with $I > 3\sigma(I)$, data/parameter ratio 8.49. The structure was solved by Patterson and Fourier methods. After anisotropic refinement, the calculated idealized positions of H atoms (0.96 Å from the parent C atoms) all occurred in positive electron density regions. No attempt was made to locate the H atoms at C(8). Final full-matrix least-squares refinement, with the fixed contribution of H atoms ($B = 1.3B_{eq}$ Å^2), converged to $R = 0.065$, $R_w = 0.073$, and GOF = 4.76. The crystal structure contains two crystallographically independent molecules (A and B).

and CpRu(CO) fragments joined by an Fe–Ru single bond that is supported by a bridging η^4-C(O)C(Ph)=C=CH$_2$ ligand. The latter is attached to Fe through the CO carbon and the internal C=C and to Ru through the terminal C=C. The C=C bond distances in the allenyl fragment are normal,[4,11] and the C(6)–C(7)–C(8) bond angle is 145°. The presence of an acyl CO is spectroscopically indicated by an IR band at 1761 (w-m) cm^{-1} and by a ^{13}C NMR resonances at δ 223.4. The ^{13}C resonance of the CH$_2$ group at δ 15.8 appears as a doublet of doublets (J_{CH} = 162.6 and 170.1 Hz), consistent with sp^2 hybridization of the carbon atom.[12,13]

Surprisingly, reaction between the congeneric propargyl complex PhC≡CCH$_2$Fe(CO)$_2$Cp and Fe$_2$(CO)$_9$ in pentane at 25 °C for 40 h affords as the major product (≥60% yield) a binuclear complex with a structure entirely different from that of **2**. The product (CO)$_3$Fe[η^4-C(O)C(Ph)=C(Fe(CO)$_2$Cp)=CH$_2$] (**4**)[14] was isolated after chromatography of the reaction mixture on alumina and crystallization from 1:1 CH$_2$Cl$_2$–pentane. Its molecules[8,15] (Figure 2) consist of an allylcarbonyl ligand that is η^4-bonded to Fe(CO)$_3$ through the CO and the three allyl carbons and η^1-attached to Fe(CO)$_2$Cp through its central allyl carbon. This allylcarbon (A) rather than a metallacyclic (B) formulation is supported by the value of the geminal coupling constant for the CH$_2$ protons (J = 3.0 Hz).[16] A vinylketene (C) representation[17] probably also contributes to the bonding description of **4**.



A



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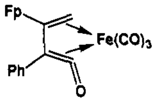
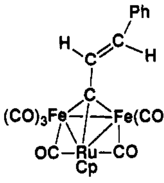


C

The formation of the two structurally different products **2** and **4** from reactions of similar metal–propargyl complexes with Fe$_2$(CO)$_9$ may be rationalized by the mechanism shown in Scheme I. This mechanism has some features in common with that proposed for the cycloaddition reactions of RC≡CCH$_2$ML$_n$.[1,2] Initially, the propargyl C≡C combines with a coordinatively unsaturated Fe(CO)$_4$ species to give a binuclear iron acetylene complex, which rearranges to a dipolar metal allene complex bearing Fe(CO)$_3$ as the negative terminus. This zwitterion then collapses by attack of the negative Fe(CO)$_3$ either at the coordinated allene (for M = Fe) or at the M(CO)$_2$ with loss of CO (for M = Ru). The observed selectivity may be due to the relative strength of the incipient Fe–M bond, the suceptibility of M(CO)$_2$ to attack by Fe(CO)$_3^-$, the propensity of M(CO)$_2$Cp to decarbonylation, or a combination of these factors.

Complex **2** serves as a convenient starting material for the preparation of heterotrinuclear metal clusters. Thus, reaction of **2** with ca. 2 equiv of Fe$_2$(CO)$_9$ in hexane at reflux for 10 min, followed by chromatography on alumina, affords dark green Fe$_2$(CO)$_6$Ru(CO)Cp(μ_3-η^3-C(Ph)=C=CH$_2$) (**5**)[8,18,19] and **3**[8,20] as major products. Whereas the formation of **3** from **2** by the addition of Fe(CO)$_3$ to the Fe–Ru bond and decarbonylation of the bridging allenylcarbonyl ligand appears quite straightforward, the formation of "capped" **3** involves rearrangement of the allenyl fragment with hydrogen migration and is still under investigation.



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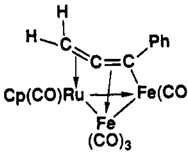

5

Stirring a 1:1 solution of **2** and (PPh$_3$)$_2$Pt(C$_2$H$_4$) in THF at 0 °C for 5 h, followed by chromatography on alumina, affords two different FeRuPt clusters as well as a Ph$_3$P-substitution derivative of **2**, (PPh$_3$)(CO)$_2$Fe(μ-η^4-C(O)C(Ph)=C=CH$_2$)Ru(CO)Cp (**6**).[8] The trinuclear clusters are presently under stuctural investigation.

