1400 cm^{-1} and a weaker band at 2100 cm^{-1}. The reaction of $CSCl_2$ and $Pt(PPh_3)_2(C_2H_4)$ gave a green solid with bands due to the PPh_3 ligand and a yellow solid which had a strong band at 1400 cm^{-1} and a weak band at 2105 cm^{-1}. The reaction of $CSCl_2$ with $Pt(PPh_3)_2(C_2H_4)$ in the presence of halide acceptor BCl_3 in benzene gave a brown solid with a very intense ir band at 1400 cm^{-1} and a weaker band at 2100 cm^{-1}. This latter band which may be due to Pt–H stretching arising from hydrolysis of a Pt(II)–CS complex was diminished in intensity when stringent procedures were adopted to exclude water and oxygen, but a product completely free from the 2100-cm^{-1} band could not be prepared. We suggest that the product with the intense band at 1400 cm^{-1} is $[Pt(PPh_3)_2(CS)Cl]^+$, but attempts to recrystallize this compound in various solvents and in the presence of PF_6^- and BPh_4^- resulted in the disappearance of the ν(CS) band at 1400 cm^{-1} and evolution of hydrogen sulfide. Cationic platinum(II) carbonyl complexes are highly susceptible to nucleophilic attack at CO,[10] and the CS ligand is more readily attacked by nucleophiles than the CO ligand.[1,11]

Experimental Section

Thiophosgene from Aldrich Chemical Co. was used without further purification. Previously reported procedures were used to prepare $Ir(PPh_3)_2(N_2)Cl$, $Ir(CO)(PPh_3)_2Cl$, $Rh(PPh_3)_3Cl$, $[Rh(CO)_2Cl]_2$, $[Rh(CO)_2Cl]_2$, $[Rh(CO)_2(PPh_3)Cl]_2$, $Rh(PPh_3)_2(CO)Cl$, $Pt(PPh_3)_3$, $Pt(PPh_3)_2(C_2H_4)_2$, and $[Ir(PPh_3)_2(CO)(CH_3CN)]PF_6$.[12] Benzene was distilled from P_4O_{10} and stored over molecular sieves. All reactions were conducted in a nitrogen atmosphere. Infrared spectra were obtained in Nujol and hexachlorobutadiene (hcb) mulls with a Perkin-Elmer Model 621 spectrophotometer. Only frequencies other than those due to the PPh_3 ligand are reported herein, and frequencies reported herein are for Nujol mulls except in the 1370-cm^{-1} region where hcb mulls were employed. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.

Trichlorobis(triphenylphosphine)thiocarbonyliridium(III), $[Ir(PPh_3)_2(CS)Cl_3]$. Thiophosgene (0.18 ml, 2.3 mmol) was added to 720 mg (0.93 mmol) of $Ir(PPh_3)_2(N_2)Cl$ in 30 ml of benzene. The tan solid which formed was recrystallized twice from dichloromethane–ethanol to give 680 mg (80%) of pale-yellow crystals, mp 193° dec. *Anal.* Calcd for $IrC_{37}H_{36}Cl_3P_2S{\cdot}CH_2Cl_2$: C, 47.93; H, 3.38; Cl, 18.6; S, 3.36. Found: C, 47.45; H, 3.52; Cl, 20.5; S, 3.45. ν(CS) 1368 (hcb) (vs); ν(Ir–Cl) 308 (w), 273 (w), 282 (sh) cm^{-1}.

Dichlorobis(triphenylphosphine)thiocarbonylcarbonyliridium(III) Hexafluorophosphate, $[Ir(PPh_3)_2(CO)(CS)Cl_2]PF_6$. A solution of 668 mg (0.72 mmol) of $[Ir(PPh_3)_2(CO)(CH_3CN)]PF_6$ and 0.08 ml (1.0 mmol) of thiophosgene in 20 ml of dichloromethane was stirred for 20 min. The solvent was evaporated under reduced pressure to 5 ml and 40 ml of diethyl ether was added to precipitate 630 mg of pale-white solid. The product was recrystallized from dichloromethane–diethyl ether to give 480 mg (67%) of bone-white crystals, mp 135° dec: ν(CS) 1409 (vs); ν(CO) 2127 (s); $\nu(PF_6)$ 842 (vs); ν(Ir–Cl) 305 (w), 295 (w) cm^{-1}. *Anal.* Calcd for $IrC_{38}H_{30}OCl_2F_6P_3S$: C, 45.46; H, 3.01; Cl, 3.19; S, 7.07. Found: C, 45.61; H, 2.98; Cl, 3.62; S, 6.77.

Trichlorobis(triphenylphosphine)thiocarbonylrhodium(III), $[Rh(PPh_3)_2(CS)Cl_3]$. Thiophosgene (0.08 ml, 1.0 mmol) was added to 463 mg (0.50 mmol) of $Rh(PPh_3)_3Cl$ in 15 ml of benzene. The reaction mixture was stirred at room temperature for 1 hr. The red-brown solid (252 mg, 65%) was recrystallized from dichloromethane–benzene and washed with diethyl ether, mp 141° dec: ν(CS) 1364 (hcb) (vs) (lit. value 1362 cm^{-1} (C_6H_6))[8]; ν(Rh–Cl) 295 (w), 282 (w), 270 (w) cm^{-1}. *Anal.* Calcd for $RhC_{37}H_{30}Cl_3P_2S$: C, 57.14; H, 3.88; Cl, 13.68; S, 4.11. Found: C, 56.92; H, 3.63; Cl, 13.50; S, 4.98.

