TELLURIUM AND SELENIUM DERIVATIVES OF IRON AND RUTHENIUM CARBONYLS

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SUMMARY

Reaction of $M_3(CO)_{12}$ (M = Fe, Ru) with diphenyl diselenide and diphenyl ditelluride have been studied. The dinuclear compounds $[M(CO)_3EPh]_2$ (E = Se, Te) are obtained as the only carbonylated products in the case of M = Fe, but for M = Ru the dinuclear species are minor reaction products. Major products are two forms of polymeric $[Ru(CO)_2(EPh)_2]_n$ (E = Se, Te). Molecular weight measurements indicate that the lower molecular weight polymer has 6–7 units per molecule whereas the heavier one has n = 12–14.

INTRODUCTION

In an investigation of the comparative donor properties of tellurium, selenium, and sulfur in transitional metal complexes, we have described in previous reports[1,2] from this laboratory the reactions between some π-cyclopentadienylmetal carbonyl substrates and Ph_2E_2 (E = S, Se, Te). Pure metal carbonyl substrates are now being studied, and this paper reports results obtained for reactions of the trinuclear iron and ruthenium carbonyls $M_3(CO)_{12}$ with diphenyl ditelluride and diphenyl diselenide. Hieber and co-workers have previously studied the reactions of some iron carbonyls with diaryl dichalcogenides. Thus, from $Fe_3(CO)_{11}$ and Ph_2S_2 they obtained dinuclear $[Fe(CO)_3SPh]_2$ and with bis(p-methoxyphenyl) ditelluride and the same iron substrate the complex $[Fe(CO)_3(TeC_6H_4OCH_3)]_2$ was gotten[3,4]. More recently the novel dicarbonyl, trinuclear complexes $[Fe(CO)_2(EPh)_2]_3$ [E = S, Se) were reported as having been obtained after a mixture of iron pentacarbonyl and Ph_2E_2 was irradiated with UV light[5]. During the course of the work reported herein the reaction of diphenyl disulfide with $Ru_3(CO)_{12}$ was reported[6] to give several polynuclear compounds. Similar compounds had been obtained previously from reactions of the dodecacarbonyl with thiols[7]. Complexes with ruthenium–selenium or ruthenium–tellurium bonds have apparently not been previously reported.

EXPERIMENTAL

Materials

The carbonyls $M_3(CO)_{12}$ (M = Fe, Ru) were obtained from Alfa Inorganics,

Inc. Other materials and procedures used were described previously[2].

Preparation of the complexes

IR and mass spectral data are given in Tables 1, 2, and 3.

Reaction of Fe$_3$(CO)$_{12}$ with Ph$_2$Te$_2$. Diphenyl ditelluride (3.28 g, 8 mmoles) and Fe$_3$(CO)$_{12}$ (2.52 g, 5 mmoles) were dissolved in 100 ml of benzene and the solution was taken to reflux temperature. Within a few minutes a color change from green to deep red occurred as a gas was evolved. An IR spectrum of a sample withdrawn after 1 h showed Fe$_3$(CO)$_{12}$ to be absent. The reaction mixture was filtered, the filtrate was taken to dryness under reduced pressure, and the residue so obtained was twice recrystallized from dichloromethane/hexane. Dark red crystals of [Fe(CO)$_3$TePh]$_2$ were obtained, 3.2 g (60%), m.p., 104–106 (decompn.). (Found: C, 31.59; H, 1.79; Fe, 16.34; Te, 36.75; mol.wt. in CHCl$_3$, 675; mol.wt. from mass spectrum, 689. C$_{18}$H$_{10}$Fe$_2$O$_6$Te$_2$ calcd.: C, 31.37; H, 1.58; Fe, 16.21; Te, 37.03%; mol.wt., 689.)

