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Reactions of 1, 1'-Dialkynylferrocene with Octacarbonyldicobalt

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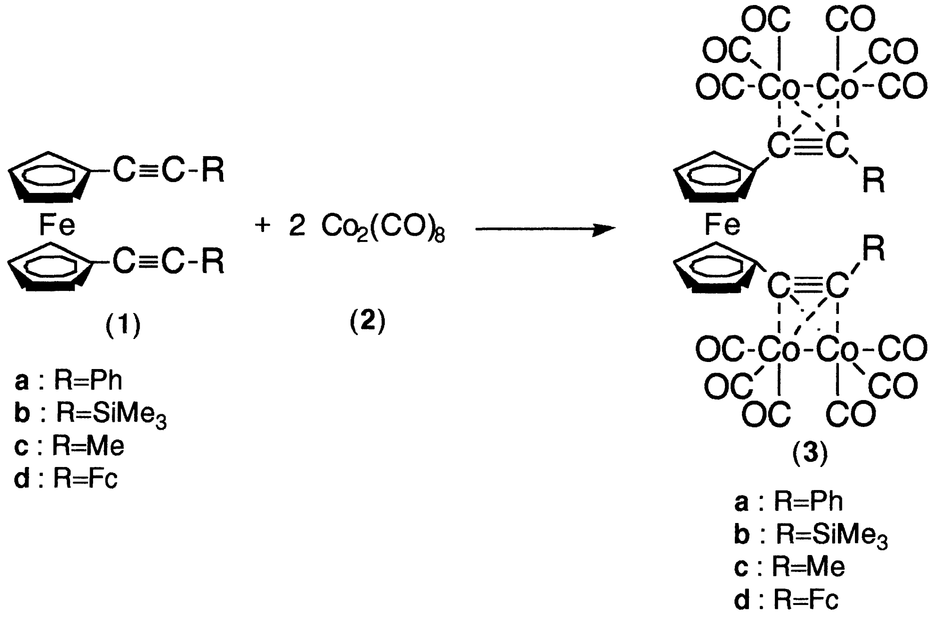
The reaction of 1, 1'-dialkynylferrocene ($(\eta^5\text{-}C_5H_4C{\equiv}CR)_2Fe$) (**1**) (R=Ph, $SiMe_3$, Me, Fc; Fc=ferrocenyl) with excess octacarbonyldicobalt (**2**) results in the formation of dark green complexes ($(\eta^5\text{-}C_5H_4C{\equiv}CR)_2Fe\{Co_2(CO)_6\}_2$ (**3**) (R=Ph, $SiMe_3$, Me, Fc), in which a $Co_2(CO)_6$ group coordinates to each of the two C≡C bonds of **1**. When 1, 1'-di(phenylethynyl)ferrocene (**1a**) was treated with an equimolar amount of **2**, $(\eta^5\text{-}C_5H_4C{\equiv}CPh)_2Fe\{Co_2(CO)_6\}$, as well as **3a**, was obtained.

Many ferrocene derivatives with donor atoms such as phosphorus and sulfur at 1,1'-positions that coordinate some transition metals were prepared.$^{1)}$ Previously we have reported the syntheses of some (ferrocenyl)silyl transition metal complexes, in which transition metal atoms are linked by dimethylsilylene group to ferrocene.$^{2)}$ In recent years, the intramolecular interaction between transition metal and central iron atom of ferrocene has become one of the most interesting topics in the chemistry of ferrocenyl transition metal complexes.$^{3)}$

On the other hand, it is well known that acetylene is able to coordinate to a variety of organometallic complexes in a lot of bonding mode.$^{4)}$ Octacarbonyldicobalt (**2**) reacts easily with acetylene to give the μ-acetylene complexes $Co_2(CO)_6(RC{\equiv}CR')$,$^{5)}$ and the reaction of **2** with ethynylferrocene also gave $Co_2(CO)_6(HC{\equiv}CFc)$ ($Fc=(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$).$^{6)}$ Titanocene acetylide complex $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti\text{-}(C{\equiv}CPh)_2$ reacts with **2** to give $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CPh)_2Co(CO)$, in which two acetylide groups act as a bidentate chelate ligand.$^{7)}$

Thus, we have examined the reaction of 1, 1'-dialkynylferrocene with **2**, which may afford a novel ferrocenyl complex or cluster. In this communication we would like to report on the synthesis and characterization of $(\eta^5\text{-}C_5H_4C{\equiv}CR)_2Fe\{Co_2(CO)_6\}_2$ (R=Ph, $SiMe_3$, Me, Fc) (**3**).

