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(*Z*)-Diiodo(2-iodo-2-phenylvinyl)(phenyl)tellurium $PhIC=CHTeI_2Ph$: Synthesis and Complexing Properties in a Reaction with Iron Pentacarbonyl

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Abstract—Electrophilic addition of $PhTeI_3$ to phenylacetylene (PhC_2H) in boiling THF stereoselectively gave (*Z*)-diiodo(2-iodo-2-phenylvinyl)(phenyl)tellurium $PhIC=CHTeI_2Ph$ (**I**). In a reaction with $Fe(CO)_5$, this complex easily eliminated two iodine atoms from tellurium to give PhTe–CH=CPhI. This ligand was coordinated to iron in a monodentate fashion through the Te atom in the resulting complex $(CO)_3FeI_2(PhTeHC=CPhI)$ (**II**). The reaction also yielded the known complex $Fe(CO)_4I_2$ (**III**). The structures of complexes **I**–**III** were determined by X-ray diffraction analysis. The Fe–Te bond in structure **II** is substantially shortened.

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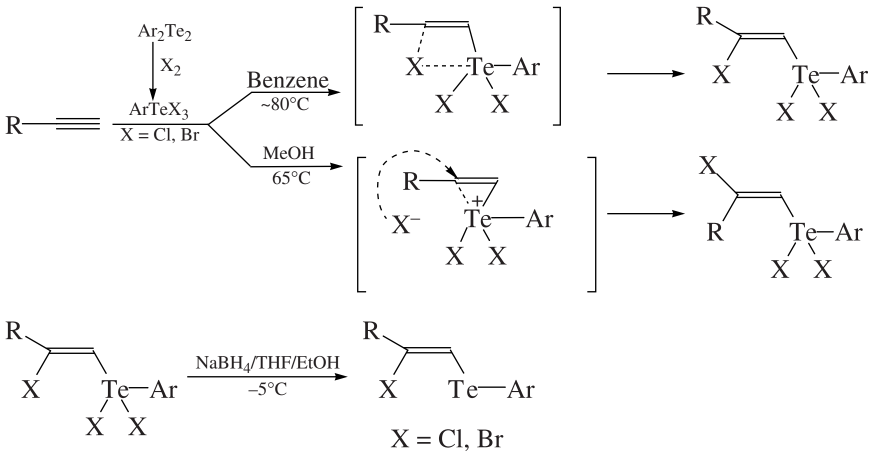
Aryltellurium trihalides $ArTeX_3$ (X = Cl or Br) [1] obtained from stoichiometric amounts of diaryl ditelluride and elemental halogen have found use in organic chemistry because of their tendency toward stereo- and regioselective electrophilic addition to the triple C–C bond of terminal acetylenes, giving (aryl)dihalo(halovinyl)tellurium(IV) [2, 3]. It has been demonstrated that reflux of $ArTeX_3$ with acetylene can yield Z- and E-isomers, depending on the solvent polarity. Further reduction with $NaBH_4$ or $Na_2S_2O_3$ can afford the corresponding aryl halovinyl tellurides (Scheme 1):



The behavior of aryltellurium triiodides in such reactions has not been documented hitherto. According to X-ray diffraction data, triiodo(phenyl)tellurium in the crystal forms dimers with bridging iodine atoms [4]. We found it interesting to study its reaction with phenylacetylene and reactions of the resulting (aryl)diiodo(iodovinyl)tellurium(IV) with iron pentacarbonyl. The latter reactions could be assumed to be similar to a known oxidative addition of diiodo(diphenyl)tellurium(IV) to $Fe(CO)_5$ [5]:

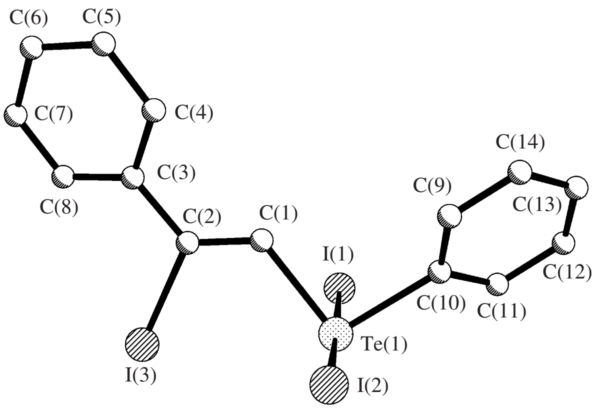
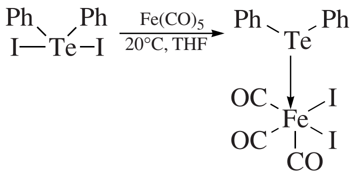


Fig. 1. Molecule **IA** in crystal structure **I**.



