The Chemistry of Bis(fulvalene)divanadium

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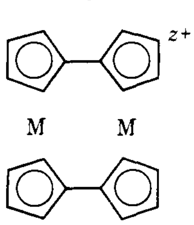
Abstract: Neutral bis(fulvalene)divanadium, $(C_{10}H_8)_2V_2$, was synthesized from the fulvalene dianion and $VCl_2 \cdot 2THF$. The compound was chemically oxidized in acetone to the mixed-valence monocation and to the dication. $(C_{10}H_8)_2V_2$ was also carbonylated to give $(C_{10}H_8)_2V_2(CO)_2$ with terminally bonded carbon monoxide. This dicarbonyl was also oxidized to a mono- and a dication. Oxidation of $(C_{10}H_8)_2V_2$ in acetonitrile gave the $[(C_{10}H_8)_2V_2(CH_3CN)_2{}^{2+}]$ ion. These compounds were characterized by elemental analysis, infrared and electronic spectroscopy, cyclic voltammetry, and magnetic susceptibility. The electronic structures of these derivatives are discussed in light of the chemistry of other metallofulvalene complexes and of metallocenes.

Recent studies in metallofulvalene chemistry have shown that these compounds are not completely described by assuming a metallocene-like electron configuration. The apparent delocalization of the odd electron in each of the mixed-valence monocations and the observed diamagnetism of every compound prepared to date with an even number of electrons suggest that strong interactions take place between the two metal centers.



M = Cr,[1] Fe,[2,3] Co,[4] Ni[5]
z = 0, 1, 2
M = Mo[6]
z = 0

In order to investigate the interactions between metal centers in electron-deficient systems, we have pursued the synthesis of bis(fulvalene)divanadium and its mono- and dications, and have attempted to demonstrate its coordinative unsaturation. The results of these studies are herein reported.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer as halocarbon or Nujol mulls, and are reported in units of cm^{-1}. Ultraviolet, visible, and near-infrared spectra were obtained using a Cary Model 14 spectrophotometer. Mass spectra were obtained on an AEI MS 12 mass spectrometer. Magnetic susceptibility measurements were obtained on solid samples using a Princeton Applied Research (PAR) Model 155 variable-temperature vibrating magnetometer. Solution magnetic moments were obtained using the Evans NMR method[7] with a Varian Associates Model T-60 NMR spectrometer. Cyclic voltammograms were recorded with a PAR Model 173 potentiostat/galvanostat equipped with Model 174 universal programmer and Model 179 digital coulometer, using a platinum disk or wire working electrode and a standard calomel or silver/silver nitrate reference electrode. All potenitals are reported referenced to the SCE. EPR spectra were kindly recorded by Mr. Wayne Glad and Mr. Jim Roe of the University of California, Berkeley, using a Varian Associates Model V 4502 EPR spectrometer. All melting points were taken with capillary tubes sealed under nitrogen.

Reagent grade solvents and chemicals were used throughout. Tetrahydrofuran (THF), benzene, toluene, hexane, and pentane were distilled from sodium benzophenone ketyl and stored under nitrogen. Acetone was dried over potassium carbonate, distilled from potassium permanganate, and finally distilled from potassium carbonate. Acetonitrile was distilled either from P_2O_5 or from boric anhydride. Pyridine was distilled from barium oxide. All aforementioned solvents were distilled and stored under nitrogen.

Other reagents were used without further purification. Solutions of n-butyllithium (ca. 2.4 M in hexane) were obtained from Alfa Inorganics. NH_4PF_6 was obtained from Ozark-Mahoning. Na(DME)-C_5H_5 was prepared according to the method of Smart and Curtis.[8] Ferrocenium hexafluorophosphate was prepared by oxidizing ferrocene with ferric chloride in water/acetone (3/1 v/v), precipitating the cation with aqueous NH_4PF_6, and recrystallizing the blue product at room temperature from acetone/ethanol with the addition of a small amount of anhydrous ferric chloride.

All operations were performed under a nitrogen atmosphere using standard Schlenk tube techniques or in a Vacuum Atmospheres inert atmosphere box unless otherwise stated. Medium-pressure reactions were performed in Fisher-Porter bottles (Lab-Crest Division, Warminister, Pa.).

Elemental analyses were performed by the University of California, Berkeley, Analytical Laboratories and by Spang Microanalytical Laboratory, Eagle Harbor, Mich.

Bis(fulvalene)divanadium(II,II) $[(\eta^5:\eta^5\text{-}C_{10}H_8)_2V_2{}^{II,II}]$ from $VCl_2 \cdot 2THF$. In a drybox, a 1-L, three-necked, round-bottom flask equipped with a stopcock inlet and a magnetic stir bar was charged with VCl_3 (18.1 g, 115 mmol) and a few small grains of NaH (50% dispersion in mineral oil), and was capped with a rubber septum. THF (250 mL) was added via cannula. A reflux condenser was attached against a nitrogen counterstream, and the suspension was heated to reflux with stirring for 15 h to give a purple solution with an orange precipitate. The flask was cooled to room temperature and zinc dust (3.75 g, 57.4 mmol) was added against a nitrogen stream. The reaction mixture was again stirred at reflux for 12 h to give a purple solution with a green precipitate of $VCl_2 \cdot 2THF$ and $ZnCl_2 \cdot x THF$.[9]

Simultaneously a 500-mL round-bottom flask with a side-arm stockcock and a magnetic stir bar was charged in the drybox with $NaC_5H_5 \cdot DME$ (41.1 g, 231 mmol). The addition of THF (350 mL) via cannula gave a pink solution which was then cooled to −78 °C. I_2 (30.66 g, 121 mmol) was added against a N_2 stream, and the reaction mixture was warmed to room temperature for 20 min with vigorous stirring to give a dark red solution. The flask was immediately rechilled to −78 °C, butyllithium (97 mL, 2.6 mol, in hexane, 250 mmol) was added via syringe, and the mixture was warmed to room temperature with stirring to give a pale pink suspension of the fulvalene dianion.

The fulvalene dianion suspension (at room temperature) was then quickly added to the refluxing $VCl_2 \cdot 2THF$ suspension via cannula. The combined reaction mixture was refluxed for 1 h and then cooled to −30 °C overnight to give a dark purple suspension.

The suspended material was collected by filtration in the drybox, washed with THF (2 × 100 mL), and dried in vacuo. Sublimation of this crude purple solid at ca. 230 °C and <0.01 mm pressure yielded dark purple $(C_{10}H_8)_2V_2{}^{II,II}$ (9.26 g, 25.9 mmol, 45% based on VCl_3) which was pure enough for most purposes. Resublimation provided an analytically pure sample. The compound is stable above 300 °C in a nitrogen atmosphere but is pyrophoric.

Anal. Calcd for $C_{20}H_{16}V_2$: C, 67.06; H, 4.50. Found: C, 67.31; H, 4.64.

