final recrystallization noted above, at room temperature (20 °C) for octants $+h,\pm k,\pm l$, $+h,+k,\pm l$, and $+h,+k,+l$ for triclinic, monoclinic, and orthorhombic crystals, respectively. Crystal data are given in Table IIIa and data collection and refinement information in Table IIIb. Coordinates and bond distances and angles are given in Tables IV-XVII and numbering systems are given in Figures 1-3. Much additional data are available in the supplementary material. Compounds **1** and **5** were studied with a Picker FACS-III diffractometer (B-filter), **6** was studied with an Enraf-Nonius CAD4 diffractometer (graphite monochromator), and the remainder were studied on Syntex P2_1 diffractometers (graphite monochromator). For compound **5** the principal crystallographic information is in ref 31. $\theta/2\theta$ scans were used throughout. For all compounds scattering factors and anomalous dispersion factors were taken from ref 30. Final refinement was by large-block least-squares methods, using anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were refined for all except compound **2**.

Final computing for compounds **1-3** and **5** used a local version of ORFLS, CRYM, and XRAY-72 on an IBM 370 computer; for compound **4**, SHELXTL was used on a Data General DG30 computer.

For all except compound **1**, the structure was solved by Patterson methods. For compound **1** superposition was used, based on the nickel position, to reveal all the atoms of the complex. The pyridine in this complex is disordered about a center of symmetry.

For compound **2** the systematic absences indicate either space group *Pnma* or *Pn*2_1*a*. The former implies that the molecule lies on a crystallographic mirror plane. The first was initially selected and shown to be correct by successful refinement. A similar choice exists for compounds **5** and **6**, and in both cases, the centrosymmetric space group is found. For compound **5** the cation and one $[ClO_4]$ group lie on a mirror plane, the other anion being on a twofold axis. For compound **6** the cation and both anions lie on mirror planes. The molecule of compound **4** lies on an inversion center.

In compounds **6** and **7** the relatively large residual electron density is attributed to highly disordered solvent.

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Supplementary Material Available: Listings of anisotropic thermal parameters and H atom coordinates for compounds **1-4**, relationships between original and present numbering for compound **5**, anisotropic thermal parameters and H atom coordinates for compounds **5-7**, and dimensions of PF_6^- groups in compounds **6** and **7** (17 pages); listings of structure factors for compounds **2-4**, **6**, and **7** (173 pages). Ordering information is given on any current masthead page. Structure factors for compounds **1** and **5** are included in ref 31. Order No. 75-11,400 from University Microfilms, Ann Arbor, MI.

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Notes

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Structure of $[(\eta\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$, a Comparison of M-CS and M-CO Bonding

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From the time of the preparation and structural determination of the first transition-metal thiocarbonyl complex,[1] it was recognized that M-CS bond distances are shorter than corresponding M-CO distances, as initially established for $(PPh_3)_2(Cl)Rh(CS)$, 1.787 (10) Å, and $(PPh_3)_2(Cl)Rh(CO)$, 1.86 Å.[2] This M-CS bond shortening and a variety of spectroscopic data have been interpreted to indicate that, in general, CS is s stronger π-accepting ligand than CO, a conclusion with which there is general agreement.[3-6] However, Andrews[7] suggested, on the basis of ν(CS) and ν(CO) infrared stretching frequency trends, that the π-acceptor/σ-donor ratio varies more for the CS ligand than for CO as the electron richness of the metal is varied. In electron-rich complexes, CS has a higher π-acceptor/σ-donor ratio than CO, but in electron-poor systems CO has a higher π-acceptor/σ-donor ratio. This crossover occurs when ν(CO) force constants for the CO ligand are greater than 17.1 mdyn/Å. This argument suggests that if π-donation from the metal is the most important factor determining M-CS bond distances, M-CO distances should be longer than M-CS distances in electron-rich complexes, but the reverse would be true in electron-poor systems. Up to this point, all accurate X-ray structural determinations of complexes where M-CO and M-CS bond distance comparisons can be made are for electron-rich complexes where k_{CO} is less than 17.1 mdyn/Å. In this paper, we report the structure of the cationic complex $(\eta\text{-}C_5H_5)Fe(CO)_2(CS)^+$, whose k_{CO} value is 17.4 mdyn/Å.[7]

Experimental Section

The complex $[(\eta\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$ (**1**) was prepared and crystallized as described previously.[8]