EXPERIMENTAL

All manipulations dealing with the synthesis and isolation of the complexes were carried out under pure argon in dehydrated solvents. IR spectra were recorded on a Specord 75IR spectrophotometer for pellets with KBr and solutions in heptane.

Synthesis of $PhTeI_2HC=CPhI$ (I). Triiodo(phenyl)tellurium (1.15 g, 2 mmol) (prepared from $PhTe_2$ (0.4 g) and I_2 (0.75 g)) and phenylacetylene (0.22 ml, 2 mmol) were refluxed in THF (30 ml) for 12 h. The solvent was removed in a water aspirator vacuum. The orange red residue was washed with light petroleum. The product was extracted with CH_2Cl_2 and precipitated by concentrating the extract with heptane in a water aspirator vacuum. Crystals suitable for X-ray diffraction analysis were grown from a concentrated solution of complex **I** in CH_2Cl_2–heptane (1 : 1).

For $C_{14}H_{11}I_3Te$ (M = 687.55) anal. calcd. (%): C, 24.46; H, 1.61.

Found (%): C, 24.70; H, 1.85.

IR (KBr, cm^{-1}): 720 s, 680 s, 650 s.

Synthesis of $(CO)_3FeI_2(PhTe–CH=CPhI)$ (II) and $Fe(CO)_4I_2$ (III). Iron pentacarbonyl (0.04 ml, 0.28 mmol) was added in one portion at room temperature to a magnetically stirred orange red solution of complex **I** (0.16 g, 0.23 mmol) in diethyl ether (30 ml). Stirring was continued for an additional 30 min. The reaction mixture turned deep red and homogeneous and no longer contained the starting complex **I** (TLC data). The solution was concentrated with heptane (5 ml) *in vacuo* to slight turbidity. The concentrate was kept at –10°C for 12 h. The dark red crystalline precipitate that formed consisted of thick needles of complex **II** and prisms of the known complex **III** [6].

Below are the IR spectra and elemental analysis data for complexes **II** and **III**.

IR (KBr, cm^{-1}): 2125 s, 2085 s, 2070 s. IR (heptane, cm^{-1}): 2125 m, 2075 s, 2060 m.

For $C_{17}H_{11}TeI_3O_2Te$(II) (M = 827.43)		
anal. calcd. (%):	C, 24.68;	H 1.34.
Found (%):	C, 20.88;	H 0.87.
For $C_4FeI_2O_4$(III) (M = 421.70)		
anal. calcd. (%):	C, 11.39.	

The complexes are unstable under the conditions of column chromatography. The crystals of complexes **II** and **III** for X-ray diffraction analysis were selected by mechanical separation.

X-ray diffraction analysis. Selected crystallographic parameters and a summary of data collection and refinement for structures **I–III** are given in Table 1. All structures were solved by the direct method and refined by the least-squares method on F^2 in the anisotropic (for H atoms, isotropic) approximation with the SHELXTL program package [7]. The hydrogen atoms were located geometrically. Selected bond lengths and angles in structures **I–III** are given in Tables 2 and 3. Atomic coordinates and other structural parameters of complexes **I–III** have been deposited with the Cambridge Crystallographic Data Center (CCDC nos. 688683 (I), 690063 (II), and 688684 (III); see http://www.ccdc.cam.ac.uk/data_request/cif).

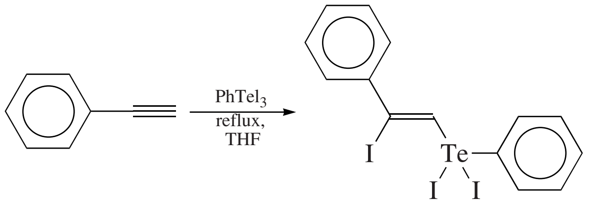
RESULTS AND DISCUSSION

We carried out a reaction of $PhTeI_3$ with phenylacetylene in boiling THF. More prolonged reflux was required, in contrast to analogous reactions with (aryl)dibromotellurium(IV) and (aryl)dichlorotellurium(IV) usually completed in 3–10 h. The resulting dark orange crystals of the adduct were stable in air and soluble in polar organic solvents. According to X-ray

