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Metal Complexes of Telluroether: Crystal Structure of $(Ph_2Te)Fe(CO)_3I_2$ and $(Ph_2Te)W(CO)_5$

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Introduction

Although the chemistry of transition metal–thioether complexes is extensive,[1] iron–telluroether complexes are less well-known,[1-3] and few X-ray diffraction measurements of iron–telluroether complexes have been reported.[1,4] The reason is probably the perception that iron–telluroether chemistry is similar to that with thioether.[1,2] Iron–telluroether complexes suffer from inherent instability and are difficult to isolate as crystalline solids.[1,2,5] Here we report the first crystalline iron(II)–telluroether complexes.[3] The observation of transfer of the diphenyl telluroether ligand from Fe(II) to W(0) in the reaction of $(Ph_2Te)Fe(CO)_3I_2$ with $W(CO)_5(THF)$ provides a comparison of the relative stability of bonding of diphenyl telluroether toward the $W(CO)_5$ and $Fe(CO)_3I_2$ fragments.

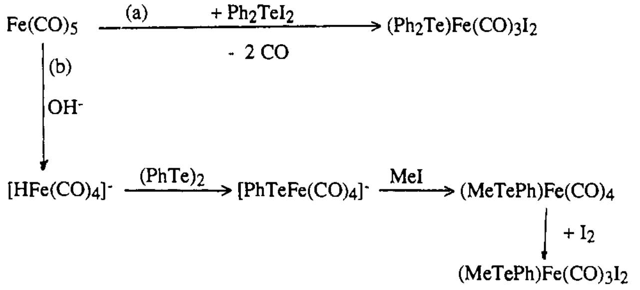
Results and Discussion

Iron pentacarbonyl reacted rapidly with Ph_2TeI_2, obtained as a brown solid by addition of I_2 to diphenyl telluroether in diethyl ether solution,[6,7] in tetrahydrofuran (THF) at ambient temperature to give a dark brown-red solution from which the moderately air- and light-sensitive crystalline solid $(Ph_2Te)Fe(CO)_3I_2$ was isolated in 93% yield after recrystallization with hexane. The reaction proceeded by oxidative addition of the I–I bond to Fe(0) and ligand displacement, as shown in Scheme 1a. $(Ph_2Te)Fe(CO)_3I_2$ is stable either as a solid or in organic solution under N_2 atmosphere at room temperature, but decomposes at $T > 55$ °C.

The analogous $(MeTePh)Fe(CO)_3I_2$ was prepared via facile oxidative addition of I_2 to freshly prepared oily $(MeTeR)Fe(CO)_4$, obtained by methylation of $[RTeFe(CO)_4]^-$,[2] in equimolar proportions in THF at room temperature (Scheme 1b).

The structure of $(Ph_2Te)Fe(CO)_3I_2$ was confirmed by X-ray diffraction of a single crystal. The distinctive IR ν_{CO} spectrum of $(Ph_2Te)Fe(CO)_3I_2$ contains one strong band and two medium bands at 2087 s, 2042 m, and 2025 m cm^{-1}, in contrast to two strong bands (ν_{CO}) in the anionic *fac*-$[Fe(CO)_3(TePh)_3]^-$ in THF.[5] We attribute this to the unsymmetrical bonding environment around the iron metal atom in $(Ph_2Te)Fe(CO)_3I_2$.

Scheme 1



An ORTEP drawing of the structure of $(Ph_2Te)Fe(CO)_3I_2$ determined from X-ray diffraction of a single-crystal appears in Figure 1. In crystals of this monomeric complex, the coordination geometry around the Fe(II) center is a distorted octahedron. The length, 2.585(2) Å, of the $Fe-Te(Ph)_2$ bond in $(Ph_2Te)Fe(CO)_3I_2$ is comparable to another $Fe-Te(Me)_2$ distance, 2.533(1) Å, of the structurally characterized, corresponding cationic iron–telluroether complex $[CpFe(CO)_2(TeMe_2)]^+$.[4]

The intramolecular Te···I contact distances in $(Ph_2Te)Fe(CO)_3I_2$ are in the range 3.423(2)–3.486(2) Å, which is greater than Te–I bond length 2.928(1) Å in the α-Ph_2TeI_2 free ligand[7] but much smaller than 4.35 Å, the sum of the van der Waals radii of tellurium and iodide.[8] Although the result (Te···I contact distance average 3.454(2) Å) indicates the absence of direct Te–I bonding, intramolecular Te···I interactions (I–Fe–Te average 83.55(7)°) are considered to be significant in $(Ph_2Te)Fe(CO)_3I_2$

The intramolecular I(1)···I(2) contact distance is 3.759(3) Å (I(1)–Fe–I(2) 92.58(6)°) in $(Ph_2Te)Fe(CO)_3I_2$.