X-ray Crystallographic Analysis. A crystal of the title compound was mounted on a glass fiber, positioned on a goniometer head, and then placed on a four-circle diffractometer designed and built at Ames Laboratory.[9] The crystal was cooled to 143 K, and 10 independent reflections selected from preliminary ω-oscillation programs were used as input to an automatic indexing program.[10] The resulting reduced cell scalars indicated monoclinic symmetry. Unit cell parameters were determined by a least-squares refinement of tuned 2θ values for 12 independent reflections ($24 < 2\theta < 39°$). The space group $C2/c$ was selected on the basis of the observed extinctions hkl ($h + k = 2n + 1$) and $h0l$ ($l = 2n + 1$) and a statistical test indicating the presence of a center of symmetry. Equivalent data were averaged ($R_{av} = 0.040$), yielding 2320 unique observed reflections. Crystallographic data are given in Table I.

All non-hydrogen atom positions, except those for two fluorine atoms and one carbonyl oxygen, were found from a sharpened Patterson map by using the Patterson analysis computer program ALCAMPS.[11] The remaining atoms were found from subsequent electron density map calculations. The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined by a combination of block-matrix/full-matrix least-squares calculations.[12] Hydrogen atom positions and

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Table I. Crystallographic Data

empirical formula	$C_8H_5O_2SPF_6Fe$
fw	366.0
cryst system	monoclinic
space grp	$C2/c$
a, Å	15.427 (2)
b, Å	13.825 (1)
c, Å	13.215 (21)
β, deg	121.58 (1)
V, Å^3	2400.9 (5)
Z	8
cryst size, mm	0.30 × 0.30 × 0.10
μ(Mo Kα), cm^{-1}	13.56 cm^{-1} (empirical corr applied)
ρ_{calcd}, g/cm^3	2.025
temp, K	143
radiation (monochromated) (λ, Å)	Mo Kα (0.710 34)
scan type	ω-scan
std reflcns	3 remeasd periodically—no observable change in intensity
reflcns measd	hkl, $\bar{h}\bar{k}l$, $\bar{h}k\bar{l}$
reflcns collcd	3658 collcd, 2752 obsd ($F \geq 3\sigma(F)$), 2320 symmetry unique
max 2θ, deg	55
R^a	0.048
R_w	0.064

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

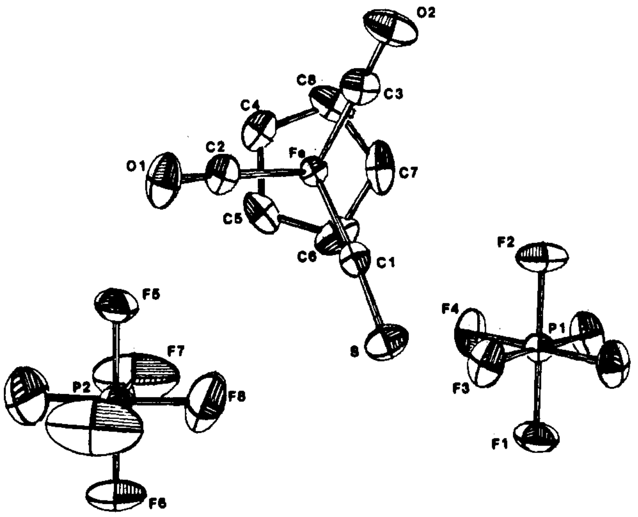

Figure 1. Structure of $[(C_5H_5)Fe(CO)_2(CS)]PF_6$ (**1**). Thermal ellipsoids are scaled to enclose 50% of the electron density.

Table II. Atom Coordinates (×10^4) and Isotropic Thermal Parameters[a] (Å^2 × 10^3) for $[(C_5H_5)Fe(CO)_2(CS)]PF_6$ (**1**)