Table 1. Selected crystallographic parameters and a summary of data collection and refinement for structures I–III

Parameter	Value		
	I	II	III
Diffractometer	Bruker APEX II CCD		
Radiation (λ, Å)	MoK_{α} (0.71073)		
Temperature	296(2)		
Space group	$P2_1/c$	$C2/c$	$C2/c$
a, Å	11.2403(5)	7.078(2)	26.375(5)
b, Å	8.5755(4)	10.906(2)	10.0848(16)
c, Å	36.3256(17)	12.633(3)	17.701(3)
β, deg	98.068(1)	92.268(5)	103.441(4)
V, Å^3	3466.8(3)	974.4(4)	4579.3(13)
Z	8	2	8
ρ(calcd), g/cm^3	2.635	2.137	2.400
μ, mm^{-1}	7.042	5.816	5.964
F(000)	2448	580	2992
θ scan range, deg	2.01–29.00	3.23–28.98	1.59–29.00
Scan mode	ω		
Number of measured reflections	37252	3653	24582
Number of independent reflections (N_1)	9193 = 0.0562)	1277 (R_{int} = 0.0320)	6079 (R_{int} = 0.0300)
Number of reflections with $I > 2(I)$ (N_2)	5294	1076	4810
Number of parameters refined	325	51	226
GOOF (F^2)	0.973	1.033	1.023
R_1 for N_2	0.0415	0.0264	0.0364
wR_2 for N_1	0.0919	0.0686	0.1006
$\Delta\rho_{max}/\rho_{min}$, e Å^{-3}	1.326/–1.604	0.871/–0.590	1.926/–1.230

diffraction data, the adduct is the (*Z*)-isomer of diiodo(2-iodo-2-phenylvinyl)(phenyl)tellurium(IV) (**I**):



(**I**)

The unit cell of crystal structure **I** comprises two crystallographically independent molecules **IA** (Fig. 1) and **IB**. In their two sublattices, the Te–I distances are 2.9098(7)–2.9308(7) Å and 2.8777(7)–2.9723(7) Å. These values are close to the sum of the covalent Te and I radii [8] and to normal bond lengths in diorganotellurium(IV) diiodides [4]. The Te···I distances differ only slightly; this can be explained by the packing effect in the crystal, viz., nonvalent Te···I and I···I interactions. Independent molecules **IA** are united in the crystal through the I(1)···Te(1) contacts (3.665(1) Å). Molecules **IB** are linked by the Te(1*A*)···I(2*A*) contacts (3.752(1) Å) into centrosymmetric dimers, which form chains via the I(1*A*)···I(3*A*) contacts (3.775(1) Å). It should be noted that the interactions in chains differ in both contact length and direction. For instance, the angle C(1)Te(1)I(1) is 165.7(1)° for the chains of molecules **IA** and 175.8° for molecules **IB** (Fig. 2).

Table 2. Selected bond lengths and angles in the crystallographically independent molecules IA and IB of complex I

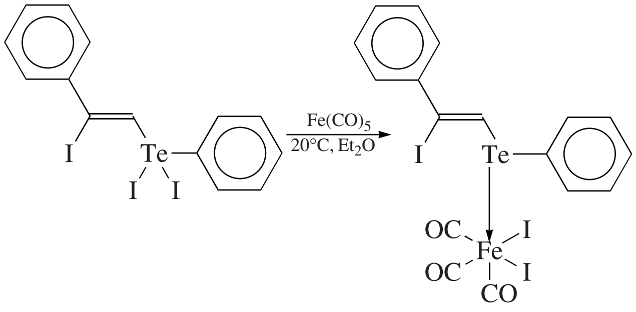
Bond	d, Å	Bond	d, Å
IA		IB	
Te(1)–C(1)	2.109(6)	Te(1*A*)–C(1*A*)	2.097(6)
Te(1)–C(10)	2.126(6)	Te(1*A*)–C(10*A*)	2.129(6)
Te(1)–I(2)	2.9098(7)	Te(1*A*)–I(1*A*)	2.8777(7)
Te(1)–I(1)	2.9308(7)	Te(1*A*)–I(2*A*)	2.9723(7)
C(1)–C(2)	1.310(8)	C(1*A*)–C(2*A*)	1.299(8)
C(2)–I(3)	2.110(6)	C(2*A*)–I(3*A*)	2.113(6)
Angle	ω, deg	Angle	ω, deg
I(2)Te(1)I(1)	178.14(2)	I(1*A*)Te(1*A*)I(2*A*)	175.04(2)
C(2)C(1)Te(1)	124.3(5)	C(2*A*)C(1*A*)Te(1*A*)	123.8(5)
C(1)C(2)I(3)	118.1(5)	C(1*A*)C(2*A*)I(3*A*)	117.0(5)