IR: 3090 m, 1760 w, 1700 w, 1680 w, 1590 w, 1540 w, 1425 s, 1395 w, 1370 m, 1295 s, 1115 s, 1068 m, 1056 m, 1042 s, 1029 sh, 1003 s, 922 m, 846 m, 840 m, 834 s, 797 s, 780 s, 760 m, 722 w, 693 w, 642 w, 450 m cm^{-1}.

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Mass spectrum [70 eV, *m/e* (rel intensity)]: 51 (46), 55 (44), 57 (49), 63 (35), 65 (32), 66 (20), 67 (35), 69 (27), 77 (39), 78 (32), 91 (60), 102 (26), 103 (13), 104 (17), 115 (97), 116 (13), 117 (44), 127 (38), 128 (100), 129 (99), 130 (85), 131 (38), 132 (41), 179 (3), 358 (21), 359 (4).

Bis(fulvalene)divanadium(III,III) Bis(hexafluorophosphate), $[(\eta^5:\eta^5\text{-}C_{10}H_8)_2V_2^{2+}](PF_6^-)_2$. In a drybox, a 100-mL round-bottom flask with a side-arm stopcock and a magnetic stir bar was charged with $(C_{10}H_8)_2V_2$ (0.25 g, 0.70 mmol) and $[(C_5H_5)_2Fe^+](PF_6^-)$ (0.23 g, 0.70 mmol). Dry, oxygen-free acetone (12 mL) was added via syringe. The reaction mixture was stirred under N_2 for 20 min to give a dark purple solution.

The purple solution was filtered through paper via cannula, the flask was washed with about 3 mL of acetone, and the wash was added to the filtrate. *n*-Pentane (ca. 5 mL) was added to the filtrate and a curdy brown precipitate separated. The mother liquor was then removed by filtration through paper via cannula and slowly chilled to −78 °C to yield black crystals. The crystals were isolated by filtration (Schlenk filter tube), washed with pentane (1 × 3 mL), and dried in vacuo. The black, crystalline product (0.17 g, 0.34 mmol, 48% yield) was analytically pure. A second crop, suitable for most purposes, could be obtained from the filtrate.

$[(C_{10}H_8)_2V_2^+](PF_6^-)$ does not melt below 280 °C in sealed capillaries and is stable briefly in air.

Anal. Calcd for $C_{20}H_{16}F_6PV_2$: C, 47.74; H, 3.21; P, 6.15; V, 20.25. Found: C, 47.58; H, 3.44; P, 6.10; V, 19.8.

IR: 3640 br, m, 3115 w, 1445 m, 1435 m, 1420 m, 1308 w, 1166 w, 1127 w, 1111 w, 1070 m, 1055 m, 1014 m, 835 br, s, 741 w, 730 w, 723 w, 641 m, 560 s cm^{-1}.

Bis(fulvalene)divanadium(III,III) Bis(hexafluorophosphate), $[(\eta^5:\eta^5\text{-}C_{10}H_8)_2V_2^{2+}](PF_6^-)_2$. In a drybox, a 100-mL round-bottom flask with a side-arm stopcock and a magnetic stir bar was charged with $(C_{10}H_8)_2V_2$ (1.16 g, 3.24 mmol) and $[(C_5H_5)_2Fe^+](PF_6^-)$ (2.16 g, 6.53 mmol). The flask was removed from the box and chilled to −70 °C. Acetone (50 mL), prechilled to −60 °C, was added via cannula, and the reaction mixture was stirred under N_2 at −70 °C for 1 h to give a purple solution.

The solution was filtered through a Schlenk filter tube prechilled to −30 °C. The solid residue was washed with cold acetone (3 × 7 mL) and the washes were added directly to the filtrate. The purple filtrate was then stirred at −30 °C while *n*-pentane (100 mL) was added slowly from a dropping funnel. A dark purple precipitate was deposited and was collected by filtration, washed with pentane (1 × 5 mL), and dried in vacuo. The dark purple, microcrystalline product (1.51 g, 2.33 mmol, 72% yield) was pure enough for most purposes. Recrystallization from cold acetone/pentane with the addition of a trace of $[(C_5H_5)_2Fe^+](PF_6^-)$ gave an analytical sample. $[(C_{10}H_8)_2V_2^{2+}]$-$(PF_6^-)_2$ lightens and turns olive green above 130 °C in sealed capillaries, but does not melt below 280 °C. The compound is air sensitive in the solid state and in solution.

Anal. Calcd for $C_{20}H_{16}F_{12}P_2V_2$: C, 37.06; H, 2.49; P, 9.56. Found: C, 37.00; H, 2.56; P, 8.65.

IR: 3550 br, m, 3120 m, 1664 br, m, 1449 m, 1407 m, 1362 w, 1300 br, m, 1170 br, m, 1129 w, 1070 w, 1055 m, 1033 w, 1023 m, 933 sh, 840 br, s, 742 m, 724 m, 709 w, 627 w, 560 s cm^{-1}.

Bis(fulvalene)dicarbonyldivanadium, $(\eta^5:\eta^5\text{-}C_{10}H_8)_2(CO)_2V_2^{II,II}$. In a drybox, a Fisher-Porter medium-pressure bottle (Lab-Crest Division, Warminster, Pa.) was charged with $(C_{10}H_8)_2V_2$ (1.50 g, 4.19 mmol) and a magnetic stir bar. THF (220 mL) was added via cannula; the bottle was purged with carbon monoxide and then pressured to 150 psi. The reaction mixture was then stirred for 20 h to give a dark green solution.

The pressure was relieved and the bottle was taken into the drybox. The solution was pressure filtered through Celite into a 1-L round-bottom flask equipped with a side-arm stopcock and a magnetic stir bar. The flask was capped with a rubber septum and passed out of the box.

A dropping funnel was attached to the flask against a nitrogen counterstream and hexane (ca. 350 mL) was added dropwise to the stirring solution. The olive-green, microcrystalline product precipitated out. The flask was chilled to −70 °C overnight and then the product was isolated by filtration, washed with hexane (2 × 15 mL), and dried in vacuo. The dark green $(C_{10}H_8)_2(CO)_2V_2$ (1.35 g, 3.26 mmol, 78% yield) is pure enough for most purposes. An analytical sample was obtained by slowly cooling a THF/pentane solution (1/1 v/v).

$(C_{10}H_8)_2(CO)_2V_2$ is air stable; however, traces of $(C_{10}H_8)_2V_2$ can lead to conflagration, and the compound is best handled in an inert atmosphere. $(C_{10}H_8)_2(CO)_2V_2$ darkens above 155 °C in sealed capillaries, but does not melt below 280 °C. Attempts to sublime the compound yield $(C_{10}H_8)_2V_2$ at ca. 200 °C with some decomposition.

Anal. Calcd for $C_{22}H_{16}O_2V_2$: C, 63.79; H, 3.89; V, 24.59. Found: C, 63.94; H, 4.02; V, 24.20, 24.24.