Reaction of Fe$_3$(CO)$_{12}$ with Ph$_2$Se$_2$. Diphenyl diselenide (2.50 g, 8 mmoles) and Fe$_3$(CO)$_{12}$ (2.52 g, 5 mmoles) were added to 80 ml of benzene and the solution was refluxed for 1 h. Removal of solvent under reduced pressure left a yellow-red solid which was first recrystallized from dichloromethane/hexane and then a benzene solution of the solid so obtained was chromatographed on an alumina column. Elution with 7/4 hexane/benzene caused an orange-red band to move down the column and this was followed by a red-brown band which moved more slowly. A small amount of yellow solid recovered from the eluate corresponding to the slower moving band exhibited no absorptions in the IR carbonyl region and was discarded. From the eluate corresponding to the first band there was obtained red, crystalline [Fe(CO)$_3$-SePh]$_2$, 3.0 g (65%) m.p., 94–96° (decompn.). (Found: C, 37.02; H, 2.12; Fe, 18.72; Se, 26.97; mol.wt. in CHCl$_3$, 572. C$_{18}$H$_{10}$Fe$_2$O$_6$Se$_2$ calcd.: C, 36.16; H, 1.67; Fe, 19.69; Se, 26.41%; mol.wt., 598.)

Reaction of Ru$_3$(CO)$_{12}$ with Ph$_2$Te$_2$. Diphenyl ditelluride (1.04 g, 2.55 mmoles) in 20 ml of benzene was added dropwise with stirring to Ru$_3$(CO)$_{12}$ (1.07 g, 1.66 mmoles) dissolved in 150 ml of benzene. The mixture was maintained at 60° for 4 h as it was monitored periodically by means of thin layer chromatography and IR spectroscopy. After 4 h a thin layer chromatogram showed (in order of decreasing R_f values) a spot corresponding to Ru$_3$(CO)$_{12}$, a light yellow spot, and an orange spot; there was no TLC evidence suggesting the presence of Ph$_2$Te$_2$ in the reaction mixture at this time. The volume of the mixture was reduced to 30 ml, and it was chromatographed on a silica gel column. Petroleum ether eluted a broad yellow band (Band I). A second band was light orange in color (Band II) and was eluted with 4/1 benzene/-chloroform while a third band, which was dark orange (Band III) in color, moved very slowly and was extracted from the silica gel with chloroform. An IR spectrum of the Band I eluate showed it to be a mixture of unreacted Ru$_3$(CO)$_{12}$ and [Ru(CO)$_3$-TePh]$_2$. The mixture was separated by preparative layer chromatography, and afforded 100 mg of yellow [Ru(CO)$_3$TePh]$_2$, m.p., 105–107° decompn.). (Found: C, 28.16; H, 1.80; mol.wt. in CHCl$_3$, 735. C$_{18}$H$_{10}$O$_6$Ru$_2$Te$_2$ calcd.: C, 27.81; H, 1.29%; mol.wt., 778.) Band II was collected in three fractions, each of which showed carbonyl absorptions at 1974, 2030, and 2080 cm^{-1}. The only noticeable difference in the spectra was the relative intensity of the 2080 cm^{-1} absorption. The third fraction from Band II was the only one affording sufficient amount of material for characteri-

zation, and the dark orange plates obtained are formulated as $[Ru(CO)_2(TePh)_2]_n$, m.p. $>200°$ (decompn.). [Found: C, 30.27; H, 2.10; mol.wt. in $CHCl_3$, 3700 ($n=$ 6 to 7). $C_{14}H_{10}O_2RuTe_2$ calcd.: C, 29.68; H, 1.77%.] From the Band III extract was obtained a solid which constituted ca. 90% of isolated products from this reaction, Recrystallization of the solid from dichloromethane/hexane yielded an orange-brown powder formulated as $[Ru(CO)_2(TePh)_2]_n$, m.p. 200–220° (decompn.). [Found: C, 29.92; H, 1.89; Te, 44.54; mol.wt. in $CHCl_3$, 7800 to 8200 ($n=$ 12 to 14). $C_{14}H_{10}$-O_2RuTe_2 calcd.: C, 29.68; H, 1.77; Te, 45.05%.] When the reaction was repeated with a Ph_2Te_2 to $Ru_3(CO)_{12}$ molar ratio greater than 3 to 2 in an attempt to cause the $Ru_3(CO)_{12}$ to completely react, thereby eliminating a portion of the rather tedious separation, the only isolated products were the two polymeric materials.