atoms	x	y	z	U
Fe	1877 (0)[b]	1688 (0)	1932 (0)	43 (1)
S	1450 (1)	3354 (1)	−73 (1)	75 (1)
O(1)	−338 (2)	1679 (21)	881 (3)	98 (3)
O(2)	1859 (3)	−24 (2)	605 (3)	110 (3)
C(1)	1672 (3)	2569 (3)	839 (3)	55 (3)
C(2)	512 (3)	1658 (3)	1310 (3)	65 (3)
C(3)	1855 (3)	650 (3)	1092 (3)	66 (3)
C(4)	2276 (3)	1342 (3)	3685 (3)	74 (3)
C(5)	2231 (3)	2354 (3)	3533 (3)	77 (3)
C(6)	2961 (3)	2613 (3)	3242 (3)	89 (4)
C(7)	3444 (3)	1764 (4)	3208 (4)	94 (5)
C(8)	3026 (3)	988 (3)	3488 (3)	89 (4)
P(1)	0	1021 (1)	7500	52 (1)
P(2)	0	4451 (1)	2500	64 (1)
F(1)	0	−124 (2)	7500	47 (5)
F(2)	0	2169 (3)	7500	121 (5)
F(3)	1213 (2)	1017 (2)	8290 (2)	101 (3)
F(4)	48 (2)	1024 (2)	6320 (2)	98 (3)
F(5)	0	3307 (3)	2500	162 (7)
F(6)	0	5599 (3)	2500	133 (5)
F(7)	−894 (4)	4447 (3)	1186 (3)	267 (6)
F(8)	−812 (4)	4425 (3)	2862 (5)	247 (7)
H(4)	1864 (39)	952 (39)	3846 (45)	
H(5)	1723 (42)	2777 (44)	3542 (49)	
H(6)	3074 (39)	3245 (37)	3126 (47)	
H(7)	3954 (41)	1726 (36)	2996 (50)	
H(8)	3241 (36)	382 (35)	2579 (44)	

[a] Equivalent isotropic thermal parameters obtained via $U = (a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ac(\cos\beta)\,\beta_{13})/6\pi^2$, where the anisotropic temperature factor has the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Estimated standard deviations are given in parentheses for the least significant digit.

Table III. Bond Lengths (Å) and Angles (deg) in $[(C_5H_5)Fe(CO)_2(CS)]PF_6$ (**1**)

Fe–C(1)	1.788 (4)	C(1)–Fe–C(2)	88.7 (2)
Fe–C(2)	1.816 (4)	C(1)–Fe–C(3)	96.1 (2)
Fe–C(3)	1.803 (4)	C(2)–Fe–C(3)	93.4 (2)
Fe–C(4)	2.117 (4)	Fe–C(1)–S	176.2 (3)
Fe–C(5)	2.099 (4)	Fe–C(2)–O(1)	176.0 (4)
Fe–C(6)	2.097 (4)	Fe–C(3)–O(2)	177.2 (4)
Fe–C(7)	2.105 (4)	C(8)–C(4)–C(5)	107.6 (4)
Fe–C(8)	2.119 (4)	C(4)–C(5)–C(6)	107.8 (4)
S–C(1)	1.521 (4)	C(5)–C(6)–C(7)	108.0 (4)
O(1)–C(2)	1.124 (5)	C(6)–C(7)–C(8)	107.9 (4)
O(2)–C(3)	1.134 (5)	C(7)–C(8)–C(4)	108.8 (4)
C(4)–C(5)	1.409 (6)	F(1)–P(1)–F(2)	180.0
C(5)–C(6)	1.412 (6)	F(1)–P(1)–F(3)	89.8 (2)
C(6)–C(7)	1.403 (7)	F(1)–P(1)–F(4)	90.2 (1)
C(7)–C(8)	1.399 (7)	F(2)–P(1)–F(3)	90.2 (1)
C(8)–C(4)	1.401 (6)	F(2)–P(1)–F(4)	89.9 (1)
P(1)–F(1)	1.583 (4)	F(3)–P(1)–F(4)	90.0 (2)
P(1)–F(2)	1.587 (4)	F(5)–P(2)–F(6)	180.0
P(1)–F(3)	1.595 (3)	F(5)–P(2)–F(7)	89.8 (2)
P(1)–F(4)	1.599 (2)	F(5)–P(2)–F(8)	88.7 (2)
P(2)–F(5)	1.582 (4)	F(6)–P(2)–F(7)	90.2 (2)
P(2)–F(6)	1.587 (4)	F(6)–P(2)–F(8)	91.3 (2)
P(2)–F(7)	1.553 (5)	F(7)–P(2)–F(8)	87.6 (2)
P(2)–F(8)	1.560 (5)		

isotropic thermal parameters were also refined. The final difference map was featureless. The non-hydrogen scattering factors were from ref 13, and those for iron and phosphorus were modified for the real and imaginary parts of anomalous dispersion.[14] Hydrogen scattering factors were those of Stewart et al.[15] Weights were based on $1/\sigma_F^2$ and slightly adjusted prior to the final refinement such that $\overline{\omega\Delta^2}$ was approximately constant as a function of $|F_o|$.

