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Structure and Reactivity of Iron(0)-Phenyltellurolate [PPN][PhTeFe(CO)$_4$]

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Anionic iron(0) tetracarbonyl with terminal phenyltellurolate ligand PhTe$^-$, [PhTeFe(CO)$_4$]$^-$, has been synthesized and characterized. The title compound was obtained by addition of (PhTe)$_2$ to [PPN][HFe(CO)$_4$] THF solution dropwise. [PPN][PhTeFe(CO)$_4$] crystallizes in the monoclinic space group C c, with a = 16.119(4) Å, b = 13.141(3) Å, c = 19.880(8) Å, β = 93.04(3)°, V = 4205(2) Å^3, and Z = 4. The [PhTeFe(CO)$_4$]$^-$ anion is a trigonal-bipyramidal complex in which the phenyltellurolate ligand occupies an axial position with Fe-Te bond length 2.630(5) Å and the Fe-Te-C(Ph) angle is 103.4(5)°. The neutral iron(0)-telluroether compound, (PhTeMe)Fe(CO)$_4$, was prepared by alkylation of the [PhTeFe(CO)$_4$]$^-$. Protonation of [PhTeFe(CO)$_4$]$^-$ and reaction of $H_2Fe(CO)_4$ and (PhTe)$_2$ ultimately lead to formation of the known dimer $Fe_2(\mu\text{-TePh})_2(CO)_6$ and H_2.

INTRODUCTION

The ligand chemistry of thiolate RS$^-$ (R = alkyl or aryl) is well developed: several complexes with terminal and bridging RS$^-$ and RSe$^-$ ligands have been reported.[1] However the ligand chemistry of tellurolate has received little attention,[2] and structural data on terminal iron-tellurolates, in particular, are rare.[3] Presumably the lack of well characterized metal-tellurolate complexes reflect the sparse synthetic procedures. Synthetic approaches to metal-tellurolate complexes, to our knowledge, involve insertion of tellurium into the metal-alkyl bond,[4] metathesis between an alkali-metal tellurolate and a metal halide,[5] a tellurolysis pathway;[6] and oxidative addition of PhTeTePh to low-valent [PhTeFe(CO)$_4$]$^-$ (E = Te, Se) and nucleophilic cleavage of the Te-Te bond by metal hydrides.[7,8]

We have established that the reaction of [PPN][HFe(CO)$_4$] with diphenylditelluride in doubly molar proportions gives rise to *fac*-[PPN][Fe(CO)$_3$(TePh)$_3$] via intermediate [PPN][PhTeFe(CO)$_4$] complex.[7] The research has been extended to synthesis of iron(II)-mixed-phenylchalcogenolate *fac*-[PPN][Fe(CO)$_3$(TePh)$_n$(SePh)$_{3-n}$] (n = 0, 1, 2, 3) complexes.[8]

About the reactivity of iron-tellurolates, we report here the structure and reactivity of the unprecedented iron(0)-phenyltellurolate complex [PPN][PhTeFe(CO)$_4$].

EXPERIMENTAL SECTION

Manipulations, transfer and reactions of samples were carried out under standard Schlenk techinques (N_2 atmosphere) and in a nitrogen atmosphere glovebox. Solvents were distilled under N_2 from appropriate drying agents (hexane and tetrahydrofuran (THF) from Na/benzophenone; diethyl ether from lithium aluminium hydride; acetonitrile from CaH_2/P_2O_5) and then stored in dried, N_2-filled flasks over activated 4 Å molecular sieves. A nitrogen purge was used on these solvents prior to use and transfers to the reaction vessels were via stainless steel cannula under positive pressure of N_2. The reagents iron pentacarbonyl, $HBF_4 \cdot OEt_2$, methyl iodide, phenylmagnesium bromide, bis(triphenylphosphoranylidene)ammonium chloride, tellurium powder (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-7 FTIR) using 0.1-mm sealed KBr solution cells. NMR spectra were performed on Bruker AC 300 spectrometer. Analyses of carbon, hydrogen and nitrogen were made on a Heraeus CHN-O Rapid.

Syntheses of [PPN][PhTeFe(CO)$_4$]

To a light brown solution of [PPN][HFe(CO)$_4$][9] (0.707 g, 1 mmol) in THF (5 mL) was slowly added diphenylditelluride[10] THF solution (0.409 g, 1 mmol in 5 mL) drop by drop, and occasionally monitored by IR at ambient temperature. After the reaction was completed, the brown-red solution was then concentrated to 3 mL, and hexane was slowly added to precipitate a brown solid. The mother liquor was cannuled out and the solid was dried under vacuum. Recrystallization of the product from a minimum volume of THF, layering it with 4-fold proportion of hexane, and then cooling to 0 °C for two weeks afforded brown crystals of

[PPN][PhTeFe(CO)$_4$]: isolated yield 96%; IR (THF) 1900vs, 2002w cm^{-1}; ^{13}C NMR (CD_3CN) δ 219.4 (s) (CO), 118.2-138.6 (m) (C_6H_5); Anal. Calcd for $C_{46}H_{35}NO_4P_2TeFe$: C, 60.63; H, 3.88; N, 1.54, Found: C, 60.24; H, 4.04; N, 1.40.