Reaction of $Ru_3(CO)_{12}$ with Ph_2Se_2. Diphenyl diselenide (0.94 g, 3 mmoles) in 20 ml benzene was added dropwise to 200 ml of benzene containing $Ru_3(CO)_{12}$ (1.28 g, 2 mmoles). The mixture was heated at 60° for 3 h at which time TLC showed that all the Ph_2Se_2 had reacted. Solvent was removed under reduced pressure, the residue was dissolved in 20 ml of dichloromethane, and the solution was applied to five 20×20 cm preparative layer silica plates. Development with petroleum ether caused a band of $Ru_3(CO)_{12}$ (Band I) to separate from a yellow band (Band II) and another yellow band (Band III) with more material remaining near the origin. Bands I, II and III were scraped from the plates and extraction of the silica gel with CH_2Cl_2 yielded 100 mg and 2 mg of yellow solids from Bands II and III respectively. The carbonyl region of the IR spectra of the materials showed absorptions at 2006 vs (br), 2052 vs, and 2091 s cm^{-1} with the only difference in the two materials being in the relative intensities of the absorptions. Yellow solid II (from Band II) melts at 97° and, in a thermogravimetric analysis, lost mass (presumably CO) very slowly above 150° and at a considerably greater rate above 250°. While yellow solid III could not be characterized because of the small amount obtained, yellow solid II is formulated as $[Ru(CO)_3SePh]_2$. (Found: C, 32.16; H, 2.10: Se, 23.49; mol.wt. in $CHCl_3$, 644. $C_{18}H_{10}O_6Ru_2Se_2$ calcd.: C, 31.69; H, 1.47; Se, 23.14%; mol.wt., 682.)

The preparative plates were returned to developing chambers after Bands I, II and III were removed and with 2/1 benzene/petroleum ether a yellow band (Band IV) separated from a yellow-orange band (Band V) which was separated from an orange band (Band VI) that remained at the origin. Each of the bands was removed and extracted with CH_2Cl_2. Band IV gave about 2 mg of a light yellow solid whose IR spectrum included bands at 1963 w, 2007 m, 2024 s, 2054 m, 2081 m, and 2105 w, but which was not further characterized. From Band V was gotten 100 mg of an orange plate-like solid which is formulated as $[Ru(CO)_2(SePh)_2]_n$, m.p., ca. 200° (decompn.). [Found: C, 36.17; H, 3.03; Ru, 21.62; mol.wt. in $CHCl_3$, ca. 3200 (n ca. 7). $C_{14}H_{10}$-O_2RuSe_2 calcd.: C, 35.84; H, 2.13; Ru, 21.55%.] From Band VI was obtained the major product of the reaction as a dark yellow powder which is formulated as $[Ru(CO)_2(SePh)_2]_n$, m.p., ca. 200° (decompn.). [Found: C, 35.05; H, 2.41; Ru, 22.03; Se, 33.38; mol.wt. in $CHCl_3$, 6700 (n ca. 14). $C_{14}H_{10}O_2RuSe_2$ calcd.: C, 35.84; H, 2.13; Ru, 21.55; Se, 33.66%.]

Instrumentation and analyses

Instrumentation used for IR, mass spectral, osmometric molecular weight, and melting point measurements was the same as previously mentioned[2].

Analyses for carbon and hydrogen were carried out by Mr. R. Seab of the Department of Chemistry, Louisiana State University. Iron and ruthenium analyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee, and iron, selenium, and tellurium analyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany.

RESULTS AND DISCUSSION

Dinuclear complexes $[M(CO)_3EPh]_2$ (E=Se, Te; M=Fe, Ru) are the first products to be isolated from the reactions of the dodecacarbonyls with the diphenyl dichalcogenides. However, when M=Ru, the dinuclear complexes react further with Ph_2E_2 to form two series of polymeric materials $[Ru(CO)_2(EPh)_2]_n$, where n is approximately seven in one series and approximately fourteen in the other.

The reactions of $Fe_3(CO)_{12}$ were carried out with a molar excess of Ph_2E_2 and chromatographic separations gave no indication of carbonylated products other than $[Fe(CO)_3EPh]_2$. However, when an excess of Ph_2E_2 was used in the reactions of $Ru_3(CO)_{12}$ and the reactions were allowed to proceed until TLC indicated that the ruthenium substrate had completely reacted, only polymeric products were isolated. Using a 2 to 3 ratio of $Ru_3(CO)_{12}$ to Ph_2E_2 in these reactions led to a product mixture consisting of about 90% polymeric compounds and 10% dinuclear compounds. It is clear that the tendency toward substitution of CO by chalcogen is greater with the ruthenium dinuclear compounds than with the corresponding iron complexes.