IR: 3125 m, 3100 sh, 1875 br, s, 1555 m, 1445 s, 1410 s, 1380 s, 1375 sh, 1360w, 1350 w, 1273 w, 1198 w, 1109 sh, 1104 m, 1071 w, 1060 sh, 1052 m, 1029 s, 1026 sh, 1010 sh, 1007 m, 934 w, 896 sh, 890 sh, 886 sh, 880 s, 869 s, 865 sh, 840 w, 835 w, 827 w, 809 w, 790 sh, 783 s, 743 sh, 730 m, 726 m, 690 m, 637 w, 598 w, 539 s, 536 sh, 527 s, 494 sh, 480 s, 462 sh, 457 w, 434 w cm^{-1}.

Solution IR in THF: ν_{CO} at 1970 sh, 1960 s, 1900 s, 1870 w cm^{-1}.

Bis(fulvalene)dicarbonyldivanadium(II,III) Hexafluorophosphate, $[(\eta^5:\eta^5\text{-}C_{10}H_8)_2(CO)_2V_2^{II,III\,+}](PF_6^-)$. In a drybox, a 100-mL round-bottom flask with a side-arm stopcock and a magnetic stir bar was charged with $(C_{10}H_8)_2(CO)_2V_2$ (0.40 g, 0.97 mmol) and $[(C_5H_5)_2Fe^+](PF_6^-)$ (0.32 g, 0.97 mmol). THF (35 mL) was added via cannula and the reaction mixture was stirred vigorously under N_2 for 90 min to yield a dark brown, microcrystalline precipitate. The product was isolated by filtration, washed with THF (2 × 2 mL), and dried in vacuo to give 0.38 g of $[(C_{10}H_8)_2(CO)_2V_2^+](PF_6^-)$ (0.68 mmol, 70%). Attempts to purify the compound by recrystallization from acetone lead to immediate loss of CO and the isolation of $[(C_{10}H_8)_2V_2^+](PF_6^-)$.

$[(C_{10}H_8)_2(CO)_2V_2^+](PF_6^-)$ is air sensitive, but does not darken or melt below 280 °C in sealed capillaries.

Anal. Calcd for $C_{22}H_{16}F_6O_2PV_2$: C, 47.2; H, 2.9. Found: C, 46.2; H, 3.7.

IR: 3610 br, W, 3120 m. 2055 s, 2010 s, 1960 s, 1915 s, 1450 m, 1440 m, 1425 m, 1415 m, 1400 w, 1303 w, 1160 m, 1109 m, 1082 w, 1078 w, 1072 w, 1054 m, 1042 sh, 1019 sh, 1014 m, 944 sh, 940 m, 830 br, s, 742 m, 738 m, 735 sh, 726 w, 722 w, 639 w, 562 sh, 559 s, 556 s, 524 m, 496 m, 480 w, 461 w cm^{-1}.

Bis(fulvalene)dicarbonyldivanadium(III,III) Bis(hexafluorophosphate), $[(\eta^5:\eta^5\text{-}C_{10}H_8)_2(CO)_2V_2^{2+}](PF_6^-)_2$. A 100-mL round-bottom flask with a side-arm stopcock and a magnetic stir bar was charged with $(C_{10}H_8)_2V_2(CO)_2$ (1.02 g, 2.46 mmol) and $[(C_5H_5)_2Fe^+](PF_6^-)$ (1.64 g, 4.95 mmol). The flask was capped with a rubber septum and purged with carbon monoxide. Acetone (45 mL) was added via syringe and the reaction mixture was stirred under CO for 10 min to give a deep purple solution. The solution was immediately filtered through Celite (Schlenk filter tube) into a round-bottom flask with a side-arm stopcock and a magnetic stir bar, and a dropping funnel was attached to the flask against a CO counterstream. The dropwise addition of *n*-pentane (70 mL) yielded a dark precipitate.

The product was isolated by filtration washed with pentane (3 × 15 mL), and dried in vacuo. The dark purple $[(C_{10}H_8)_2(CO)_2V_2^{2+}]$-$(PF_6^-)_2$ thus obtained is pure enough for most purposes (1.32 g, 1.88 mmol, 76% yield). Analytically pure material was prepared by reducing the volume of a saturated acetone solution under a slow stream of CO followed by cooling to give orange crystals. $[(C_{10}H_8)_2V_2(CO)_2^{2+}](PF_6^-)_2$ may be handled in air. The compound gradually darkens above 155 °C but does not melt below 280 °C.

Anal. Calcd for $C_{22}H_{16}F_{12}P_2O_2V_2$: C, 37.52; H, 2.99; P, 8.80. Found: C, 37.38; H, 2.23; P, 8.68.

IR: 3130 m, 3100 sh, 2055 s, 2005 s, 1445 m, 1405 m, 1289 w, 1260 w, 1210 w, 1180 w, 1152 w, 1127 w, 1082 m, 1073 sh, 1051 m, 1014 m, 950 sh, 935 w, 906 sh, 887 s, 835 br, s, 777 sh, 750 w, 722 w, 683 m, 568 sh, 563 sh, 560 s, 528 s, 498 m, 474 m cm^{-1}.

Solution IR in acetone: ν_{CO} at 2050, 2005 cm^{-1}.

Bis(fulvalene)bis(acetonitrile)divanadium(III,III) Bis(hexafluorophosphate), $[(\eta^5:\eta^5\text{-}C_{10}H_8)_2(CH_3CN)_2V_2^{III,III}](PF_6^-)_2\cdot CH_3CN$. In a drybox, a 100-mL round-bottom flask equipped with a side-arm stopcock and a magnetic stir bar was charged with $(C_{10}H_8)_2V_2$ (0.30 g, 0.84 mmol) and $[(C_5H_5)_2Fe^+](PF_6^-)$ (0.54 g, 1.63 mmol). Dry, oxygen-free acetonitrile (15 mL) was added via syringe, and the mixture was stirred for 3 h at room temperature to give a yellow-brown solution. The solution was filtered (Schlenk tube filter), and toluene (65 mL) was added dropwise via syringe while the solution was stirred. A brown, microcrystalline precipitate separated. The flask was chilled to −70°C; the precipitate was isolated by filtration, washed with toluene (1 × 10 mL), and dried in vacuo. The air-sensitive product

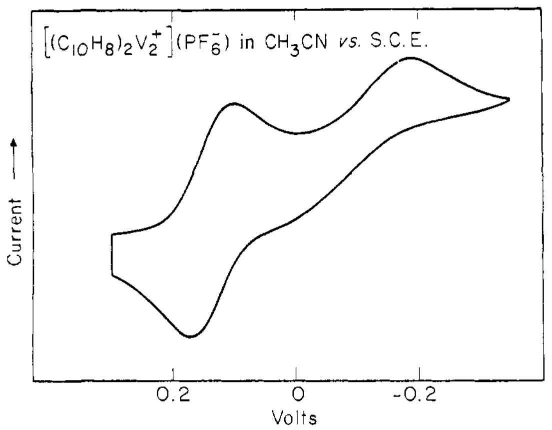


Figure 1. The cyclic voltammogram of bis(fulvalene)divanadium(**II**,**III**) hexafluorophosphate (ca. 10^{-3} M) in acetonitrile, $(Et_4N^+)(ClO_4^-)$ (0.5 M) as supporting electrolyte, referenced to the SCE.