Preparation of (PhTeMe)Fe(CO)$_4$

The starting material [PPN][PhTeFe(CO)$_4$] (0.912 g, 1 mmol) was placed in a Schlenk flask (50 mL) and dissolved in THF (5 mL). A portion of MeI (64 μL, 1 mmol)) was syringed into the [PPN][PhTeFe(CO)$_4$] THF solution. The solution was stirred for 20 min at 0°C, and a white precipitate of PPNI settled out. The THF solvent was removed under vacuum and the brown-red residue was extracted with hexane. Upon removal of hexane in vacuum, a red-brown oil (PhTeMe)Fe(CO)$_4$ was obtained. Attempts to obtain this neutral product as solid were unsuccessful. IR (THF) 1937s, 1961m, 2041m, (hexane) 1943s, 1947sh, 1974m, 2048m cm^{-1}; ^{1}H NMR (CD_3CN) δ 2.42 (CH_3); ^{13}C NMR (CD_3CN) δ 215.2 (CO). The spectral properties are consistent with alkylation at tellurium of phenyltellurolate of [PhTeFe(CO)$_4$]$^-$.

Reaction of [PPN][PhTeFe(CO)$_4$] and HBF$_4$·OEt$_2$

A portion (0.912 g, 1 mmol) of [PPN][PhTeFe(CO)$_4$] was loaded into a Schlenk flask (50 mL) and dissolved in THF (5 mL) at ambient temperature. Et_2O·HBF_4 solution (230 μL, 1 mmol) was syringed into the mixture. The reaction mixture was stirred for half hour. A red-brown solution and a white precipitate were formed. The solvent was removed under vacuum (2 mL left) and hexane (20 mL) was added to extract the red-brown product. The reaction mixture was monitored by IR to confirm the presence of the known [PhTeFe(CO)$_3$]$_2$ dimer:[11] IR (THF) 2054m, 2018vs, 1982s, 1965sh cm^{-1}, (hexane) 2056m, 2021vs, 1990m, 1982sh cm^{-1}. Recrystallization of the neutral product from a minimum amount of hexane, and then cooling to 0 °C for three weeks afforded brown-red crystals of [Fe(CO)$_3$(μ-TePh)]$_2$ dimer.

Reaction of H$_2$Fe(CO)$_4$ and (PhTe)$_2$

Into a Schlenk flask (20 mL) was loaded [PPN][HFe(CO)$_4$] (0.354 g, 0.5 mmol) and a portion (5 mL) of THF. A portion (115 μL, 0.5 mmol) of Et_2O·HBF_4 solution was syringed into the flask at -78 °C. The reaction mixture was stirred for 2 min, and then diphenylditelluride (0.5 mmol) THF solution was added into the flask by cannula. Upon warming to room temperature, the dimer [Fe(CO)$_3$(TePh)]$_2$ was formed:[11] IR (THF) 2054m, 2018vs, 1982s, 1965sh cm^{-1}.

Table 1. Crystallographic Data

Formula	$C_{46}H_{35}NO_4FeTeP_2$
F_w	911.17
Color	brown
Cryst size, mm	0.20 x 0.40 x 0.50
Cryst system	monoclinic
Space group	C c
a, Å	16.119(4)
b, Å	13.141(3)
c, Å	19.880(8)
β, deg	93.04(3)
V, Å^3	4205(2)
Z	4
F(000)	1711
λ (Mo K$_\alpha$)	0.71069 Å
D_{calc}, g/cm^3	1.439
2θ(max), deg	45
Scan range	
h	-17 to 17
k	0 to 14
l	0 to 21
No. of reflcns	2742
No. of unique reflcns	2742
No. of reflcns. obsd (I > 2σ (I))	1640
T_{max}/T_{min}	1.00/0.93
R (all data)	0.061 (0.114)
R_w (all data)	0.057 (0.060)
GOF	2.17
Resid. peak, e/Å^3	0.700
Resid. hole, e/Å^3	-0.780

X-ray Crystal Structure Determination of [PPN][PhTeFe(CO)$_4$]