TABLE 1

CARBONYL STRETCHING FREQUENCIES (cm^{-1}) FOR THE DINUCLEAR COMPLEXES $[M(CO)_3X]_2$

M	X	v_1	v_2	v_3	v_4	Solvent	Ref.
Fe	SEt	2073	2037	2000	1991	CCl_4	15
Fe	SPh	2078	2041	2009	2001	CCl_4	15
Fe	SePh	2061	2031	1998	1991	C_6H_{12}	a
Fe	TePh	2058	2021	1990	1983	C_6H_{12}	a
Ru	SPh	2086	2058	2014	1973	CCl_4	6
Ru	SePh	2081	2052	2006 (br)		$CHCl_3$	a
Ru	TePh	2073	2044	2002 (br)		$CHCl_3$	a

^{a} This work.

Shown in Table 1 are carbonyl stretching frequencies for the dinuclear complexes $[M(CO)_3EPh]_2$ (M = Fe, Ru; E = S, Se, Te). The similar IR patterns are taken as evidence of comparable structures. An X-ray study[8] of $[Fe(CO)_3SEt]_2$ has shown it to have a folded Fe_2S_2 ring with an *anti*-conformation of alkyl groups (I). This structural information, in conjunction with NMR and IR spectral data[9,10], suggests that a

(I)   (II)
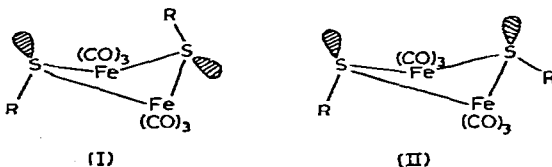
second isomer of $[Fe(CO)_3SR]_2$ complexes has a *syn*-arrangement (II) of groups in the bridging unit. Both *anti*- and *syn*-isomers were previously observed for the iron complexes $[Fe(CO)_3SR]_2$ (R = Et, PhCH$_2$, and Me) whereas with R = tert-butyl only the *anti*-isomer was detected, and it was suggested[10] that the steric factors might be prohibitive in regard to existence of the *syn*-isomer for bulky R-groups. No isomers were found for the (phenylseleno)- and (phenyltelluro)iron complexes reported herein, but TLC offered some evidence for the existence of isomers of $[Ru(CO)_3SePh]_2$, although only one isomer was isolated in sufficient quantity for characterization. In the

TABLE 2

CARBONYL STRETCHING FREQUENCIES (cm^{-1}) FOR $[Ru(CO_2)(EPh)_2]_n$[a]

E	v_1	v_2	v_3
Se[b]	2096 m	2037 s	1974 m (br)
Se[c]	2105 w	2037 s	1974 m (br)
Te[b]	2085 m	2030 s	1974 m (br)
Te[c]	2095 w	2027 s	1974 m (br)

[a] Recorded in CHCl$_3$ solution. [b] Lower molecular weight polymer ($n = 6-7$). [c] Higher molecular weight polymer ($n = 12-14$).

context of the steric rationale advanced by Bor for iron–sulfur complexes, it would seem that isomers would be much more likely for the larger ruthenium atom, particularly with selenium and tellurium as bridging atoms.

Mass spectra of the $[Fe(CO)_3EPh]_2$ compounds have weak peaks for the parent molecular ions and for ions corresponding to loss of two to five CO groups.

TABLE 3

MASS SPECTRA RELATIVE ABUNDANCES OF $[Fe(CO)_3EPh]_2$[a]

Ion	Relative abundances		
	E = S	E = Se	E = Te
$Fe(CO)_6E_2Ph_2^+$	8.2	4.4	6.2
$Fe_2(CO)_5E_2Ph_2^+$	0.8		
$Fe_2(CO)_4E_2Ph_2^+$	16.3	9.7	3.0
$Fe_2(CO)_3E_2Ph_2^+$	8.2	3.8	4.9
$Fe_2(CO)_2E_2Ph_2^+$	5.7	3.2	2.5
$Fe_2(CO)E_2Ph_2^+$	13.2	7.9	3.6
$Fe_2E_2Ph_2^+$	100	61.6	43.8
$Fe_2E_2Ph^+$	51	19.5	vw
$Fe_2E_2^+$	41.7	100	100
FeE_2^+		w	w
Fe_2E	16.3	w	m
Fe_2^+	2.8		
Fe^+	4.8	w	m

[a] Taken at 70 eV; data for E = S from ref. 11.