(0.31 g, 0.40 mmol, 48%) was recrystallized from acetonitrile/toluene. Elemental analyses on several crystalline samples failed to establish the stoichiometry of the complex. However, an X-ray crystal structure analysis performed by Day and Fredrich[10] on a crystal grown from acetonitrile/benzene has verified the anticipated stoichiometry and established the structure of the complex.

IR: 3545 br, m, 3125 br, m, 2940 w, 2320 m, 2290 m, 1610 w, 1580 w, 1490 m, 1455 m, 1410 m, 1370 w, 1264 w, 1060 w, 1032 w, 840 br, s, 740 m, 560 s cm^{-1}.

Results and Discussion

Reaction Chemistry. An efficient synthesis has been developed for bis(fulvalene)divanadium utilizing an in situ preparation of the fulvalene dianion.[8] The slow addition of the ligand to a refluxing suspension of $VCl_2·2THF$ in THF furnishes the dark purple, neutral compound in moderate yield. $(C_{10}H_8)_2V_2$ is insoluble in common organic solvents with the exception of pyridine. This compound undergoes oxidation with 1 equiv of ferrocenium hexafluorophosphate in acetone to give the black-purple monocation, and with 2 equiv at −70 °C to give the dark purple dication. Analogous tervalent $(C_5H_5)_2VX$ compounds are prepared by the reaction of vanadocene with alkyl and aryl halides.[11]

$(C_{10}H_8)_2V_2$, like $(C_5H_5)_2V$, is coordinatively unsaturated. Both undergo carbonylation at modest pressures to yield $(C_{10}H_8)_2V_2(CO)_2$ and $(C_5H_5)_2V(CO)$,[12] respectively. Oxidation of $(C_{10}H_8)_2V_2(CO)_2$ with 1 equiv of ferrocenium hexafluorophosphate in THF gives the brown, microcrystalline $[(C_{10}H_8)_2V_2(CO)_2{}^+](PF_6{}^-)$. Attempts to dissolve this compound in polar solvents lead to the immediate loss of CO. The dication $[(C_{10}H_8)_2V_2(CO)_2{}^{2+}](PF_6{}^-)_2$, prepared by oxidizing the neutral dicarbonyl with 2 equiv of ferrocenium in acetone, gives relatively stable orange solutions as long as a CO atmosphere is maintained. However, solid samples redissolve incompletely.

The oxidation of $(C_{10}H_8)_2V_2$ with 2 equiv of ferrocenium hexafluorophosphate in acetonitrile leads to isolation of a bis(acetonitrile) adduct, $[(C_{10}H_8)_2V_2(CH_3CN)_2{}^{2+}](PF_6{}^-)_2·CH_3CN$, which has been characterized by X-ray crystallography.[10] Attempts to prepare a monocationic acetonitrile adduct gave only the bis(acetonitrile) dication and unreacted starting material.

Infrared Spectra. $(C_{10}H_8)_2V_2$ exhibits an infrared spectrum which is very similar to those of $(C_{10}H_8)_2Cr_2$[1] and $(C_{10}H_8)_2Fe_2$.[3] However, the cations have spectra which differ substantially from those of other metallofulvalene cations. (In fact, no obvious trends appear in the infrared spectroscopic behavior of the various binary metallofulvalene complexes studied to date.)

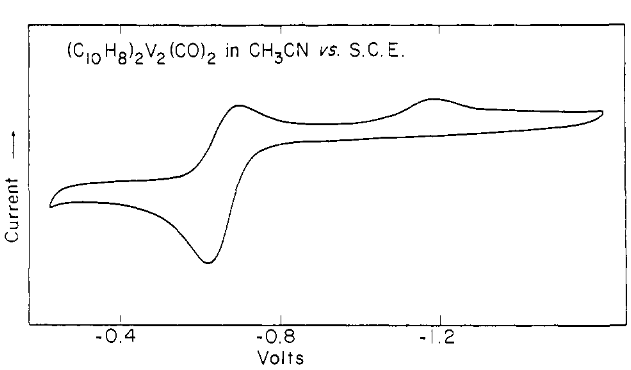


Figure 2. The cyclic voltammogram of bis(fulvalene)dicarbonyldivanadium(**II**,**II**) (ca. 10^{-3} M) in acetonitrile, $(Et_4N^+)(ClO_4^-)$ (0.5 M) as supporting electrolyte, referenced to the SCE.

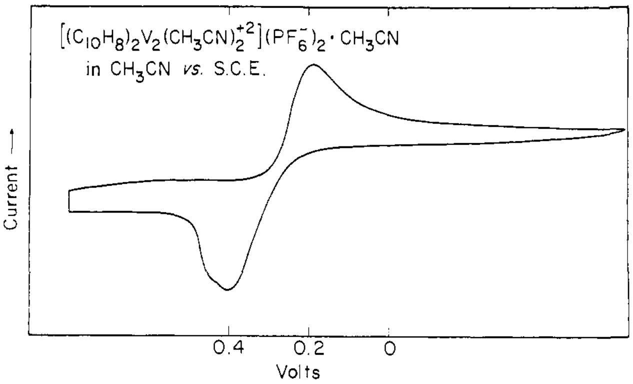


Figure 3. The cyclic voltammogram of bis(fulvalene) bis(acetonitrile)-divanadium(**III**,**III**) bis(hexafluorophosphate)-acetonitrile (ca. 10^{-3} M) in acetonitrile, $(Et_4N^+)(ClO_4^-)$ (0.1 M) as supporting electrolyte, referenced to the SCE.

The bis(fulvalene)dicarbonyldivanadium complexes (z = 0, +1, +2) all exhibit C–O stretching bands in the terminal region of the spectrum. The bands move to higher energy upon oxidizing the neutral compound to the monocation, as would be expected. Subsequent oxidation to the dication does not alter the positions of the bands. An unexpected feature of these spectra is the multiplicity of bands observed. The neutral and monocationic complexes both exhibit four absorptions in this terminal CO region. A possible explanation is that a pair of isomers exist with cis and trans dispositions of the carbonyl groups. The dicarbonyl dication displays the two anticipated absorption bands. The entire infrared spectra of the neutral and monocationic dicarbonyls are generally more complex than that of the dication, particularly in the carbon–carbon stretching region and the low-energy region (which has been correlated with ring-metal tilting bands[3]), further suggesting that two isomers may be present.

The infrared spectrum of $[(C_{10}H_8)_2V_2(CH_3CN)_2{}^{2+}]$ displays the anticipated aromatic C–H stretch as well as the alkyl C–H bands of the acetonitrile methyl group. Two C–N bands appear in the triple-bond region of the spectrum, at higher frequency than in uncoordinated CH_3CN. A similar increase in frequency is observed in $[(C_5H_5)_2V(CH_3CN)_2{}^{2+}](PF_6{}^-)_2$.[13] A band does not appear for the CH_3CN of crystallization (revealed by the X-ray crystallographic data), perhaps due to its being buried under the broad bands of the coordinated nitriles.