The foregoing syntheses of the Fe$_2$Ru and FeRuPt complexes suggest that **2** may be a versatile reagent for the preparation of various heteronuclear FeRuM clusters containing bridging allenyl and related ligands. We are presently exploring these synthetic possibilities.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (through Grant CHE-8420806 to A.W.) and Ministero Pubblica Istruzione (Rome, Italy). High-field NMR and

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(12) Jackman, L. M. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd Ed.; Pergamon: New York, 1969; Chapter 4-5.

(13) Additional selected spectroscopic data for **2**: IR (C$_6$H$_6$) ν(CO) 2041 (s), 1996 (s), 1975 (s), 1968 (sh) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.00 (s, Cp), 4.07, 3.69 (2 d, J = 6.0 Hz, CH$_2$); ^{13}C{^{1}H} NMR (CDCl$_3$, 220 K) δ 214.3, 210.6, 204.7 (FeCO), 201.8 (RuCO), 185.5 (=C=), 87.3 (Cp), 47.0 (*C*Ph).

(14) Selected spectroscopic data for **4**: IR (C$_6$H$_6$) ν(CO) 2055 (s), 2023 (m), 1992 (vs), 1983 (sh), 1780 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.64 (s, Cp), 2.75, 2.00 (2 d, J = 3.0 Hz, CH$_2$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 233.19 (FeC=O), 215.61, 215.29 (Fe(CO)$_3$), 210.00 (CpFe(CO)$_2$), 140.21 (*C*Ph), 86.77 (Cp), 73.15 (CFe), 54.74 (CH$_2$).

(15) Crystal data for **4**: space group $P\bar{1}$ with a = 8.967 (2) Å, b = 9.304 (3) Å, c = 12.533 (4) Å, α = 98.02 (3)°, β = 104.84 (2)°, γ = 105.48 (3)°, V = 949.6 (5) Å^3, Z = 2, and D_{calc} = 1.609 g cm^{-3}; data collected at 294 ± 1 K with Mo Kα radiation, λ(Kα) = 0.71069 Å, μ = 15.6 cm^{-1}, 2θ limits 6–60°, 4121 unique reflections with $I > 3\sigma(I)$, data/paramester ratio 16.2. The structure was solved by Patterson and Fourier methods. After anisotropic refinement, the calculated idealized positions of H atoms (0.96 Å from the parent C atoms) all occurred in positive electron density regions. Final full-matrix least-squares refinement, with the fixed contribution of H atoms (B = 1.3 B_{eq} Å^2), converged to R = 0.032, R_w = 0.032, and GOF = 0.65.

(16) Reference 12, Chapter 4-1.

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(18) Selected spectroscopic data for **5**: IR (C$_5$H$_{12}$) ν(CO) 2052 (m), 2013 (s), 1987 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.26 (s, Cp), 3.21, 3.03 (2 d, J = 2.4 Hz, CH$_2$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 210.4 (FeCO), 201.8 (RuCO), 186.6 (=C=), 150.2 (=CPh), 87.2 (Cp), 13.3 (CH$_2$).

(19) Crystal data for **5**: space group $P2_1/c$ with a = 8.068 (3) Å, b = 15.333 (4) Å, c = 16.849 (3) Å, β = 95.11 (1)°, V = 2076.0 (4) Å^3, Z = 4, and D_{calc} = 1.885 g cm^{-3}; data collected at 297 ± 1 K with Mo Kα radiation, λ(Kα) = 0.71069 Å, μ = 21.2 cm^{-1}, 2θ limits 6–56°, 3753 unique reflections with $I > 3\sigma(I)$, data/parameter ratio 13.4. The heavy-atom positions were determined by the Patterson method. The whole structure was then determined by conventional Fourier methods. After anisotropic refinement, the calculated idealized positions of H atoms (0.96 Å from the parent C atoms) all occurred in positive electron density regions. Final full-matrix least-squares refinement, with the fixed contribution of H atoms ($B = 1.3B_{eq}$ Å^2), converged to R = 0.037, R_w = 0.042, and GOF = 1.77.

(20) Selected spectroscopic data for **3**: IR (C$_6$H$_{14}$) ν(CO) 2055 (s), 2022 (vs), 2012 (s), 1983 (m), 1973 (m), 1876 (w-m), 1839 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 9.18, 7.04 (2 d, J = 15.2 Hz, CH=CH), 5.43 (s, Cp); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 288.8 (μ_3-C), 215.4 (CO), 152.5, 129.1 (CH=CH), 96.7 (Cp). These data compare well with those of the structurally elucidated (by X-ray diffraction) Fe$_2$(CO)$_6$RuCp(μ_2-CO)$_2$(μ_3-η^1-CCH=CH$_2$), which differs from **3** only by replacement of the Ph group with H.[21]

(21) Shuchart, C. E.; Wojcicki, A.; Calligaris, M.; Nardin, G. To be submitted for publication.

mass spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant 79-10019). We also thank the Johnson Matthey Co. for a loan of ruthenium trichloride.