In Table 3 mass spectral data for analogous sulfur[11], selenium, and tellurium compounds are listed. It is interesting that relative abundances of the $Fe_2E_2^+$ ions decrease in the order of E as S < Se, Te. Also significant is the appearance of FeE_2^+ ions when E = Se and Te but not when E = S. These data may be an indication of iron–chalcogen bond strengths decreasing in the order of E as Te, Se > S.

Attempts to obtain mass spectra of the dinuclear ruthenium compounds were disappointing in that no peaks were observed that could be assigned to ions containing ruthenium–chalcogen or ruthenium–ruthenium bonds. This behavior is at first surprising in view of the presumed metal–metal bond in $[Ru(CO)_3EPh]_2$. Thermogravimetric plots of these compounds revealed no mass loss until 150–160°. Residual material removed from the thermogravimetric balance after heating to ca. 200° had an IR spectrum which was different from the spectra of the unheated samples. Apparently, loss of carbon monoxide is accompanied by aggregation of the dinuclear units to give non-volatile polymers (vide infra).

The polymeric materials isolated from the reactions of Ph_2E_2 (E = Se, Te) with $Ru_3(CO)_{12}$ are of formula $[Ru(CO)_2(EPh)_2]_n$ and were found in two degrees of polymerization. The lower weight polymers have about six to seven units per molecule and the higher weight ones consist of approximately twelve to fourteen units per molecule. The low molal solubility of these materials causes some uncertainty in the osmometric molecular weight results. However, several determinations were made on each material and on materials from different reactions and these measurements fell always in the above-mentioned limits. The lower molecular weight polymers containing Se and Te described here, i.e. $[Ru(CO)_2(EPh)_2]_{6-7}$ compare both in IR spectra (Table 2) and number of structural units with a sulfur polymer $[Ru(CO)_2(SPh)_2]_n$ reported by two groups[6,7]. An insoluble iron compound with an analogous empirical formula, $[Fe(CO)_2(SCH_3)_2]_m$ but of an unknown degree of aggregation, had been reported earlier[12]. For the ruthenium–sulfur polymer a structural analogy to the presumed kinked-chain halogen-bridged polymers $[Ru(CO)_2X_2]_n$ (II) was suggested[7].

(III)
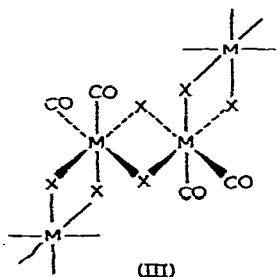
However, the presence of three bands (and possibly four considering the broadness of the lowest energy absorption) in the carbonyl region of the IR spectra of the chalcogen-bridged polymers of ruthenium would suggest a different symmetry than in the halogen-bridged dicarbonyl complexes of iron[13] and ruthenium[14] $[M(CO)_2I_2]_n$, or the halogen-bridged dinitrosyl complexes of molybdenum and tungsten[13] $[M(NO)_2-X_2]_n$ where only two bands are observed. Also, the halogen-bridged polymers are insoluble in common solvents, quite unlike the chalcogen-bridged polymers reported here which are soluble in CH_2Cl_2 and $CHCl_3$. The kinked-chain structure (III) does not require metal–metal bonding in order to conform to the 18-electron rule, and

considering the much greater polymerization tendency of the ruthenium dinuclear complexes $[Ru(CO)_3EPh]_2$ relative to the iron dinuclear compounds, it would be surprising if a ruthenium polymer without metal–metal bonding could be so easily formed at the expense of a dinuclear species containing a metal–metal bond. And it would seem that a chain structure might be of quite variable length and not yield only two classes of polymers where the heavier class is essentially double the molecular weight of the lighter class. While it is not profitable to speculate further about the structures, we do believe for the reasons given above that a cluster arrangement may be more likely than a chain structure. Whatever the structure, the compounds are quite stable. They decompose thermally only when heated above 200° and can be repeatedly recrystallized from mixed solvents in air without apparent decomposition.

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