The two Te–C bonds (2.118(7) and 2.068(8) Å) in $(Ph_2Te)Fe(CO)_3I_2$ have an average length of 2.093(8) Å which corresponds to the sum of the radii, 2.10 Å, of Te (1.37 Å) and sp^2 C (0.73 Å),[8] and parallels the Te–C bond length of 2.13(2) Å in the Ph_2TeI_2 free ligand.[7]

$(Ph_2Te)Fe(CO)_3I_2$ reacted with $W(CO)_5(THF)$ in THF at ambient temperature to yield an orange yellow solution from which the air-stable crystalline solid $(Ph_2Te)W(CO)_5$ was isolated in 62% yield after removal of solvent and recrystallization with hexane. Attempts to isolate, and observe spectrally, an intermediate were unsuccessful.

According to its crystal structure, $(Ph_2Te)W(CO)_5$ has an almost regular octahedral coordination geometry (Figure 2). The $W-TePh_2$ bond of length 2.809(1) Å is comparable with the W–Te bond of length 2.784(1) Å in pentacarbonyl(3-phenyl-2-tellurobicyclo[2.2.1]hept-5-ene)tungsten.[9] The C(6)–Te–C(12) bond angle 94.8(5)° indicates a greatly distorted tetrahedral disposition of electron pairs about the tellurium atom.

Experimental Section

All reactions were performed under nitrogen using standard Schlenk techniques. Reagents were purchased from Aldrich Chemical Co. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-7 FTIR) using 0.1-mm sealed KBr solution cells. NMR spectra were measured on a Bruker AC 200 spectrometer. UV–visible spectra were recorded on a GBC 918 spectrophotometer. Elemental analysis was made on a CHN analyzer (Heraeus).

Synthesis of $(Ph_2Te)Fe(CO)_3I_2$. The neutral $(Ph_2Te)Fe(CO)_3I_2$ was prepared by dissolving Ph_2TeI_2 (805 mg, 1.5 mmol) in THF (10 mL)[6,7] and treating it with $Fe(CO)_5$ (198 μL, 1.5 mmol) added via microsyringe. The reaction occurs immediately with observable evolution of gaseous CO. The dark brown-red solution was then concentrated after stirring

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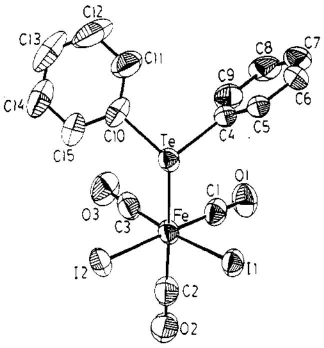

Figure 1. ORTEP drawing and labeling scheme for $(Ph_2Te)Fe(CO)_3I_2$. Thermal ellipsoids represent the 50% probability level.

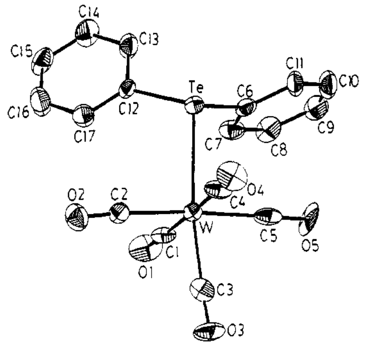

Figure 2. ORTEP drawing and labeling scheme for $(Ph_2Te)W(CO)_5$ with thermal ellipsoids drawn at the 50% probability level.

for 20 min at room temperature. Slow addition of hexane (5 mL) and storage for 2 weeks at 4 °C produced a dark brown-red crystalline product (935 mg, 93% yield). IR ν_{CO} (THF): 2087 s, 2042 m, 2025 m cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.5–8.0(m) ppm (C_6H_5). ^{13}C NMR (CD_3COCD_3): δ 211.6(s) (*C*O), 136.5 (s), 131.9 (s), 131.0 (s), 120.5 (s) ppm (C_6H_6). Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1}, cm^{-1})]: 323 (28 224), 357 (15 876). Anal. Calcd for $C_{15}H_{10}O_3TeI_2Fe$: C, 26.67; H, 1.49. Found: C, 26.85; H, 1.64.

Preparation of (MeTePh)Fe(CO)$_3$I$_2$. The complex $(MeTePh)Fe(CO)_3I_2$ was made by combining I_2 (127 mg, 0.5 mmol) and freshly prepared oily $(MeTePh)Fe(CO)_4$ (addition of MeI to [PPN][PhTeFe(CO)$_4$] (456 mg, 0.5 mmol)) in THF (5 mL)[2] and stirring the mixture for 5 min at ambient temperature. The dark brown-red solution was layered with hexane (5 mL); storage for 2 weeks at 4 °C led to formation of dark brown-red crystals (287 mg, 94% yield) of the product. IR ν_{CO} (THF): 2085 s, 2038 m, 2018 m cm^{-1}. ^1H NMR (CD_3COCD_3): δ 2.8 (s) (CH_3), 7.5–8.1 (m) ppm (C_6H_5). ^{13}C NMR (CD_3COCD_3): δ 211.8 (CO), 117.8, 130.2, 131.0, 134.2 (C_6H_5, $\mathit{C}H_3$, unresolved). Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1}, cm^{-1})]: 334 (24 861), 365 (18 181).