Discussion

Structure of $[(\eta\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$ (1). Atomic coordinates and isotropic thermal parameters are given in Table II, while selected bond distances and angles are given in Table III. The structure is shown projected onto the cyclopentadienyl (Cp) ring in Figure 1. This structure is composed of discrete cationic ($(C_5H_5)Fe(CO)_2(CS)^+$) and anionic (PF_6^-) species. The coordination about the iron atom is very nearly octahedral, with the carbonyl (C(2) and C(3)) and thiocarbonyl (C(1)) carbons occupying three of the six positions and the Cp ring, acting as a tridentate ligand, occupying the remaining three positions. There

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(12) Calculations were carried out on a VAX 11/780 computer. Structure factor calculations and least-squares refinements were done by using the block-matrix/full-matrix program ALLS (Lapp, R. L.; Jacobson, R. A. U.S. Department of Energy Report IS-4708; Iowa State University, Ames, IA, 1979), Fourier series calculations were done by using the program FOUR (Powell, D. R.; Jacobson, R. A. U.S. Department of Energy Report IS-4737; Iowa State University, Ames, IA, 1980), and for molecular drawings the program ORTEP was used (Johnson, C. K. U.S. Atomic Energy Commission Report ORNL-3794; Oak Ridge National Laboratory, Oak Ridge, TN, 1970). An empirical absorption correction was carried out by using the diffractometer Φ-scan data and the program ABSN (Karcher, B. A. Ph.D. Dissertation, Iowa State University, Ames, IA, 1981).

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Table IV. Differences between M–CO and M–CS Bond Distances in Carbonyl–Thiocarbonyl Complexes

compd	ν(CS)[a]	M–CO[b]	M–CS[b]	Δ[b]
$[CpFe(CO)_2(CS)]PF_6$[c]	1348	1.803 (4), 1.816 (4)	1.788 (4)	0.022
$(\eta\text{-}C_6H_5CO_2Me)Cr(CO)_2(CS)$[d]	1225	1.847 (3), 1.850 (2)	1.792 (2)	0.057
$(\eta^6\text{-tetralone})Cr(PPh_3)(CO)(CS)$[e]	1170–1201[f]	1.85 (1)	1.75 (1)	0.10

[a] cm^{-1}. [b] Å. [c] This work. [d] Saillard, J.-Y.; LeBorgne, G.; Grandjean, D. *J. Organomet. Chem.* **1975**, *94*, 409. [e] Korp, J. D.; Bernal, I. *Cryst. Struct. Commun.* **1980**, *9*, 821. [f] Not reported for this compound. Values given are for the similar compounds: $(\eta\text{-}C_6H_5CO_2Me)Cr(PPhMe_2)(CO)(CS)$, 1170 cm^{-1} (Jaouen, G.; Meyer, A.; Simonneaux, G. *Tetrahedron* **1975**, *31*, 1889); $(\eta\text{-}C_6H_5CO_2Me)Cr[P(OEt)_3](CO)(CS)$, 1201 cm^{-1} (Jaouen, G.; Dabard, R. *J. Organomet. Chem.* **1974**, *72*, 377).

are two symmetry-independent PF_6^- groups, each with one phosphorus and two fluorines lying on twofold axes. The PF_6^- group containing P(1) is clearly resolved, with fluorine thermal parameters comparable to those for carbon and oxygen atoms. The other group is more disordered but approximated by the four independent positions F(5), F(6), F(7), and F(8). The cyclopentadienyl ring is planar within experimental error.

The Fe–CS bond distance (1.788 (4) Å) in **1** is considerably longer than that (1.662 (3) Å) in the more electron-rich Fe(CS)(OEP)[16] (OEP = octaethylporphyrin), consistent with the idea that there is more π-bonding to the CS in the latter compound. The shorter C–S distance in **1** (1.521 (4) Å) as compared with that (1.559 (3) Å) in Fe(CS)(OEP) is also expected because of reduced π-electron donation from the Fe to the π^* orbitals of CS in **1**. Even though the Fe–CS distance (1.788 (4) Å) in **1** is relatively long, it is still much shorter than Fe–CS distances in the bridging thiocarbonyl complexes $[(C_5H_5)Fe(CO)(\mu\text{-}CS)]_2$ (1.90–1.91 Å)[17] and $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CS)$ (1.889 (8) Å).[18]