Crystal data are collected in Table 1. Brown crystals of [PPN][PhTeFe(CO)$_4$] were mounted on glass fibers with epoxy cement. The unit cell parameters were obtained from 25 reflections with 2θ angle in the range from 15.54° to 18.90°. Diffraction measurements were carried out on a Nonius diffractometer (Mo K$_\alpha$ radiation). The monoclinic space group C c was assigned from statistics of intensity distribution and successful least squares refinement. The final least-squares cycle was based on 315 parameters and 1640 out of 2742 reflections. The final model of refinement is that all the nonhydrogen atoms of anion and P, N atoms of cation were refined anisotropically, the phenyl carbon atoms of PNP cation were refined isotropically, and all hydrogen atoms were fixed in their idealized positions. The final re-

Table 2. Selected Bond Lengths/Å and Bond Angles/deg

Bond Lengths/Å			
Te-Fe	2.630(5)	C(1)-O(1)	1.12(2)
Te-C(5)	2.06(3)	C(2)-O(2)	1.11(3)
Fe-C(1)	1.76(2)	C(3)-O(3)	1.20(4)
Fe-C(2)	1.83(2)	C(4)-O(4)	1.18(3)
Fe-C(3)	1.67(3)	C(5)-C(6)	1.41(3)
Fe-C(4)	1.76(2)	C(5)-C(10)	1.41(4)
Bond Angles/deg			
Fe-Te-C(5)	103.4(5)	C(2)-Fe-C(4)	91.2(12)
Te-Fe-C(1)	83.4(8)	C(3)-Fe-C(4)	114.7(13)
Te-Fe-C(2)	174.6(9)	Fe-C(1)-O(1)	174.1(21)
Te-Fe-C(3)	92.7(16)	Fe-C(2)-O(2)	165.6(24)
Te-Fe-C(4)	86.3(8)	Fe-C(3)-O(3)	175(5)
C(1)-Fe-C(2)	94.4(11)	Fe-C(4)-O(4)	177.6(22)
C(1)-Fe-C(3)	117.9(14)	Te-C(5)-C(6)	120.0(16)
C(1)-Fe-C(4)	126.6(10)	Te-C(5)-C(10)	125.0(21)
C(2)-Fe-C(3)	92.7(19)	P(1)-N-P(2)	142.7(9)

siduals of the refinement were R = 0.061 and R_w= 0.057. Selected bond lengths and angles appear in Table 2.

RESULTS AND DISCUSSION

Reaction of 1 equiv [PPN][$HFe(CO)_4$] with 2 equiv $(PhTe)_2$ in THF at room temperature (25 °C) leads to the formation of moderately air-, and light-sensitive, dark purple crystalline solid *fac*-[PPN][$Fe(CO)_3(TePh)_3$] via the intermediate iron(0)-phenyltellurolate [PPN][$PhTeFe(CO)_4$] identified by √(CO) FTIR.[7] The title compound, iron(0)-phenyltellurolate, was alternatively prepared by addition of 1 equiv diphenylditelluride (in THF) to 1 equiv [PPN][$HFe(CO)_4$] THF solution drop by drop, monitored by FTIR, and isolated as brown-red solid accompanied by formation of benzenetellurol which is known to decompose at ambient temperature (Eq. 1).

$$[PPN][HFe(CO)_4] + PhTeTePh \longrightarrow [PPN][PhTeFe(CO)_4] + PhTe\text{-}H \quad (1)$$

The mechanism of this hydride/tellurolate exchange reaction in iron-carbonyl-hydride complex is presumed to go via a nucleophilic replacement; however the single-electron-transfer pathway cannot be excluded as there are no kinetic data.

The [PPN][$PhTeFe(CO)_4$] salt is a stable crystal in the absence of air at 5 °C (at least 2 weeks). In THF solution [PPN][$PhTeFe(CO)_4$] is stable to prolonged (at least 2 h) periods at 60 °C.

An almost regular trigonal-bipyramidal structure, an idealized local C_{3v} symmetry for the $Fe(CO)_4$ unit, is retained in THF solution as indicated by the occurrence of two carbonyl stretching bands, 1900vs, 2002w cm^{-1}. The former is assumed to be a composite of A_1^1 and E vibrational modes and the latter is assigned to the A_1^2 vibration. The ^{13}C NMR spectrum show only one signal in the CO region, indicating that the [$PhTeFe(CO)_4$]$^-$ anion is fluxional, scrambling equatorial and axial carbonyl ligands.

The nucleophilicity of iron(0)-phenyltellurolate is evident in reactions with electrophiles such as MeI and Brønsted acids. [$PhTeFe(CO)_4$]$^-$ reacts readily with methyl iodide at 0 °C to yield a hexane-soluble product of which the spectral properties are consistent with alkylation at tellurium (Eq. 2).