1, 1'-Bis(phenylethynyl)ferrocene (**1a**), which was prepared by the reaction of 1, 1'-diiodoferrocene$^{8)}$ and phenylacetylene in the presence of $(Ph_3P)_2PdCl_2$ and $Cu(OAc)_2$ catalyst in diisopropylamine under reflux,$^{9)}$ was treated with slightly excess **2** in hexane for 2h at room temperature under a nitrogen atmosphere. The color of the reaction mixture changed from brown to purple and finally to green with the progress of the reaction. After purification by column chromatography on alumina using hexane as an eluent under a nitrogen atmosphere followed by recrystallization from hexane, dark green crystals of **3a** were obtained in 62% yield. Complex **3a** is stable to air in the solid state and soluble in common organic solvents. The IR spectrum of **3a** showed very strong absorptions in the CO stretching region indicating that cobaltcarbonyl groups coordinate to the alkynyl groups of **1a**. The ^{1}H NMR spectrum of **3a** exhibited two triplets at δ 4.54 and 4.32 assigned to the protons of cyclopentadienyl rings and two multiplets at δ 7.89-7.87 and 7.16-7.06 assigned to the protons of phenyl groups. In the ^{13}C NMR spectrum acetylenic carbon resonances were observed at δ 92.62 and 91.77, which are in lower magnetic field than those of **1a** at δ 87.94 and 87.59, and a resonance due to the carbonyl appeared at δ 199.74. These data are consistent with the structure of **3a**, which is produced by the coordination of a $Co_2(CO)_6$ group to each of the two $C\equiv C$ bonds of **1a**, and the composition of **3a** was determined by the elemental analysis.[10]



(1)

a : R=Ph
b : R=SiMe3
c : R=Me
d : R=Fc

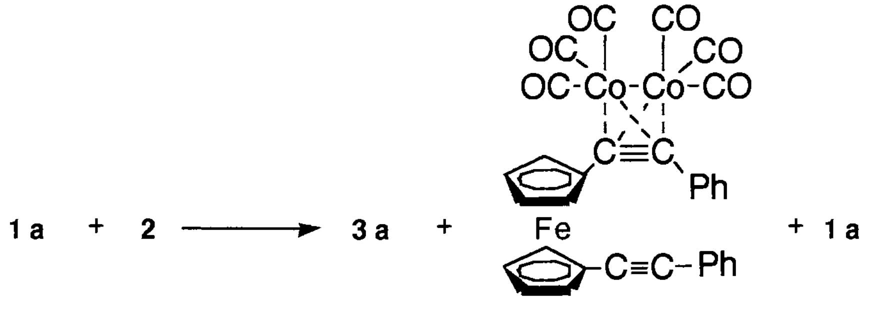
(2)

(3)

a : R=Ph
b : R=SiMe3
c : R=Me
d : R=Fc

Similar treatments of 1, 1'-bis(trimethylsilylethynyl)ferrocene (**1b**) and 1, 1'-dipropynylferrocene (**1c**)[11] with **2** gave **3b** in 27% yield and **3c** in 89% yield, respectively. Furthermore 1, 1'-bis(ferrocenylethynyl)-ferrocene[12] (**1d**) that was prepared by the reaction of 1, 1'-diiodoferrocene and ethynylferrocene[9] in a similar condition to that of **1a** also reacted with **2** to give dark green crystals of **3d** in 74% yield. These complexes were also characterized by spectroscopic analyses, and the satisfactory elemental analysis data were available.[13]

It should be noted that the reaction of **1a** with equimolar amount of **2** afforded not only **3** (17% yield) but also a new complex **4** (22% yield), and 20% of **1a** was recovered. The appearance of four ν_{CO} absorptions in the IR spectrum of **4** suggests the coordination of cobaltcarbonyl group to acetylene. The ^{1}H NMR of **4** showed four resonances of the Cp ring protons at δ 4.48, 4.40, 4.23 and 4.00. In the ^{13}C NMR spectrum four signals of acetylenic carbons were observed at δ 92.36, 91.89, 88.25 and 87.41, the chemical shifts of the two former signals are close to those of **3a**, and those of the two latter signals are similar to those of **1a**. These NMR data suggest that two $CpC\equiv CPh$ groups of **4** are magnetically unequivalent. Microanalytical data in conjunction with these spectroscopic data proved to characterize complex **4**, in which a $Co_2(CO)_6$ group coordinates to one of the two $C\equiv C$ bonds of **1a**.[14] From this result we have found that the coordination of a $Co_2(CO)_6$ group to one of the two $C\equiv C$ bonds does not affect the coordination to the other $C\equiv C$ bond.