Cyclic Voltammetry. The cyclic voltammograms of the $(C_{10}H_8)_2V_2{}^z$, $(C_{10}H_8)_2V_2(CO)_2{}^z$, and $[(C_{10}H_8)_2V_2(CH_3CN)_2{}^{2+}]$ systems are shown in Figures 1–3. The cyclic voltammogram of $[(C_{10}H_8)_2V_2{}^+](PF_6{}^-)$ exhibits one quasi-reversible half-wave and one irreversible wave. The $+2 \rightleftarrows +1$

Table I. Cyclic Voltammetry Data for Metallofulvalene Compounds[a]

compd	$E_{+2\rightleftharpoons+1}$	(ΔE_p[b])	$E_{+1\rightleftharpoons0}$	(ΔE_p[b])	$\Delta E_{1/2}$[c]
$[(C_{10}H_8)_2V_2]^z$	+0.14	(70)	−0.09	(195)	0.23
$[(C_{10}H_8)_2V_2(CO)_2]^z$	−0.66	(75)	−1.18	(highly irreversible)	0.52
$[(C_{10}H_8)_2V_2(CH_3CN)_2]^z$	+0.30	(220)			
$[(C_{10}H_8)_2Cr_2]^z$[1]	−0.18	(82)	−0.84	(77)	0.66
$[(C_{10}H_8)_2Fe_2]^z$[3]	+0.72		+0.13		0.59
$[(C_{10}H_8)_2Co_2]^z$[4]	−0.07		−0.95		0.88
$[(C_{10}H_8)_2Ni_2]^z$[5]	+0.12	(64)	−0.29	(72)	0.41

[a] Potentials given in volts vs. SCE. All samples were run in CH_3CN with the exception of $[(C_{10}H_8)_2Ni_2]^z$, which was run in $(CH_3)_2CO$. [b] $\Delta E_p \equiv$ difference in potentials under anodic and cathodic sweeps, in mV. [c] $\Delta E_{1/2} = (E_{+2\rightleftharpoons+1}) - (E_{+1\rightleftharpoons0})$.

Table II. Magnetic Moments of Metallofulvalenes and Metallocenes (Solid Samples Unless Otherwise Indicated)

compd	μ_{eff}, μ_B	unpaired electrons	ref
$(C_5H_5)_2V$	3.78	3	15
$(C_5H_5)_2V\ I$	2.81	2	12
$(C_{10}H_8)_2V_2$	0	0	*a*
$[(C_{10}H_8)_2V_2^+](PF_6^-)$	0–1.2 solid 0.8–1.3 soln	1	*a*
$[(C_{10}H_8)_2V_2^{2+}](PF_6^-)_2$	0	0	*a*
$(C_5H_5)_2V(CO)$	1.76	1	12
$(C_5H_5)_2V(CO)I$	0	0	12
$(C_{10}H_8)_2V_2(CO)_2$	0	0	*a*
$[(C_{10}H_8)_2V_2(CO)_2^+](PF_6^-)$	1.7	1	*a*
$[(C_{10}H_8)_2V_2(CO)_2^{2+}](PF_6^-)_2$	0.9–2.1	2	*a*
$[(C_{10}H_8)_2V_2(CH_3CN)_2^{2+}]$-$(PF_6^-)_2 \cdot CH_3CN$	3.0 solid 2.9 soln	2	*a*

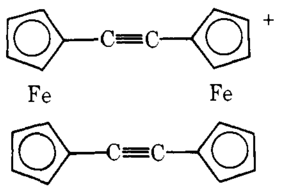
[a] Present study.

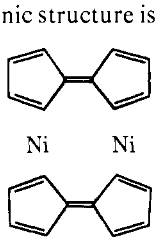
couple occurs at a potential comparable to that in the $(C_{10}H_8)_2Ni_2$ system. However, the $+1 \rightleftharpoons 0$ couple appears at a potential relatively close to that of the first and is highly irreversible, the anodic scan revealing virtually zero current flow. It appears that neutral $(C_{10}H_8)_2V_2$ may be unstable to the conditions of the voltammetry experiment. The compound is unchanged after stirring overnight in 50/50 THF/acetonitrile, perhaps owing to the severe solubility limitations. However, refluxing for 18 h in pure acetonitrile leads to some decomposition. The relatively small $\Delta E_{1/2}$ (separation of the waves) distinguishes this compound from the other bis(fulvalene)dimetal complexes.

The cyclic voltammograms of $[(C_{10}H_8)_2V_2(CH_3CN)_2^{2+}](PF_6^-)_2 \cdot CH_3CN$ and $(C_{10}H_8)V_2(CO)_2$ also display irreversibility. The former exhibits only a single wave with a large value for ΔE_p, the peak-to-peak separation, suggesting that the reduction product undergoes rapid subsequent reaction. This conclusion would be consistent with our inability to prepare a neutral or monocationic bis(acetonitrile) adduct. The dicarbonyl compound exhibits two peaks under the cathodic scan at −0.70 and −1.18 V vs. SCE, but only a single anodic peak at −0.620 V. The irreversibility of the couples is consistent with the observed instability of the dicarbonyl monocation in solution. The ratio of the anodic to cathodic peak currents for the wave centered at −0.66 V is about 1.6:1.0. One possible explanation is that the decomposition products undergo oxidation under the anodic scan.

Magnetic Properties. The magnetic moments of vanadocenes and bis(fulvalene)divanadium complexes are summarized in Table II. While $(C_5H_5)_2V$ has a 15-electron configuration with three unpaired electrons, the fusing of two vanadocene-like moieties in $(C_{10}H_8)_2V_2$ leads to the pairing of these free electrons. Removal of two electrons leaves the diamagnetic dication. Similarly, while $(C_5H_5)_2Cr$ and $[(C_5H_5)_2Cr^+]$ have 16- and 15-electron configurations with two and three unpaired electrons, respectively, $(C_{10}H_8)_2Cr_2$ and $[(C_{10}H_8)_2Cr_2^{2+}]$ both have all electrons paired.[1] Similar behavior is observed in the iron, cobalt, and nickel metallocenes and metallofulvalenes. It bears reiterating that the dication, of the *singly fused* biferrocenium dication, $[(C_{10}H_8)(C_5H_5)_2Fe_2^{2+}]$, is paramagnetic with two unpaired electrons, one on each metallocene moiety.[14] Only with the rigid doubly fused geometry are all electrons paired.

Two possible mechanisms may be operative in the electron pairing in metallofulvalene systems. There may be direct, through-space metal-metal interactions, or a ligand-propagated, superexchange mechanism. On the basis of magnetic susceptibility data, Hendrickson[3] has proposed that relatively weak antiferromagnetic couplings (ca. 400 cm^{-1}), which are considerably weaker (and over greater distances) than formal metal-metal bonds, might lead to diamagnetic behavior in the $[(C_{10}H_8)_2Fe_2^{2+}]$ dication. Alternatively, electron exchange might occur via conjugated bridging ligands, as was suggested by the delocalization in the monocation of [2.2]ferrocenophane-1,13-diyne.[16] The X-ray crystal structure of $(C_{10}H_8)_2Ni_2$[17] indicates that this type of ligand-propagated electron pairing is responsible in part for the diamagnetism of this electron-rich complex. The bond lengths in the complex suggest that the electronic structure is one contributing resonance structure. It appears, however, that other resonance structures also contribute to the ground-state electron distribution.





