infrared spectrum of the final products showed the presence of ClF, $FClO_2$, and $TeClF_5$.

Tellurium Chloride Pentafluoride. The identity of the material was established by comparison of its ^{19}F nmr spectrum with that reported in the literature.[1] $TeClF_5$ is a colorless liquid, bp 13.5 ± 1.0°, mp (under its own vapor) −28 ± 1.0°. It is unreactive toward mercury at room temperature and can be kept in dry metal and glass apparatus. The infrared spectrum of the gas in the range 4000–250 cm^{-1} showed several absorptions with the most prominent ones occurring at 727 (vs), 410 (s), 317 (vs), and 259 (s) cm^{-1} in substantial agreement with Peacock, *et al.*,[1] who reported very strong bands at 726 and 317 cm^{-1}. A detailed analysis of the vibrational spectrum of $TeClF_5$ is in progress.[5]

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Registry No. $TeClF_5$, 21975-44-0; ClF, 7790-89-8; TeF_4, 15192-26-4; $TeCl_4$, 10026-07-0; TeO_2, 7446-07-3.

(5) W. V. F. Brooks, M. Eshaque, C. Lau, and J. Passmore, to be submitted for publication.

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Sign of the Electric Field Gradient in Dioxidized Biferrocenylene

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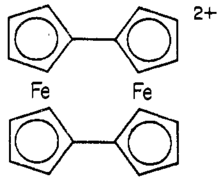
Iron-57 Mossbauer spectroscopy shows that ferrocene has a quadrupole splitting of 2.4 mm/sec and the ferricenium ion a splitting ranging from 0.0 to 0.08 mm/sec.[2-4] Collins[5] determined that for ferrocene the electric field gradient V_{zz} is *positive.* A recent[6] ligand field treatment of ferrocene shows that ferrocene has the configuration $(a_{1g})^2(e_{2g})^4$. If the contributions to the field gradient for the two different types of electrons are taken as $V_{zz}(a_{1g}) = -{}^4/_7\langle r^{-3}\rangle$ and $V_{zz}(e_{2g}) = {}^4/_7\langle r^{-3}\rangle$, then ferrocene is calculated to have a relatively large *positive* field gradient in agreement with experimental results.[5] The collapse in quadrupole splitting observed for ferricenium ion is (qualitatively) explicable in terms of the loss of an e_{2g} electron.

In our studies[7-9] of mixed-valence biferrocene-like compounds it has been found[9] that dioxidized biferrocenylene, I, which formally contains two Fe(III) ($S = {}^1/_2$) centers, has a large quadrupole splitting of 2.950 (1) mm/sec (PF_6^- salt) at 298°K. Because we are very interested in electron exchange in mixed-valence $[Fe^{II}Fe^{III}]$ and related $[Fe^{III}Fe^{III}]$ materials, this unusally large quadrupole splitting for an iron(III) metallocene prompted a determination of the sign of the field gradient for dioxidized biferrocenylene. The results of this study are reported in the present paper.



I

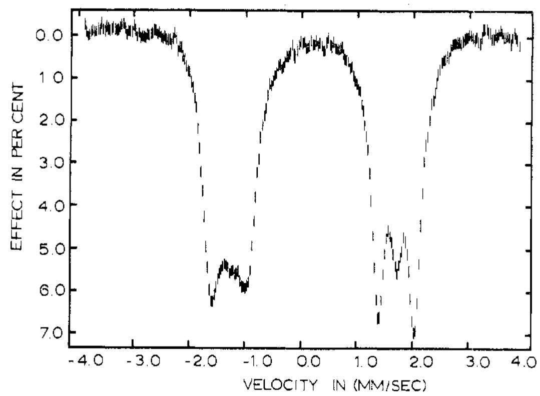


Figure 1. Magnetically perturbed (27-kG longitudinal field) ^{57}Fe Mossbauer spectrum for a sample of biferricenylenium bis(hexafluorophosphate) at 4.2°K. The velocity scale is referenced to Co in Cu source.