Table 3. Selected bond lengths and angles in structure **II**

Bond	*d*, Å
III	
Te(1)–C(1)	2.100(5)
Te(1)–C(9)	2.110(6)
C(1)–C(2)	1.325(7)
C(2)–I(3)	2.120(5)
Fe(1)–I(1)	2.6335(9)
Fe(1)–I(2)	2.6349(9)
Te(1)–Fe(1)	2.5815(8)
Angle	**ω, deg**
C(1)Te(1)C(9)	97.2(2)
C(1)Te(1)Fe(1)	103.35(14)
C(9)Te(1)Fe(1)	100.16(15)
C(2)C(1)Te(1)	126.1(4)

In a room-temperature reaction of complex **I** with $Fe(CO)_5$ in ether, two iodine atoms are transferred from tellurium to iron with elimination of one CO group to give the known complex $Fe(CO)_4I_2$ (**II**) [6]. It was isolated and structurally characterized by X-ray diffraction data (the lengths of two *cis*-arranged Fe–I bonds are 2.6375(6) Å) (Fig. 3).

Replacement of another CO group in complex **I** by in situ generated (*Z*)-2-iodo-2-phenylvinyl phenyl telluride gives complex **III**. Its black red crystals are relatively stable in air and soluble in most organic solvents.



(I) (II)

According to X-ray diffraction data, the Te and I atoms in complex **III** are in opposition to the carbonyl groups (Fig. 4). The Fe–I distances (2.6335(9) and 2.6349(9) Å) correspond to the single bonds found in the complexes $(CO)_3FeI_2(L)$: e.g., 2.6482(7) and 2.6541(6) Å in $(CO)_3FeI_2(Te_2Ph_2)$ (**IV**) or 2.6478(7) and 2.6541(7) Å in $(CO)_3FeI_2(PhTeI)$ (**V**) [9]. At the same time, the Te–Fe distance (2.5815(8) Å), as in complexes **IV** and **V**, is substantially shorter than the sum of the covalent Fe and Te radii (2.70 Å) [8]. This is probably due to a dative interaction of the lone electron pairs on the Fe atom with the vacant *d* orbital of the Te atom, in addition to the donor–acceptor bonding between tellurium and iron.

Note that complexes **II** and **III** cannot be separated by crystallization and are unstable under the conditions of column chromatography. According to elemental analysis data, the ratio **II** : **III** is close to 30 : 70. Their