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Registry No. **1A**, 51540-60-4; **2**, 51540-62-6; **1B**, 51607-40-0; $CSCl_2$, 463-71-8; $Ir(PPh_3)_2(N_2)Cl$, 15695-36-0; $[Ir(PPh_3)_2(CO)(CH_3CN)]PF_6$, 51540-63-7; $Rh(PPh_3)_3Cl$, 14694-95-2.

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Convenient Synthesis of Tellurium Chloride Pentafluoride

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Received March 6, 1974 AIC40153+

Tellurium chloride pentafluoride was first prepared in low yield by Fraser, Peacock, and Watkins[1] by the reaction of fluorine and tellurium tetrachloride. More recently[2] $TeClF_5$ was produced as one of the products of the reaction of chlorine monofluoride and bis(perfluoroethyl) telluride and ditelluride. We wish to report the convenient synthesis of $TeClF_5$ in good yield, by the reaction of chlorine monofluoride with TeF_4, $TeCl_4$, or TeO_2.

Experimental Section

Apparatus and Materials. Techniques and apparatus are described in ref 3. Te, TeF_6, $TeCl_4$, TeO_2, and ClF were used without further purification. Tellurium tetrafluoride was prepared by the reaction of tellurium hexafluoride and tellurium metal[4] in a Monel vessel at 160–170° for 3 days. Crystalline tellurium tetrafluoride product was sublimed into the cooled top of the Monel reactor.

Tellurium Tetrafluoride and Chlorine Monofluoride. Chlorine monofluoride (7.9 mmol) was condensed in small aliquots onto tellurium tetrafluoride (3.54 mmol) in a Kel-F vessel. The reactants were warmed to room temperature after each addition and finally left overnight. Solid TeF_4 was consumed; the reaction product was a yellow liquid. Materials volatile at −78° were condensed from the reaction vessel for about 1 min and shown to contain ClF, $TeClF_5$, SiF_4, and fluorocarbons. The involatile fraction was clear liquid $TeClF_5$ (2.76 mmol).

Tellurium Tetrachloride and Chlorine Monofluoride. In a typical experiment chlorine monofluoride (31 mmol) was condensed in small aliquots onto $TeCl_4$ (5.5 mmol). The reactants were warmed to room temperature after each addition. Liquid ClF reacted with $TeCl_4$ with bubbling. The yellow liquid product consisted of a mixture of $TeClF_5$, chlorine, and impurities such as SiF_4. The ^{19}F nmr[1] of the product showed that the only tellurium species present was $TeClF_5$. Relatively pure material was obtained by condensing out about two-thirds by volume of the liquid product. The last traces of chlorine were removed by agitation with mercury giving 4.6 mmol of clear colorless liquid $TeClF_5$. The volatile products of reactions, in which less than a stoichiometric amount of ClF had been added, were examined by infrared and ^{19}F nmr. Only $TeClF_5$ was detected by these techniques, although chlorine was also present. X-Ray powder photographs of the solid showed the presence of TeF_4, but its mass spectrum showed peaks attributable to both $TeCl_4$ and TeF_4 molecular ions and fragments.

Reaction of Tellurium Dioxide and Chlorine Monofluoride. In a typical reaction chlorine monofluoride (39.5 mmol) was condensed in small aliquots onto TeO_2 (3.36 mmoles). After the first additions a deep red liquid (probably ClO_2) and oxygen were formed. The

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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.

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Sign of the Electric Field Gradient in Dioxidized Biferrocenylene

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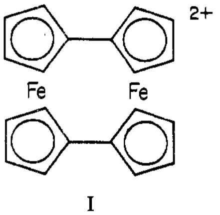
Iron-57 Mossbauer spectroscopy shows that ferrocene has a quadrupole splitting of 2.4 mm/sec and the ferricenium ion a splitting ranging from 0.0 to 0.08 mm/sec.[2-4] Collins[5] determined that for ferrocene the electric field gradient V_{zz} is *positive*. A recent[6] ligand field treatment of ferrocene 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.



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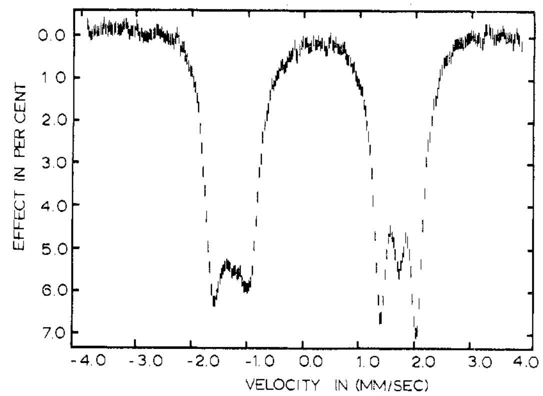

Figure 1. Magnetically perturbed (27-kG longitudinal field) ^{57}Fe Mossbauer spectrum for a sample of biferricenylenium bis(hexafluorophosphate) at 4.2°K. The velocity scale is referenced to Co in Cu source.

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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