Results and Discussion

A sample of the PF_6^- salt of I was prepared and analyzed. *Anal.* Calcd: C, 36.51; H, 2.45; Fe, 16.98. Found: C, 36.92; H, 2.48; Fe, 17.22. The 4.2°K magnetically *unperturbed* ^{57}Fe Mossbauer spectrum for this sample gives an isomer shift of 0.573 (2) mm/sec (*vs.* metallic iron) and a quadrupole splitting of 2.951 (2) mm/sec. In a previous paper[9] we proposed that the large quadrupole splitting in dication I is the result of the delocalization of the e_{2g} ($d_{x^2-y^2}$ and d_{xy} in D_{5d} symmetry) electrons throughout the molecule *via* an electron-exchange interaction between the two Fe(III) centers. The presence of such an exchange interaction has been substantiated by the observation[7] that dication I is *diamagnetic.* The interaction of the Fe(III) e_{2g} electrons could lead to a reduction in $V_{zz}(e_{2g})$ due to a decrease in $\langle r^{-3}\rangle$ for these electrons. If $V_{zz}(e_{2g})$ became very small, then the field gradient at the Fe(III) centers would be determined by the two $a_{1g}(d_{z^2})$ electrons and the field gradient would be *negative* and of a magnitude comparable to ferrocene.

The 4.2°K magnetically (27-kG longitudinal field) *perturbed* ^{57}Fe Mossbauer spectrum for the PF_6^- salt of I is shown in Figure 1. It is clear from this spectrum that the electric field gradient at the Fe(III) centers is *negative* as the above model predicted. A second piece of information is potentially available from such a spectrum. This is the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, which would give us a measure of how strongly one iron atom perturbs a second. Unfortunately, it has been shown[10] that an accurate determination of η for large quadrupole splittings from the magnetic spectrum is not easily made. From a comparison of various simulated magnetic spectra[10] it is possible to deduce that η is less than ~0.4 for our case. This probably does not tell us much about the extent of

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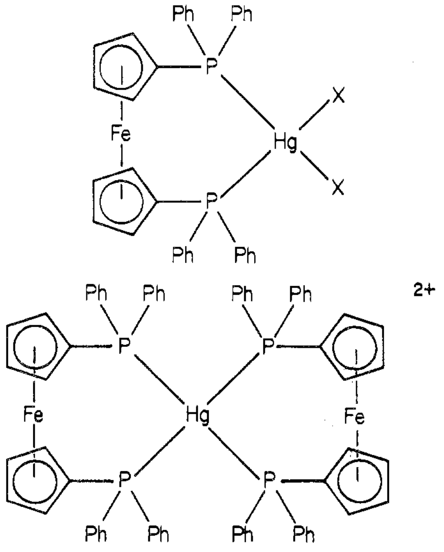
Fe–Fe interaction. If the diamagnetic nature of I is analyzed in terms of an exchange interaction (*i.e.*, $J\hat{S}_1\cdot\hat{S}_2$) between the two $S = {}^1/_2$ Fe(III) centers, the exchange parameter J is greater than ~400 cm^{-1}. This is the case because there is no appreciable population of the triplet state ($S' = S_1 + S_2 = 1$) for I up to 300°K.

The effect of lattice contributions to the electric field gradient in I has not been included in the above analysis. It is possible that the introduction of a nearby $\text{Fe}(C_5H_5)^+$ moiety (the positive charge is most certainly *not* localized on the iron atom) is partially the cause of the large negative field gradient at the other Fe(III) in cation I. The range of quadrupole splittings for the ferricenium cation as a function of the anion is very small (0–0.08 mm/sec), but perhaps this could be attributed to the greater distances involved. However, we have just reported[11] that the quadrupole splittings observed for the two species



are essentially unchanged from that observed for ferrocene, which can be taken as evidence as to the negligible influence of a partial positive charge at a distance of ~4.0 Å or greater.

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Registry No. Biferricenylenium bis(hexafluorophosphate), 51472-07-2.

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Transition Metal π Complexes. III. Reactions of Benzocycloheptatriene with the Group VIb Metal Carbonyls[1]

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Although transition metal π complexes of single and multiple ring systems are numerous,[2-7] analogous derivatives of the fused six-seven-membered carbocyclic benzocycloheptatriene (bcht) are unknown except for the two iron carbonyls $\text{Fe(CO)}_3\text{(bcht)}$ and $[\text{Fe(CO)}_3\text{(bcht)}]^+$.[8] This report describes results of an exploratory investigation of the reactions of bcht with the group VIb metal carbonyls and selected derivatives.