The Fe–CO distances (1.816 (4) and 1.803 (4) Å) in **1** are relatively long and comparable to those (1.802 (6), 1.831 (7), and 1.815 (6) Å) in $[(C_5H_5)Fe(CO)_3]PF_6$;[19] thus, CS does not measurably affect the Fe–CO distances as compared with those in $(C_5H_5)Fe(CO)_3^+$. In contrast, the Fe–CO distances (1.767 (4) and 1.775 (4) Å) in $[(C_5H_5)Fe(CO)_2(PPh_3)]Cl$,[20] containing the more electron-donating PPh_3 ligand, are significantly shorter than those in **1**.

Comparison of M–CS and M–CO Bond Distances. As discussed in the introduction, Andrews[7] concluded that the CS ligand should have a higher π-acceptor/σ-donor ratio than CO in electron-rich complexes but a lower ratio than CO in electron-poor complexes. If the π-acceptor/σ-donor ratio is largely determined by the π-acceptor character of the CX ligand, then in electron-rich complexes M–CS bonds should be shorter than M–CO bonds; this is what is observed in all known structures of carbonyl–thiocarbonyl complexes.[3–6] However, as the electron richness of the complex decreases, it is expected that CO and CS will become comparable π-acceptors and the M–CS and M–CO distances should become more equivalent.

There are few structural studies in the literature that allow a comparison of M–CO and M–CS distances in the same molecule to test this idea. However, three examples where the distances are sufficiently precise for such a comparison are given in Table IV. As the electron richness increases down the table, as measured by the decreasing ν(CS) values, the M–CS bond does indeed become shorter relative to the M–CO bond, as indicated by the difference (Δ) between the M–CS distance and the average of the M–CO bond distances. Even though k_{CO} for $CpFe(CO)_2(CS)^+$ is 17.4 mdyn/Å, which is above the point where Andrews suggests the π-acceptor/σ-donor ability of CO should be larger than that of CS, the M–CS distance is still slightly shorter than M–CO. However, the trend is in the direction predicted by Andrews' analysis.

While it would be desirable to substantiate the above trend with more data, one might nevertheless consider the chemical consequences of the relative change in CS and CO bonding with electron density on the complex. In electron-rich $L_xM(CO)_y(CS)$ complexes, the CS ligand should be bonded more strongly than CO, and substitution reactions with phosphines and other ligands should result in replacement of CO, rather than CS. That this is true is documented in numerous substitution reactions.[3–6,21] The only reactions where some CS substitution occurs are those of $(C_5H_5)Fe(CO)_2(CS)^+$. Thus, $(C_5H_5)Fe(CO)_2(CS)^+$ reacts with phosphines and related ligands to give a mixture of products, $(C_5H_5)Fe(CO)(L)(CS)^+$ and $(C_5H_5)Fe(CO)_2(L)^+$;[22] it also reacts with halides (X^-) to give both $(C_5H_5)Fe(CO)(X)(CS)$ and $(C_5H_5)Fe(CO)_2X$.[23] In general, one might expect CS substitution to be a likely reaction in complexes where the ν(CS) value is as high as or higher than that (1348 cm^{-1}) of $(C_5H_5)Fe(CO)_2(CS)^+$.

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Supplementary Material Available: Listings of thermal parameters and least-squares planes (2 pages); a table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Phosphorus(V) Oxides

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Among oxides of phosphorus it is believed that phosphorus pentoxide (named according to its empirical formula, P_2O_5) is best understood.[1] Furthermore, it is stated that in addition to amorphous and glassy forms it exists in three crystalline polymorphs.[2,3] We wish to suggest that the so-called crystalline polymorphs are in fact three distinct compounds with different structural characteristics but with the same empirical formula, P_2O_5.

Structural data for the three crystalline forms based upon X-ray diffraction studies are given in Table I. There are no spectroscopic studies on any of the three solid forms.

The so-called H form[1–3] (based upon the erroneous belief that the crystals belong to the hexagonal crystal system) contains discrete P_4O_{10} molecules.[4,7] Unfortunately, the crystal structure studies[4,7] do not provide precise structural parameters even though the existence of discrete P_4O_{10} molecules is not in doubt. The reliable structural parameters of the P_4O_{10} molecule are based

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