Supplementary Material Available: A description of spectroscopic and analytical data for $[(\eta^2\text{-}CH_2{=}C{=}CPh)Ru(CO)_2Cp]BF_4$, $\overline{CH_2C(CN)_2C(CN)_2C(Ph){=}C}Ru(CO)_2Cp$, and complexes **1**–**6** and details of the structure determinations for complexes **2**, **4**, and **5**, including tables of crystal data and data collection parameters, general temperature factor expressions, positional parameters and their estimated standard deviations, and selected bond distances and angles (24 pages). Ordering information is given on any current masthead page.

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^{1}H Nuclear Magnetic Resonance Studies of the Reduction of Paramagnetic Iron(III) Alkyl Porphyrin Complexes to Diamagnetic Iron(II) Alkyl Complexes

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Summary: Reaction of $(TPP)Fe^{III}Cl$ in dichloromethane with $LiHBEt_3$ yields $(TPP)Fe^{III}Et$.[15] Reduction of $(TPP)Fe^{III}R$ to $[(TPP)Fe^{II}R]^-$ (R = *n*-propyl, ethyl) by either $LiHBEt_3$ or $KHB(i\text{-}Bu)_3$ can be accomplished in benzene/tetrahydrofuran solution, where electron exchange between the iron(III) and iron(II) alkyls is rapid. $[(TPP)Fe^{II}R]^-$ is diamagnetic and is reoxidized by dioxygen to $(TPP)Fe^{III}R$.

The paramagnetic alkyl complexes of iron(III) porphyrins have received considerable study.[1-7] We have recently reported that in toluene solution at −80 °C dioxygen readily inserts into the Fe–C bond of low-spin ($S = {}^1/_2$) $(P)Fe^{III}CR_3$ to yield the very thermally unstable, high-spin ($S = {}^5/_2$) alkyl peroxide complex $(P)Fe^{III}OOCR_3$.[8,9] Electrochemical studies have shown that $(P)Fe^{III}CR_3$ can be reduced to the iron(II) level,[2,7] but other spectroscopic and reactivity data on the iron(II) alkyl complexes $(P)Fe^{II}CR_3^-$ are lacking. Here we report on the chemical reduction of $(P)Fe^{III}CR_3$ and on the reactivity of these iron(II) alkyls toward dioxygen. Trialkylborohydride ions are effective reducing agents for this, and the general question of their reactivity toward iron prophyrins has been examined.

Treatment of $(TPP)Fe^{III}Cl$ in dichloromethane solution with lithium triethylborohydride (Super-Hydride) in tetrahydrofuran solution at room temperature in the dark results in nearly quantitative conversion to $(TPP)Fe^{III}CH_2CH_3$, which has been identified by its characteristic ^{1}H NMR resonances (pyrrole H, −18.9; methyl H, −117.2 ppm; at 23 °C in benzene). This represents an unusual case in

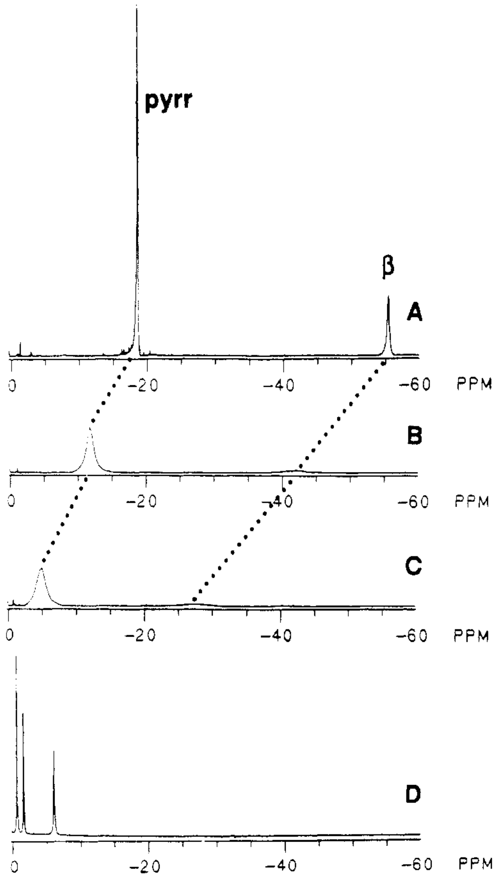

Figure 1. ^{1}H NMR spectra (300 MHz) of $(TPP)Fe^{III}CH_2CH_2CH_3$ in benzene-d_6 at 23 °C: (A) Spectrum of $(TPP)Fe^{III}CH_2CH_2CH_3$ alone; (B) spectrum after addition of 0.4 equiv of $KHB(i\text{-}Bu)_3$; (C) spectrum after addition of 0.7 equiv of $KHB(i\text{-}Bu)_3$; (D) spectrum after addition of 1.6 equiv of $KHB(i\text{-}Bu)_3$. Resonances are assigned as pyrr for pyrrole protons and β for the β-methylene of axial *n*-propyl group.

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