(4)

The electronic spectra of **3** and **4** showed some distinct bands. The λ_{max} and ε values of the lowest energy band assigned to $d_{\pi} \rightarrow \sigma^{*}$[15] are as follows, **3a**: 597 nm (ε=2.2x10^3), **3b**: 621 nm (ε=1.5x10^3), **3c**: 595 nm (ε=2.7x10^3), **3d**: 607 nm (ε=3.7x10^3) and **4**: 565 nm (ε=1.0x10^3), respectively. The λ_{max} values of the lowest energy band are dependent on the acetylenic substituent, following the series $SiMe_3$>Fc>Ph>Me. The important point to note is that the $SiMe_3$ substituent shows the strongest bathochromic shift. For the analogous complexes, $RC{\equiv}CSiMe_2H\{Co_2(CO)_6\}$, where R=$HMe_2Si$ or Ph, the order is Ph>HMe_2Si.[16] These data may indicate that two dicobalt tetrahedrane chromophores of **3** conjugate through ferrocene and vacant d-orbitals of silicone atoms.

Attempts to obtain a novel ferrocenyl cobaltcarbonyl cluster by the irradiation of ultraviolet light or thermal reaction under benzene reflux of **3a**[17] were unsuccessful, and **3a** was recovered. The reaction of **3a** under dioxane reflux gave an unstable product which could not be characterized.

Further studies including X-ray structural analysis of these complexes are now in progress.

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10) mp 124-125 °C; IR(KBr): 3150(w), 2090(vs), 2050(vs), 2030(vs), 2000(vs), 1625(w), 1585(w), 1565(w), 1480(m), 1440(m), 1385(w), 1260(w), 1080(w), 1040(m), 1025(w), 840(m), 825(m), 805(w), 760(m), 695(s), 660(m), 630(m), 605(m), 595(m), 585(m), 570(m), 540(m), 520(s), 495(s), 465(s) cm^{-1}; ^{1}H NMR(400 MHz, C_6D_6): 7.89-7.87(4H, m, Ph), 7.16-7.06(6H, m, Ph), 4.54(4H, t, J=2 Hz, Cp), 4,32(4H, t, J=2 Hz, Cp); ^{13}C NMR(C_6D_6): 199.74(CO), 138.74(Ph), 129.83(Ph), 129.27(Ph), 128.45(Ph), 92.64(C≡), 91.77(C≡), 86.61(Cp), 72.73(Cp), 71.11(Cp); UV(c-C_6H_{12}) λ_{max}=216 (ε=7.2x10^4), 430 (ε=3.3x10^3), 597 nm (ε=2.2x10^3); Anal. Found: C, 47.44; H, 1.87%. Calcd for $C_{38}H_{18}O_{12}Co_4Fe$: C, 47.64; H, 1.89%.

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13) **3b**: mp 184-187 °C (dec. in N_2); IR(KBr): 3080(w), 2965(m), 2900(w), 2095(vs), 2065(vs), 2055(vs), 2010(vs), 1990(vs), 1965(s), 1955(s), 1605(m), 1420(m), 1410(m), 1260(m), 1250(m), 1220(m), 1205(w), 1045(w), 1035(m), 940(w), 865(m), 850(s), 840(s), 820(m), 790(m), 760(w), 700(w), 660(w), 640(w), 615(m), 525(s), 505(s), 475(s), 460(s) cm^{-1}; ^{1}H NMR(400 MHz, $CDCl_3$): 4.41(4H, s, Cp), 4.34(4H, s, Cp), 0.45(18H, s, Me); ^{13}C NMR($CDCl_3$): 200.11(CO), 86.23(Cp), 72.49(Cp), 70.61(Cp), 1.25(Me). The resonances of acetylene carbon were not detected due to low solubility of **3b**. UV(c-C_6H_{12}) λ_{max}=215 (ε=4.4x10^4), 621 nm (ε=1.5x10^3); Anal. Found: C, 40.19; H, 2.60%. Calcd for $C_{32}H_{26}O_{12}Si_2Co_4Fe$: C, 40.25; H, 2.76%.