The diamagnetism of the electron-deficient metallofulvalene complexes, $(C_{10}H_8)_2V_2$ (z = 0, +2) and $(C_{10}H_8)_2Cr_2$ (z = 0, +2), presents an additional difficulty. While similar types of "electron pushing" may generate valence-bond models with even numbers of electrons, the resulting structures are even more electron deficient than the parent metallocenes. Rather than alleviating an unfavorable electron distribution, the deficiency would be exacerbated. The early transition metals also have higher reduction potentials than the later transition metals, mitigating against the type of resonance involving the concomitant oxidation of ligand and reduction of metal which may account in part for the diamagnetism of the electron-rich metallofulvalene complexes. Yet these compounds do not ex-

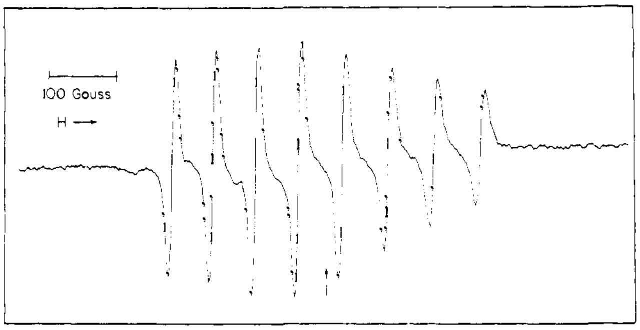
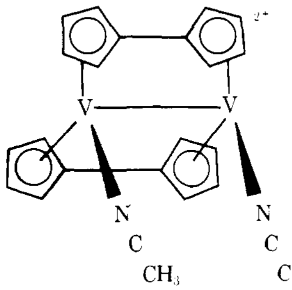
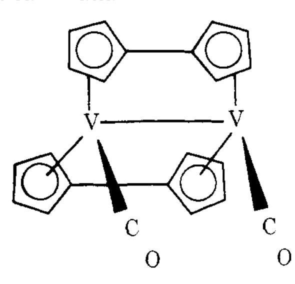


Figure 4. Electron spin resonance spectrum of a saturated solution of $[(C_{10}H_8)_2V_2^+](PF_6^-)$ in acetone at room temperature. Arrow indicates $\langle g \rangle$ 1.978.

hibit an unusual propensity for coordinating solvents in order to reduce the degree of coordinative saturation. $(C_{10}H_8)_2V_2$ and $(C_{10}H_8)_2Cr_2$ do not coordinate THF or DME, nor do their dications coordinate acetone as does the vanadocene cation.[18] The weak antiferromagnetic interactions suggested by Hendrickson, corresponding to incipient bond formation, may in fact be operative in these electron-deficient compounds.

Evidence supporting direct metal-metal interactions in fulvalene complexes of the early transition metals can be found in the magnetic properties of the vanadium carbonyl and acetonitrile adducts. The moment of 2.9 μ_B for $[(C_{10}H_8)_2V_2(CH_3CN)_2^{2+}](PF_6^-)_2{\cdot}CH_3CN$ indicates two unpaired electrons and would be consistent with a structure containing a single V-V bond leading to a 17-electron configuration about each vanadium. This formulation is supported by the crystallographic data,[10] which indicates that the vanadium atoms have slipped toward each other in order to promote direct bonding. The diamagnetism of $(C_{10}H_8)_2V_2(CO)_2$ is also consistent with this bonding model, with 18 electrons about each vanadium.





The dication $[(C_{10}H_8)_2V_2(CO)_2^{2+}](PF_6^-)_2$ is isoelectronic with the bis(acetonitrile) dication and should also bear two unpaired electrons. The observed magnetic moment is low, however, and may result from the tendency of the compound to lose CO, leaving a diamagnetic product. The observation that solid samples of $[(C_{10}H_8)_2V_2(CO)_2^{2+}](PF_6^-)_2$ redissolve only incompletely in acetone supports the view that some type of decomposition may be responsible for the low magnetic moment.

The magnetic moment of $[(C_{10}H_8)_2V_2(CO)_2^+](PF_6^-)$ indicates one unpaired electron with spin-only behavior. The solid-state EPR spectrum ($\langle g \rangle = 2.007$) unfortunately reveals no hyperfine structure, and a solution spectrum is not possible owing to the instability of the complex in solution.

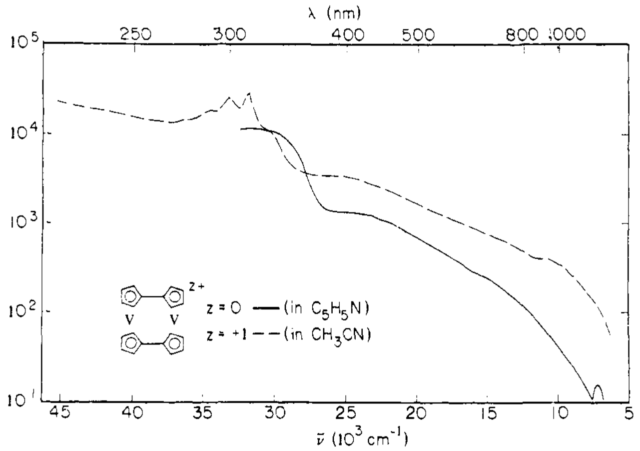


Figure 5. Electronic spectra of $(C_{10}H_8)_2V_2$ (in pyridine, solid line) and $[(C_{10}H_8)_2V_2^+](PF_6^-)$ (in acetonitrile, dashed line).

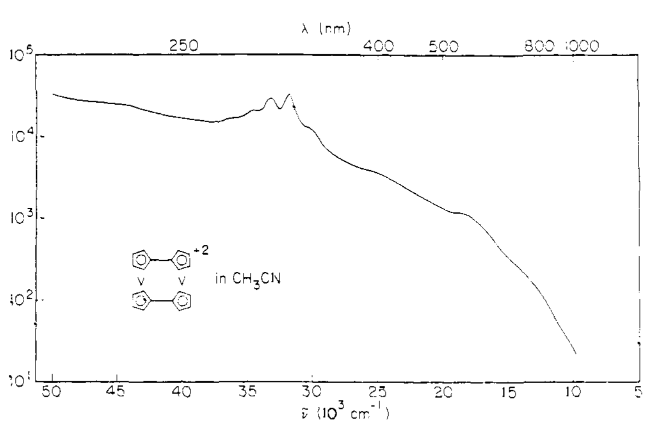


Figure 6. Electronic spectrum of $[(C_{10}H_8)_2V_2^{2+}](PF_6^-)_2$ (in acetonitrile).

The magnetic moment of $[(C_{10}H_8)_2V_2^+](PF_6^-)$, on the other hand, is consistently low. The fact that solid samples exhibit only small susceptibilities suggests that there may be intermolecular antiferromagnetic coupling in the solid state.