Experimental Section

Microanalyses were performed by M-H-W Laboratory, Garden City, Mich. Infrared spectra were recorded on a Model 621 Perkin-Elmer spectrometer. Proton nmr spectra were taken on a Varian Associates Model T-60 machine in chloroform-*d* with tetramethylsilane as an internal standard; carbon-13 spectra were obtained on a Jeol Model PFT-100 instrument. Mass spectra were recorded on a Varian Associates Model CH7 spectrometer. Dry nitrogen was used routinely for deaeration of solvents, maintenance of an inert atmosphere over reaction mixtures, and admission to evacuated vessels.

A mixture of 1,2- and 3,4-benzocycloheptatriene was synthesized according to a literature method beginning with 5-phenylvaleric acid.[9] The reactive intermediates (diglyme)Mo(CO)_3,[10] $(\text{CH}_3\text{CN})_3\text{Cr(CO)}_3$,[11] and $(\text{CH}_3\text{CN})_3\text{W(CO)}_3$[11] were also prepared by known procedures.

$\mathbf{C_{11}H_{10}Cr(CO)_3}$. Equimolar amounts of chromium hexacarbonyl and bcht were allowed to react in ethylcyclohexane at 132° for 66 hr. The resulting yellow solution was cooled at −78° for 3 hr and the crude yellow solid was collected in 30% yield (yield was depressed because of the continuous loss of Cr(CO)_6 which sublimed from the reaction solution). Sublimation (70°, 0.05 mm) produced pure, bright yellow crystals, mp 73–74°; ν(CO) 1979, 1911 cm^{-1} in hexane. *Anal.* Calcd for $\text{C}_{11}\text{H}_{10}\text{Cr(CO)}_3$: C, 60.43; H, 3.62; Cr, 18.69; O, 17.25; mol wt 278. Found: C, 59.99; H, 3.56; Cr, 18.30; O, 18.85; mol wt 300 (vpo in CHCl_3 at 37°) and 278 (mass spectrum). KBr infrared spectra (cm^{-1}): 3070 (w, br), 3045 (w, br), 2967 (w), 2900 (w), ν(CO) bands above, 1462 (sh), 1455 (m), 1428 (s), 1413 (s), 1380 (sh), 1371 (m), 1338 (w), 1318 (m), 1228 (m), 1195 (w), 1182 (w), 1163 (sh), 1157 (s), 1113 (sh), 1082 (m), 1043 (w), 1028 (m), 967 (m), 950 (m), 928 (m), 899 (m), 870 (s), 847 (s), 818 (s), 792 (s), 750 (s), 718 (w), 674 (sh), 668 (s). Carbon-13 spectra (ppm downfield from TMS): 34.3, 91.5, 94.4, 95.1, 105.8, 109.8, 128.3, 130.3, 131.6, 132.4, 234.1.

When Mo(CO)_6, (diglyme)Mo(CO)_3, W(CO)_6, or $(\text{CH}_3\text{CN})_3\text{W(CO)}_3$ was allowed to react with bcht in both hydrocarbon solvents or neat at temperatures between 25 and 160°, no isolable products could be obtained. Monitoring the metal–carbonyl stretching region indicated only very weak molybdenum product bands and complete decomposition with tungsten.

Results and Discussion

In order to establish methods that might be successful in the synthesis of benzocycloheptatriene complexes, several cycloheptatriene (cht) reactions were attempted with various group VIb metal carbonyl compounds. Those that proved most effective were (1) direct CO replacement in the hexacarbonyls by heating the reaction mixture in hydrocarbon solvents at temperatures between 100 and 132°, (2) replacement of labile groups, CH_3CN or diglyme, in their tricarbonyls in hydrocarbon solvents at temperatures from 60 to 100°, and (3) replacement of labile groups by heating the intermediate with cht in the absence of solvent.

Although the three methods produced the same cht metal

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