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TELLURIUM AND SELENIUM DERIVATIVES OF π-CYCLOPENTADIENYLIRON DICARBONYL

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SUMMARY

Reactions of the diphenyl dichalcogenides Ph_2E_2 (E=Te, Se) with [π-CpFe$(CO)_2]_2$ have been studied and several new complexes have been isolated and characterized. These include mononuclear π-CpFe$(CO)_2$EPh (E=Te, Se) and dinuclear [π-CpFe(CO)EPh$]_2$ (E=Te, Se). In the case of the dinuclear compounds two isomers were obtained and separated for selenium and a mixture of two isomers was obtained for tellurium. Comparisons of the donor properties of sulfur, selenium, and tellurium in these complexes are made.

INTRODUCTION

An investigation of the comparative donor properties of tellurium, selenium, and sulfur in transitional metal complexes is being carried out in this laboratory[1]. Emphasis at this stage is being put on the preparation and characterization of complexes containing tellurium and selenium as donor atoms as this area has been greatly neglected in coordination chemistry. The donor properties of sulfur-containing ligands have, of course, been much studied[2].

In view of the number of alkyl- and arylsulfido-derivatives of π-cyclopentadienyliron dicarbonyl that have been prepared[3-8], we have chosen to use [π-CpFe$(CO)_2]_2$ as a substrate for reactions with diphenyl ditelluride and diphenyl diselenide. It was anticipated that use of the heavier and "softer" chalcogens Se and Te for reactions with the soft substrate [π-CpFe$(CO)_2]_2$ might lead to more stable complexes than those previously prepared with the less soft sulfur derivatives.

EXPERIMENTAL

I. Materials

The diphenyl dichalcogenides, Ph–E–E–Ph (E=S, Se, Te) were obtained from commercial sources and used with further purification as was [π-CpFe$(CO)_2]_2$.

Hydrocarbon solvents were dried over sodium and deaerated before use. All reactions and work-ups were carried out under an atmosphere of nitrogen.

Column chromatographic separations were carried out using Silica Gel (70–325 mesh) and neutral and acidic alumina. For preparative thin layer chromatography Silica Gel PF-254 was coated on 20 x 20 cm plates in layers of 2 mm thickness while for analytical TLC Silica Gel GF-254 was coated on 5 x 20 cm plates in layers of 0.35 mm thickness. Proper conditions for TLC work were ascertained using silica gel-coated microscope slides[9]. Adsorbents were products of E. Merck AG, Darmstadt.

II. Preparation of complexes

IR and NMR spectral data are given in Table 1.

TABLE 1

IR AND NMR SPECTRAL DATA

Compound[a]		IR[b]			^{1}H NMR[c]
(I)	E=S	2033 s,	1990 s		4.83
(I)	E=Se	2026 s,	1984 s		4.79
(I)	E=Te	2018 s,	1976 s		4.77
(II)	E=S	1982 s			4.43[d]
(III)	E=S	1953 s,	1937 s		4.03[e]
(II)	E=Se	1975 s			4.46
(III)	E=Se	1947 s,	1931 s		4.02
(II)+(III) mixture, E=Te		1965 m,	1937 s,	1921 s	4.48, 4.11

[a] The numbers refer to structures shown in text. [b] Carbonyl stretching frequencies (cm^{-1}) recorded in cyclohexane solution. [c] Cyclopentadienyl proton signal; recorded in CS_2 solution and expressed in ppm from TMS. [d] Ref. 5 reports 4.49 ppm. [e] From ref. 5.

A. Reaction of Ph_2Te_2 with $[\pi\text{-}CpFe(CO)_2]_2$. Diphenyl ditelluride (2.87 g, 7 mmoles) and $[\pi\text{-CpFe(CO)}_2]_2$ (2.0 g, 5 mmoles) were mixed in 150 ml of benzene and the solution was heated to reflux temperature. Periodic withdrawal of small samples for IR spectra showed after 3 h that $[\pi\text{-CpFe(CO)}_2]_2$ was no longer present in the solution, whereupon the reaction mixture was cooled, filtered, and taken to dryness under reduced pressure. The resulting green solid was dissolved in diethyl ether and chromatographed on an alumina column by development with 9/1 hexane ether. A green band and a yellow band separated. The yellow eluate showed no absorptions in the carbonyl stretching region and was discarded. Solvent was removed from the green eluate to give a green tar which was recrystallized from dichloromethane/hexane at −70° to give green crystals of $\pi\text{-CpFe(CO)}_2\text{TePh}$, m.p. 66°. (Found: C, 40.36; H, 3.01; mol.wt. osmometric in $CHCl_3$, 434. $C_{13}H_{10}FeO_2Te$ calcd.: C, 40.89; H, 2.62%; mol.wt. 382).