An EPR spectrum has been obtained on an acetone solution of $[(C_{10}H_8)_2V_2^+](PF_6^-)$ (see Figure 4). The spectrum exhibits eight hyperfine lines. For a delocalized system, one would expect to observe 15 lines due to splitting of the electron spin by two equivalent vanadium (^{51}V, 99.5%, $I = 7/2$) nuclei. Such a 15-line pattern is observed for the $[(C_{10}H_8)_2Co_2^+](PF_6^-)$ monocation.[4b] This eight-line pattern suggests that $[(C_{10}H_8)_2V_2^+](PF_6^-)$ may be a trapped valence complex, with the odd electron localized on one vanadium center with a residence time of at least 10^{-7}-10^{-8} s. This spectrum is in sharp contrast to other data indicating that the mixed-valence compounds of other bis(fulvalene)dimetal systems are delocalized, fractionally valent molecules. There is no obvious explanation for this discrepancy.

Electronic Absorption Spectra. The electronic absorption spectra of the new binary metallofulvalene compounds are shown in Figures 5 and 6. The spectra differ substantially from those of the parent metallocenes and metallocene cations in multiplicity and intensity of the bands. The position of the bands for these metallofulvalene complexes are summarized in Table III.

It can be seen from Figures 5 and 6 that the spectra of $[(C_{10}H_8)_2V_2^+](PF_6^-)$ and $[(C_{10}H_8)_2V_2^{2+}](PF_6^-)_2$ in ace-

Table III. Electronic Absorption Bands (nm) for Metallofulvalenes

$(C_{10}H_8)_2V_2$ in pyridine	1390 (ϵ 16), 625 sh (295), 455 sh (1040), 423 sh (1280), 395 (1370), 328 sh (10 900), 318 (11 700)
$[(C_{10}H_8)_2V_2^+](PF_6^-)$ in CH_3CN	900 (ϵ 412), 690 w sh (706), 388 sh (3470), 326 sh (11 400), 314 (28 400), 300 (25 300), 290 (18 300), 278 sh (14 500), 243 w sh (17 100)
in $(CH_3)_2CO$	985 sh (ϵ 23), 855 sh (50), 690 sh (330), 587 (630), 465 w sh (790), 395 (6900)
$[(C_{10}H_8)_2V_2^{2+}](PF_6^-)_2$ in CH_3CN	775 w sh (ϵ 148), 530 sh (1170), 380 sh (4210), 328 sh (13 000), 314 (33 500), 300 (29 200), 290 (21 000), 280 sh (16 700), 220 sh (25 200)
in $(CH_3)_2CO$	975 sh, 740 sh, 525 sh, 380 sh, 325 sh
$(C_{10}H_8)_2V_2(CO)_2$ in CH_3CN	1010 (ϵ 9), 760 sh (120), 640 sh (210), 445 (3600), 380 (3400), 285 (4200), 245 (4900)
in $(CH_3)_2CO$	710 sh (ϵ 220), 570 w sh (800), 450 (10 500), 385 (10 000)
$[(C_{10}H_8)_2V_2(CO)_2^{2+}]$-$(PF_6^-)_2$ in CH_3CN	1010 w sh (ϵ 30), 490 sh (900), 380 sh (2300), 325 sh (7000), 312 (11 000), 300 (11 000), 287 (10 000), 240 sh (13 000)
in $(CH_3)_2CO$	990 w sh (30), 690 w sh (300), 580 w sh (620), 385 sh (5700), 320 (14 500)
$[(C_{10}H_8)_2V_2(CH_3CN)_2^{2+}]$-$(PF_6^-)_2 \cdot CH_3CN$ in CH_3CN	1250 w sh (ϵ 82), 920 (145), 525 (2300), 390 sh (2500), 327 sh (7700), 314 (11 400), 300 (11 800), 287 (11 400), 213 (43 000)
in $(CH_3)_2CO$	1000 sh (ϵ 94), 525 (1550), 390 (5000)

tonitrile are virtually identical, with minor adjustments in the low-energy region. A series of peaks occur clustered about 300 nm. The large extinction coefficients of these bands, coupled with their sharpness and high energy, suggests that they may be charge-transfer bands. In addition, the band structure in the high-energy region is strikingly similar for $[(C_{10}H_8)_2V_2(CH_3CN)_2^{2+}](PF_6^-)_2$ in acetone and acetonitrile, for $[(C_{10}H_8)_2V_2(CO)_2^{2+}](PF_6^-)_2$ in acetone and acetonitrile, and for $[(C_{10}H_8)_2Cr_2^{2+}](PF_6^-)_2$[19] in acetonitrile. The spectrum of the vanadium dication $[(C_{10}H_8)_2V_2^{2+}](PF_6^-)_2$ does not change substantially in acetone; however, that of the corresponding monocation is significantly different in acetone than in acetonitrile, particularly in the high-energy visible region.

These spectra suggest that $[(C_{10}H_8)_2V_2^+](PF_6^-)$ and $[(C_{10}H_8)_2V_2^{2+}](PF_6^-)_2$ may be unstable in acetonitrile with respect to formation of $[(C_{10}H_8)_2V_2(CH_3CN)_2^{2+}]$. The inability to prepare a bis(acetonitrile) monocation indicates that the $[(C_{10}H_8)_2V_2^+]$ monocation may disproportionate in acetonitrile. However, these results are inconsistent with the differences in behavior between $[(C_{10}H_8)_2V_2^+]$ and $[(C_{10}H_8)_2V_2(CH_3CN)_2^{2+}]$ under the cyclic voltammetry experiment. In solution $[(C_{10}H_8)_2V_2^{2+}]$ may coordinate both acetone and acetonitrile to give systems with bent geometries and similar electronic configurations. $[(C_{10}H_8)_2V_2^+](PF_6^-)$ does *not* disproportionate or oxidize in acetone to give a dication and may have a planar geometry and a different configuration.

The similarities in the spectra of $[(C_{10}H_8)_2V_2(CH_3CN)_2^{2+}]$ and $[(C_{10}H_8)_2V_2(CO)_2^{2+}]$ suggest that the geometries and electronic structures in these two isoelectronic bent metallofulvalene complexes are very similar. An alternative explanation is that the dicarbonyl complex loses CO in solution and subsequently coordinates solvent molecules. The stability of acetone solutions of $[(C_{10}H_8)_2V_2(CO)_2^{2+}]$ depends upon maintaining a CO atmosphere.