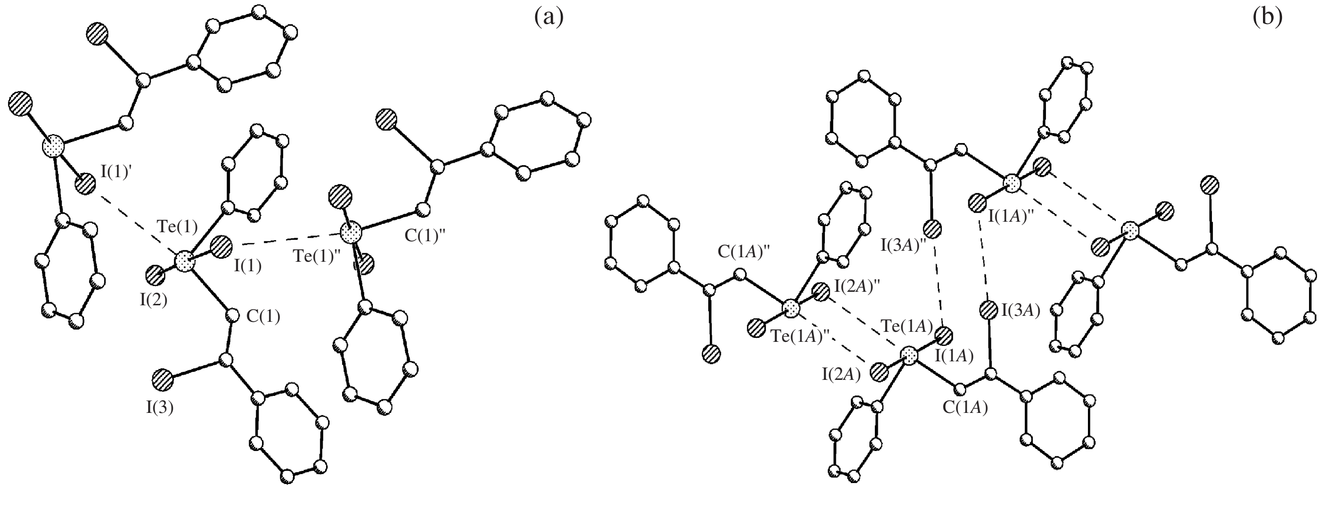


Fig. 2. Molecular packing of (a) **IA** and (b) **IB** in crystal structure **I**.

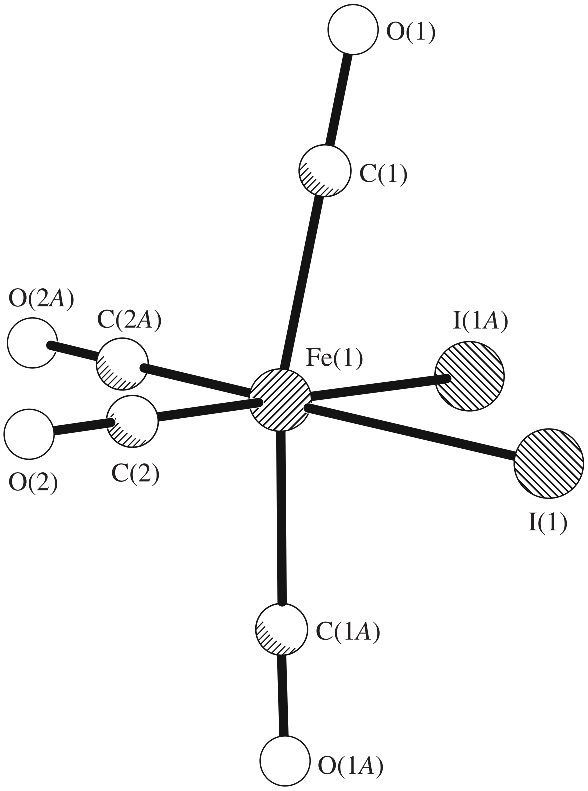


Fig. 3. Molecular structure **II** (Fe(1)–I(1) 2.6375(6) Å, Fe(1)–C(2) 1.811(4) Å, Fe(1)–C(1) 1.850(4) Å, O(1)–C(1) 1.111(5) Å, O(2)–C(2) 1.128(5) Å).

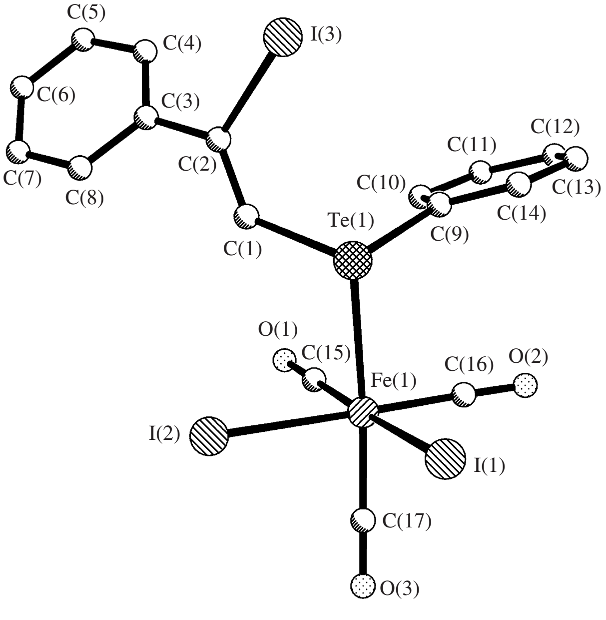


Fig. 4. Molecular structure **III**.

total IR spectrum is obviously a superposition of the known spectrum of complex **II** (2131, 2086, 2062, and 2047 cm^{-1}) in hexane [6] and the spectrum of complex **III**, which should be similar to the IR spectra of complexes **IV** and **V** in the range of CO stretching vibrations (ν, cm^{-1}: 2080 s, 2040 s, 2025 s [7]).

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