Diphenyl ditelluride (2.87 g, 7 mmoles) and $[\pi\text{-CpFe(CO)}_2]_2$ (2.0 g, 5 mmoles) were refluxed in 150 ml of benzene. A sample withdrawn after 5 h showed strong IR absorptions corresponding to $\pi\text{-CpFe(CO)}_2\text{TePh}$ and an additional band at 1917 cm^{-1}. IR spectra of samples taken after 8, 10, and 23 h of reflux indicated only a slight increase in intensity of the 1917 cm^{-1} band. In the course of examining the last sample it was noticed that successive scans through the 1800–2500 cm^{-1} region caused a growth of the 1917 band and a corresponding decrease in absorptions of the $\pi\text{-CpFe(CO)}_2\text{TePh}$ bands. Therefore, an IR heating lamp was used to irradiate the reaction mixture and after 3 h the bands due to $\pi\text{-CpFe(CO)}_2\text{TePh}$ had disappeared. The reaction mixture was taken to dryness, the residue was dissolved in dichloromethane and chromatographed on an alumina column. Development with cyclohexane caused a brown band to separate from a band due to diphenyl ditelluride. The brown eluate was taken to dryness, and the brown solid which was obtained was recrystallized from dichloromethane/ethanol to give a 60% yield of fine dark crystals of a mixture of two isomers of [π-CpFe(CO)TePh]$_2$: (Found: C, 40.45; H, 3.16, Fe, 15.73; mol.wt. osmometric in $CHCl_3$, 680. $C_{24}H_{20}Fe_2O_2Te_2$ calcd.: C, 40.73; H, 2.85; Fe, 15.80%; mol.wt., 707.) Several unsuccessful attempts using crystallization, column chromatography (silica gel and alumina), and preparative layer chromatography were made in an effort to separate the isomers. The preparative TLC approach proved to give a slight enrichment of one isomer over the other but a pure isomer was not separated.

B. Reaction of Ph_2Se_2 with [π-CpFe(CO)$_2$]$_2$. Diphenyl diselenide (2.19 g, 7 mmoles) and [π-CpFe(CO)$_2$]$_2$ (2.0 g, 5 mmoles) were mixed in 150 ml of benzene and maintained at room temperature. After 3 h IR monitoring showed a weak product band developing at 2025 cm^{-1}. However, since after 24 h at ambient conditions a substantial amount of unreacted [π-CpFe(CO)$_2$]$_2$ remained, the mixture was refluxed for 2 h at which time the [π-CpFe(CO)$_2$]$_2$ had disappeared. Solvent was removed under reduced pressure and the resulting solid was recrystallized several times from dichloromethane/hexane to yield (53%) dark crystals of π-CpFe(CO)$_2$SePh, m.p. 50–52°. (Found: C, 46.45; H, 3.20; mol.wt. osmometric in $CHCl_3$, 372, mass spectrum, 333. $C_{13}H_{10}FeO_2Se$ calcd.: C, 46.89; H, 3.03%; mol.wt., 333.)

Diphenyl diselenide (2.19 g, 7 mmoles) and [π-CpFe(CO)$_2$]$_2$ (2.0 g, 5 mmoles) were added to 150 ml of benzene. The mixture was refluxed and simultaneously irradiated with the heat lamp used in the analogous Ph_2Te_2 reaction in an effort to encourage dimer formation. After 3 h [π-CpFe(CO)$_2$]$_2$ had disappeared and π-CpFe(CO)-SePh was the principal constituent. After 6 h a broad band had begun to develop at 1928 cm^{-1}, while monomer bands had simultaneously weakened. After a total reaction period of 10 h the monomer had disappeared and solvent was removed. The residue was dissolved in dichloromethane and addition of hexane caused a brown solid to precipitate. The solid was collected and showed a single absorption at 1975 cm^{-1} in the carbonyl region. From the filtrate there was obtained, after reduction of the solvent volume and cooling of the solution, a dark crystalline material with strong absorptions at 1931 and 1947 cm^{-1} and a very weak band at 1975 cm^{-1}. The brown solid with a single absorption at 1975 cm^{-1} was chromatographed on an alumina column using 1/1 benzene/hexane as eluent, and the solid remaining after the eluate was taken to dryness was recrystallized from dichloromethane/hexane as gold-colored needles of a pure isomer* of [π-CpFe(CO)SePh]$_2$ in 30% yield, m.p. 170–172 (decompn.). (Found: C, 46.94; H, 3.43; Fe, 17.76; mol.wt. osmometric in $CHCl_3$, 601. $C_{24}H_{20}Fe_2O_2Se_2$ calcd.: C, 47.23; H, 3.33; Fe, 18.32%; mol.wt., 610.) The dark crystalline solid with strong absorptions at 1931 and 1947 cm^{-1} was likewise chromatographed on an alumina column using the same eluent and the solid obtained from the eluate was recrystallized from dichloromethane/hexane as dark crystals of a second pure isomer* of [π-CpFe(CO)SePh]$_2$ in 10% yield, m.p. 170–172. (Found: C, 46.85; H, 3.38; Fe, 17.71; mol.wt., osmometric in $CHCl_3$, 589.)