The absence of a strong absorption band in the near-infrared region of the spectrum for $[(C_{10}H_8)_2V_2^+](PF_6^-)$ (in either acetone or acetonitrile) is significant. Bands in this region have been observed for the monocations $[(C_{10}H_8)_2Cr_2^+]$,[1] $[(C_{10}H_8)_2Fe_2^+]$,[2,3] $[(C_{10}H_8)_2Co_2^+]$,[4] and $[(C_{10}H_8)_2Ni_2^+]$,[5] as well as many biferrocenyl systems.[3,16-20] Near-infrared bands in the spectra of mixed-valence compounds have been assigned to intervalence transfer transitions on the basis of theory by Hush;[21] however, the applicability of this theory to the mixed-valence monocations of binary metallofulvalene complexes has been questioned, due to the apparent delocalized nature of the ground states.[2] Loew et al.[22] have performed extended Hückel calculations on the $(C_{10}H_8)_2Fe_2$ systems and have suggested that low-energy d-d transitions may be responsible for the observed near-infrared bands in the spectrum of the monocation. In addition, near-infrared bands appear in the spectra of all of the following compounds: $(C_{10}H_8)_2V_2$ (0, +2), $(C_{10}H_8)_2V_2(CO)_2$, $[(C_{10}H_8)_2V_2(CH_3CN)_2^{2+}](PF_6^-)_2 \cdot CH_3CN$, $(C_{10}H_8)_2Cr_2$ (0, +2),[1] $(C_{10}H_8)_2Co_2$,[19] and $(C_{10}H_8)_2Ni_2$ (0, +2).[5] Although these bands are generally the most intense in the mixed-valence derivatives of these compounds, the presence of seemingly analogous near-infrared bands in other derivatives suggests that they are *not* intervalence transfer transitions associated with electron transfer from one localized metal center to another. Rather, a delocalized, fractionally valent system is more consistent with the accumulated data. These near-infrared absorption bands may then be attributable to low-energy d-d transitions generated by the interaction and splitting of two sets of metallocene-like orbitals brought together by the bridging ligand system. The degree of interaction between the constituent halves of the metallofulvalene unit is underscored by the observation that the spectra of these metallofulvalene complexes are qualitatively different from those of the parent metallocenes.

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One-Electron Reduction of Ferrideuteroporphyrin IX and Reaction of the Oxidized and Reduced Forms with Chlorinated Methyl Radicals

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Abstract: α-Hydroxyisopropyl radicals prepared by fast electron irradiation of aqueous solutions containing 2-propanol and acetone were found to reduce monomeric ferrideuteroporphyrin to ferrodeuteroporphyrin with a rate constant of 3.7×10^8 $M^{-1}\ s^{-1}$. Relaxation of the coordination sphere is found to proceed with a rate constant $k \geq 5 \times 10^5\ s^{-1}$. Irradiation of such solutions in the added presence of various concentrations of CCl_4, $CHCl_3$, or CH_2Cl_2 enabled studies to be made of the reactions of ferri- and ferrodeuteroporphyrin with chlorinated methyl radicals. No reaction of ferrideuteroporphyrin with $\cdot CCl_3$ could be detected ($k \leq 10^6\ M^{-1}\ s^{-1}$). For ferrodeuteroporphyrin it appears that a rapid reaction ($k = (2 \pm 1) \times 10^9\ M^{-1}\ s^{-1}$) gives a complex ($DPFe^{II}\text{-}\cdot CH_{3-n}Cl_n$) which undergoes further reaction as shown by transient spectral modifications. These results suggest that ferrous cytochrome P450 is likely to react rapidly with chlorinated radicals. A model for the toxicity and detoxification of CCl_4 is proposed.

Introduction

Iron porphyrins are a matter of continuing interest owing to their involvement in fundamental biological processes.[2] Their most recently recognized role is in relation to the cytochrome P450 functions,[3] one of which involves the reduction of carbon tetrachloride, a hepatotoxic molecule, resulting in the formation of trichloromethyl radicals which are responsible for lethal cellular damages.[4,5] Also, under anaerobic reducing conditions, carbon tetrachloride and other polyhalogenated compounds react with cytochrome P450 leading to new derivatives[6,7] assigned to carbene complexes.[7] The formation of these derivatives involves a two-electron reduction of the halogenated molecule and could correspond to a further step of its metabolism. Recently, dichlorocarbene complexes of ferrous porphyrins considered as models for these cytochrome P450 derivatives have been characterized.[8,9] It has been shown that these complexes are obtained in solution when ferrous porphyrins are allowed to react with carbon tetrachloride according to the overall reaction[8]

$$\begin{aligned} 3\ \text{ferroporphyrins} + 1\ CCl_4 \rightarrow 2\ &\text{ferriporphyrins} \\ &+ 1\ \text{dichlorocarbeneferroporphyrin} \end{aligned}$$

The limiting step was attributed[8] to the reduction of carbon tetrachloride by the ferroporphyrin leading to trichloromethyl radicals ($k \simeq 10^2\ M^{-1}\ s^{-1}$). Moreover, the stoichiometry of the above reaction implies that no leaking of intermediate species occurs, which suggests a fast scavenging of the $\cdot CCl_3$ radicals by the porphyrin.

The present paper deals with a pulse radiolysis study of the fast reaction of iron porphyrins, especially the ferrous form, with $\cdot CCl_3$, $\cdot CHCl_2$, and $\cdot CH_2Cl$ radicals. This approach has required the use of an efficient system for reduction of the ferriporphyrin to the ferrous state with concomitant $\cdot CCl_3$, $\cdot CHCl_2$, or $\cdot CH_2Cl$ radical formation. Therefore, we also present a study of the reduction of the ferriporphyrin by α-hydroxyisopropyl radicals.

The experiments have been performed with ferrideuteroporphyrin IX chloride (deuterohemin) in 2-propanol–phosphate buffer (pH 7.2) mixture, where this porphyrin was found to be a monomer. The only previous data on the reduction of simple monomeric porphyrins appear to have been on protohemin IX at alkaline pH,[10] on hemin *c*,[11] and on protohemin IX intercalated into sodium dodecyl sulfate micelles.[12]

Experimental Section

Materials. Ferrideuteroporphyrin IX chloride (deuterohemin) was prepared from ferriprotoporphyrin IX chloride via the resorcinol melt procedure[13] and recrystallized three times as follows. Crude deuterohemin (4 g) was dissolved in pyridine (40 mL). The solution was then filtered and added to a boiling NaCl saturated 90% acetic acid solution (550 mL) containing 35 mL of concentrated HCl. After cooling and standing for 24 h, the deuterohemin crystals were twice washed with 50% acetic acid and three times with water. Washing with ethanol and ethyl ether was performed after the last crystallization sequence. The crystals were then dried under vacuum. The purified deuterohemin moves as a single spot using polyamide 6 TLC plates (Macherey-Nagel) according to a procedure modified from Lamson et al.[14] Sodium dithionite was purchased from Merck. 2-Propanol was purified according to Baxendale and Mellows[15] to remove aldehydic and ketonic impurities. Carbon tetrachloride and methylene chloride (Baker BAR) were used without further purification. Chloroform was three times distilled before use.

Preparation of Deuterohemin Solutions. Deuterohemin being soluble only at alkaline pH, the following procedure was used to prepare neutral alcoholic solutions. Deuterohemin was dissolved in 1.5 mL of NaOH (0.1 M). The solution was diluted to 15 mL, and then 25 mL of KH_2PO_4 (10^{-2} M) was added followed by 50 mL of 2-propanol. The resulting solution was adjusted to 100 mL with phosphate buffer

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