Reaction of (Ph$_2$Te)Fe(CO)$_3$I$_2$ and W(CO)$_5$(THF). A solution of $(Ph_2Te)Fe(CO)_3I_2$ (203 mg, 0.3 mmol) in THF (5 mL) was added to $W(CO)_5(THF)$ obtained by photolysis of $W(CO)_6$ (106 mg, 0.3 mmol) in THF (15 mL) at room temperature. The reaction mixture was stirred for 0.5 h, and the solvent was removed under vacuum. Hexane was added to extract the neutral product. Recrystallization of the product from hexane and then cooling to 4 °C for 2 weeks afforded orange-yellow crystals of $(Ph_2Te)W(CO)_5$ isolated yield 62%. IR ν_{CO} (THF): 1922 sh, 1940 vs, 1982 vw, 2070 w cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.34–7.78 (m) ppm (C_6H_5). ^{13}C NMR (CD_3CN): δ 200.6(s), 198.1(s) (*C*O), 139, 137.1, 130.9, 116.3 ppm (C_6H_5). Anal. Calcd for $C_{17}H_{10}O_5TeW$: C, 33.71; H, 1.67. Found: C, 33.74; H, 1.88.

Table 1. Crystallographic Data for $(Ph_2Te)Fe(CO)_3I_2$ and $(Ph_2Te)W(CO)_5$

	$(Ph_2Te)Fe(CO)_3I_2$	$(Ph_2Te)W(CO)_5$
chem formula	$C_{15}H_{10}O_3TeFeI_2$	$C_{17}H_{10}O_5TeW$
fw	675.53	605.75
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbca*
λ, Å (Mo Kα)	0.7107	0.7107
a, Å	9.998(3)	12.892(2)
b, Å	10.139(4)	17.068(2)
c, Å	10.288(7)	16.289(2)
α, deg	103.32(4)	90.0
β, deg	97.54(4)	90.0
γ, deg	112.46(3)	90.0
V, Å^3	909.6(8)	3584.1(8)
Z	2	8
d (calcd), g cm^{-3}	2.466	2.245
μ, cm^{-1}	57.73	82.06
abs (min and max transm coeff)	0.393–1.000	0.643–1.000
$F(000)$	616	2224
T, °C	25	25
R^a	0.035	0.030
$R_w{}^b$	0.037	0.032

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for (a) $Ph_2Te)Fe(CO)_3I_2$ and (b) $(Ph_2Te)W(CO)_5$

	(a) $(Ph_2Te)Fe(CO)_3I_2$		
Fe–Te	2.585(2)	Fe–I(1)	2.564(2)
Fe–I(2)	2.636(2)	Fe–C(1)	1.770(9)
Fe–C(2)	1.823(9)	Fe–C(3)	1.727(9)
Te–C(4)	2.118(7)	Te–C(10)	2.068(8)
I(1)–Fe–I(2)	92.58(6)	I(1)–Fe–Te	83.32(7)
I(1)–Fe–C(1)	85.4(3)	I(1)–Fe–C(2)	88.0(3)
I(1)–Fe–C(3)	174.6(3)	I(2)–Fe–Te	83.78(5)
Te–Fe–C(1)	96.3(3)	Te–Fe–C(2)	165.9(3)
Te–Fe–C(3)	93.8(3)	Fe–Te–C(4)	105.6(2)
Fe–Te–C(10)	109.8(2)	C(4)–Te–C(10)	94.3(3)
	(b) $(Ph_2Te)W(CO)_5$		
W–Te	2.809(1)	Te–C(6)	2.12(1)
Te–C(12)	2.13(1)	W–C(1)	2.03(2)
W–C(2)	1.99(2)	W–C(3)	2.04(2)
W–C(4)	2.03(2)	W–C(5)	2.07(2)
C(6)–Te–C(12)	94.8(5)	Te–W–C(1)	92.8(4)
Te–W–C(2)	97.0(4)	Te–W–C(3)	172.2(4)
Te–W–C(4)	88.3(4)	Te–W–C(5)	87.1(4)
W–Te–C(6)	101.0(4)	W–Te–C(12)	109.0(4)

Crystallography. The crystal data are summarized in Table 1. The moderately air-sensitive crystal $(Ph_2Te)Fe(CO)_3I_2$ chosen for diffraction measurement was ca. 0.10 × 0.50 × 0.50 mm (the air-stable crystal $(Ph_2Te)W(CO)_5$ had crystal dimensions 0.05 × 0.20 × 0.30 mm) was mounted on a glass fiber and coated in epoxy resin. The unit-cell parameters were obtained from 25 reflections (16.62° < 2θ < 24.40° for $(Ph_2Te)Fe(CO)_3I_2$; 17.60° < 2θ < 32.00° for $(Ph_2Te)W(CO)_5$). Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation employing the $\theta/2\theta$ scan mode. A ψ scan absorption correction was made. Structural determinations were made using the NRCC-SDP-VAX package of programs.[10] Selected bond distances and angles are listed in Table 2.

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Supplementary Material Available: Complete crystallographic data, bond lengths and angles, atomic parameters, and $u(i,j)$ or U values for $(Ph_2Te)Fe(CO)_3I_2$ and $(Ph_2Te)W(CO)_5$ (8 pages). Ordering information is given on any current masthead page.

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