C. Reaction of Ph_2S_2 with [π-CpFe(CO)$_2$]$_2$. Diphenyl disulfide (1.53 g, 7 mmoles) and [π-CpFe(CO)$_2$]$_2$ (2.0 g, 5 mmoles) were dissolved in benzene and heated to reflux temperature. A sample withdrawn after 2 h showed bands characteristic of

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* Isomer purity was verified by infrared and NMR data (See Table 1).

mononuclear π-CpFe(CO)$_2$SPh, and a shoulder at 1926 cm^{-1} indicated that dinuclear [π-CpFe(CO)SPh]$_2$ had commenced to form. A relatively weak band due to the bridging carbonyl of [π-CpFe(CO)$_2$]$_2$ showed that starting material had mostly reacted after 2 h, and after 3 h there was only a very weak band at 1782 cm^{-1} due to [π-CpFe(CO)$_2$]$_2$. The reaction mixture was then cooled, filtered, and reduced in volume for chromatography on an alumina column. Elution with 3/2 hexane/benzene first, followed by elution with neat benzene, caused three bands to separate. The first eluate collected, which was a yellow solution, contained a small amount of a yellow-brown solid (2% of the solids collected) which was the "less stable" isomer of [π-CpFe(CO)SPh]$_2$; the second material obtained was the "more stable" isomer of [π-CpFe(CO)SPh]$_2$ (50% of the solids collected); and the third material, which appeared as a violet band on the column, was mononuclear π-CpFe(CO)$_2$SPh.

III. Instrumentation and analyses

IR spectra were recorded with a Beckman IR-7 instrument using cyclohexane or CS$_2$ solutions of the compounds in 0.4 mm chloride cells.

Melting points were taken in open capillaries on a Hoover melting point instrument.

Mass spectra were obtained by Mrs. Cheryl White of the Department of Chemistry, Louisiana State University, on a Varian M-66 instrument at 70 eV.

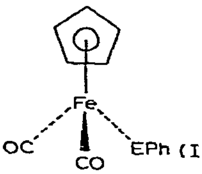
Proton magnetic resonance spectra were obtained with a Varian A-60 instrument using CS$_2$ solutions of the complexes with TMS as an internal standard.

Osmometric molecular weight measurements were determined with a Hewlett–Packard Model 302A osmometer in CHCl$_3$ solution using a 37° probe.

Carbon and hydrogen analyses were carried out by Mr. R. Seab, Department of Chemistry, Louisiana State University, and analysis for iron was done by Galbraith Laboratories, Inc., Knoxville, Tennessee.

RESULTS AND DISCUSSION

The diphenyl dichalcogenides, Ph–E–E–Ph (E=Te, Se, S[5]), react slowly at room temperature but readily in refluxing benzene with π-cyclopentadienyliron dicarbonyl dimer to give first the mononuclear complexes π-CpFe(CO)$_2$EPh, (I) (E=Te, Se, S[5]). Qualitatively, the rate of reaction of Ph$_2$E$_2$ with the substrate was observed to decrease in the order of E=S >Se >Te.