3c: mp 210-237 °C (dec. in N_2); IR(KBr): 3080(w), 2960(w), 2900(w), 2095(vs), 2055(vs), 2045(vs), 2000(vs), 1980(vs), 1420(w), 1385(w), 1365(w), 1245(w), 1205(w), 1065(w), 1050(w), 1030(w), 1015(w), 825(m), 700(m), 640(w), 565(w), 520(s), 505(s), 470(s) cm^{-1}; ^{1}H NMR(400 MHz, $CDCl_3$): 4.39(8H, s, Cp), 2.86(6H, s, Me); ^{13}C NMR($CDCl_3$): 199.78(CO), 94.72(C≡), 91.23(C≡), 86.06(Cp), 71.31(Cp), 70.16(Cp), 21.00(Me); UV(c-C_6H_{12}) λ_{max}=215 (ε=6.7x10^4), 595 nm (ε=2.7x10^3); Anal. Found: C, 40.07; H, 1.61%. Calcd for $C_{28}H_{14}O_{12}Co_4Fe$: C, 40.33; H, 1.69%.

3d: mp 180-184 °C; IR(KBr): 3070(w), 2090(vs), 2050(vs), 2030(vs), 2005(vs), 1995(vs), 1980(vs), 1545(w), 1410(w), 1380(w), 1260(w), 1200(w), 1110(m), 1040(m), 1020(w), 1000(w), 850(w), 820(m), 760(m), 640(w), 515(s), 500(s), 470(s) cm^{-1}; ^{1}H NMR(400 MHz, $CDCl_3$): 4.70(4H, br, Cp), 4.62(4H, br, Cp), 4.46(8H, br, Cp), 4,24(10H, s, Cp); ^{13}C NMR($CDCl_3$): 199.69(CO), 93.30(C≡), 91.74(C≡), 86.96(Cp), 85.93(Cp), 72.49(Cp), 70.54(Cp), 70.13(Cp), 69.84(Cp), 69.26(Cp); UV(c-C_6H_{12}) λ_{max}=221 (ε=7.2x10^4), 607 nm (ε=3.7x10^3); Anal. Found: C, 46.93; H, 1.86%. Calcd for $C_{46}H_{26}O_{12}Co_4Fe_3$: C, 47.06; H, 2.23%.

14) mp 78-80 °C; IR(KBr): 3055(w), 3045(w), 2090(vs), 2050(vs), 2005(vs), 1990(vs), 1625(w), 1590(w), 1490(m), 1480(m), 1435(m), 1385(w), 1260(w), 1200(w), 1070(w), 1040(w), 1030(m), 920(w), 825(s), 760(s), 690(s), 660(m), 625(w), 605(w), 590(w), 580(w), 570(m), 540(m), 515(s), 495(s) cm^{-1}; ^{1}H NMR(400 MHz, C_6D_6): 7.97-7.95(2H, m, Ph), 7.57-7.56(2H, m, Ph), 7.19-7.16(3H, m, Ph), 7.08-7.01(3H, m, Ph), 4.48(2H, s, Cp), 4,40(2H, s, Cp), 4.23(2H, s, Cp), 4,00(2H, s, Cp); ^{13}C NMR(C_6D_6): 199.77(CO), 138.74(Ph), 131.74(Ph), 129.97(Ph), 129.29(Ph), 128.73(Ph), 128.56(Ph), 128.17(Ph), 124.35(Ph), 92.36(C≡), 91.89(C≡), 88.25(C≡), 87.41(C≡), 86.58(Cp), 73.14(Cp), 72.73(Cp), 71.81(Cp), 71.25(Cp), 67.15(Cp); UV(c-C_6H_{12}) λ_{max}=214 (ε=4.8x10^4), 300 (ε=2.6x10^4), 436 (ε=1.9x10^3), 565 nm (ε=1.0x10^3); Anal. Found: C, 57.33; H, 2.55%. Calcd for $C_{32}H_{18}O_6Co_2Fe$: C, 57.18; H, 2.70%.

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