(I)

The IR spectral data of Table 2 allow a comparison of ν(CO) values in complexes containing some common ligands with selenium- and tellurium-containing ligands. One notes the relatively low stretching frequencies in the chalcogen complexes, and while these lower values may be a consequence of classical mass effects, they are also consistent with stronger bonding of the carbonyl groups to iron in the

TABLE 2

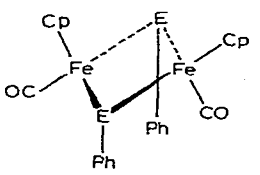
CARBONYL STRETCHING FREQUENCIES[a] OF π-CYCLOPENTADIENYLIRON DICARBONYL DERIVATIVES, π-CpFe(CO)$_2$X

X	ν_1	ν_2	Solvent	Ref.
CN	2060	2020	CCl_4	11
Cl	2050	2010	CCl_4	11
I	2044	2000	$CHCl_3$	12
CF_3S	2044	2000	Cyclohexane	7
CH_3S	2029	1981	CCl_4	5
PhS	2030	1987	CCl_4	5
PhSe	2026	1984	Cyclohexane	[b]
PhTe	2018	1976	Cyclohexane	[b]

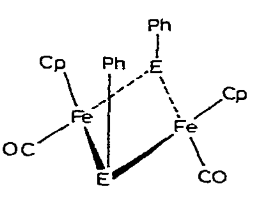
[a] Cm^{-1}. [b] This work.

chalcogen complexes. A knowledge of the relative Fe–C bond strengths in the three phenylchalcogenido-complexes would be an indirect measure of the comparative donor abilities of sulfur, selenium, and tellurium in these complexes. Unfortunately, neither the IR data nor some observations of reactivities allow one to draw an unambiguous conclusion about the Fe–C bond strengths. It is true that the tendency of the mononuclear complexes to dimerize with loss of CO decreases in the order of E as S > Se > Te, and this ability of tellurium and selenium to kinetically stabilize mononuclear complexes relative to sulfur with respect to loss of CO was also observed in the related molybdenum complexes π-CpMo(CO)$_3$EPh[1]. However, while these qualitative kinetic observations may imply stronger Fe–C bonding decreasing in the order of E as Te > Se > S if a dissociative mechanism is operative, the reactivities may also be explained in terms of nucleophilicity of E decreasing in the order of E as S > Se > Te for an associative mechanism.

As with the previously reported sulfur reactions[5], complexes (I) (E = Se, Te) lose CO when heated, and more rapidly when irradiated with visible-IR light, to give two isomers of [π-CpFe(CO)EPh]$_2$. In the case of E = Se, the two isomers were separated but with E = Te separation could not be achieved. Comparisons of IR and NMR spectra (Table 1) with spectra of the sulfur isomers suggest that structures of these new dinuclear selenium and tellurium complexes are analogous to those of the lighter congener, one of which has been shown by an X-ray study[10] to be a folded conformer of (II), and the other of which has been deduced to have structure (III) from NMR considerations[8].



(II)



(III)

Mass spectra of the dinuclear compounds were taken but in no cases was a parent molecular ion peak observed, nor was these seen any other carbonyl-containing species. The base peak was m/e 186 assigned to Cp_2Fe^+, and other intense peaks corresponded to PhE^+ (E=S, Se, Te) and Fe^+.

Greater stability of the dinuclear selenium and tellurium compounds over the sulfur compound is evidenced by the fact that the former compounds have been stored in unsealed sample bottles for three years without noticeable decomposition whereas partial decomposition of (II) (E=S) was noticed after several months of storage.

A considerably different ratio of the two dinuclear isomers was isolated from the reactions of the three different diphenyl dichalcogenides with $[\pi\text{-CpFe(CO)}_2]_2$. In the sulfur reaction it was reported[5] that (III) is obtained as ca. 1% of the isomer mixture. When E=Se, (III) is obtained as ca. 25% of the isomer mixture and for E=Te, (III) is the major dinuclear product, even after prolonged reflux with irradiation. These percentages presumably reflect the kinetically controlled processes of a single isomer (III) formation[5,8] and subsequent isomerization [(III)→(II)]. In regard to the first process it was noted above that the dinuclear formation from π-CpFe(CO)-EPh decreases in the order of E as S > Se > Te and in regard to the relative rates of isomerization a similar trend is observed. Isomerization of (III) to (II) for E=Se was observed in a CS_2 solution in an IR cell but no changes in intensity of carbonyl absorptions were seen in a 30 min period when a similar experiment was performed with a mixture of tellurium isomers. Too little is really known about the kinetics and mechanism of these very interesting isomerization processes to make a definitive statement about the relative donor properties of S, Se, and Te based on the relative rates of isomerization of these compounds. However, if cleavage of the Fe–E bond is important in the mechanism, as it may be in the sulfur case studied by Knox *et al.*[8], then the decreasing order of Fe–E bond strength is implied to be: Te > Se > S. If steric constrictions are important in promoting (III)→(II), then the stability of (III) for E=Te is understandable in view of the larger size of the bridging tellurium atoms.

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