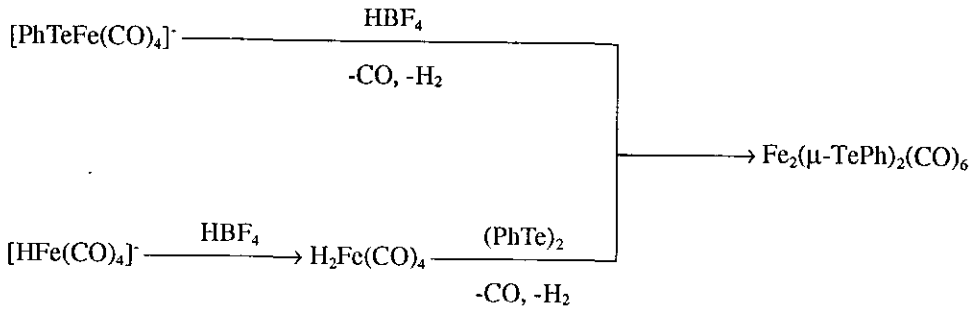
$$[PPN][PhTeFe(CO)_4] + MeI \longrightarrow (PhTeMe)Fe(CO)_4 + PPNI \quad (2)$$

The shift of ^{13}C NMR resonance to smaller values (215.2 ppm, CD_3CN) for the neutral $(PhTeMe)Fe(CO)_4$ relative to that of anionic [$PhTeFe(CO)_4$]$^-$ (219.4 ppm, CD_3CN) indicates a trend of decreasing electronic donation of the PhTeMe ligand to the iron carbonyls. This neutral iron-telluroether complex (in THF) showed three carbonyl stretching bands, 2041m, 1961m, 1937vs cm^{-1}, which has almost identical √(CO) IR spectra both in √(CO) position and in pattern with iron(0)-thioether $(PhSMe)Fe(CO)_4$,[12] iron(0)-selenoether $(PhSeMe)Fe(CO)_4$,[13] but differs greatly from that of $(PhTePh)Fe(CO)_4$.[14] The telluroether complex $(PhTeMe)Fe(CO)_4$ was isolated only as an oil, is stable either neat or in solution for at least 24 h at ambient temperature, but decomposed at T > 45 °C. This result shows the relative order of thermal stability of neutral iron-tetracarbonyl chalcogenether complexes is: $(PhTeMe)Fe(CO)_4$ > $(PhSeMe)Fe(CO)_4$ > $(PhSMe)Fe(CO)_4$, implying that a more electron-donating ligand stabilizes the iron(0)-carbonyl complexes.

The interesting reaction of the iron(0)-tellurolate derivative and Brønsted acid (HBF_4·OEt_2) was oxidation/reduction to yield the known $[(\mu\text{-}TePh)Fe(CO)_3]_2$ (Scheme I).[11] Attempts to isolate, and observe spectrally, an intermediate in protonation were unsuccessful. An analogous reaction would support the production of $Fe_2(\mu\text{-}TePh)_2(CO)_6$ dimer on addition of PhTeTePh to the thermally unstable Fe(II)-dihydride[15] $H_2Fe(CO)_4$ (Scheme I).

The single-crystal X-ray structure of the anion [$PhTeFe(CO)_4$]$^-$ has an almost regular trigonal-bipyramidal coordination geometry, with the tellurium atom of the

Scheme I



phenyltellurolate ligand occupying an axial site on the coordination sphere of iron (Fig. 1). The complex consists of a well-separated PPN^+ cation with the P-N-P angle 142.7(9)°. As given in Table 2, the deviation from the regular TBP reflects in the equatorial plane in which one $C_{(eq)}$-Fe-$C_{(eq)}$ angle opens to 126.6(1)° and the other two closes to 117.9(1)° and 114.7(1)° individually.

The Fe-Te bond length 2.630(5) Å in anionic $[PhTeFe(CO)_4]^-$ is, accidentally, the same as the average terminal Fe-Te bond distance 2.630(4) Å of *fac*-$[Fe(CO)_3(TePh)_3]^-$,[7] but is longer than the reported terminal Fe-TePh average bond length 2.598(2) Å in $[Fe_4Te_4(TePh)_4]^{-3}$ cubane.[16] The Fe-Te-C(5) bond angle 103.4(5)° indicates a slightly distorted tetrahedral disposition of electron pairs about the tellurium atom. We found significant difference between the Fe-$CO_{(ax)}$ and the Fe-$CO_{(eq)}$ distanecs (Fe-$CO_{(ax)}$ 1.83(2) Å vs average Fe-$CO_{(eq)}$ 1.73(2) Å). We also notice that the short distance of Fe-C(3). It might not be real. It might be due to the large thermal parameter of C(3) and poorly diffracted crystal.

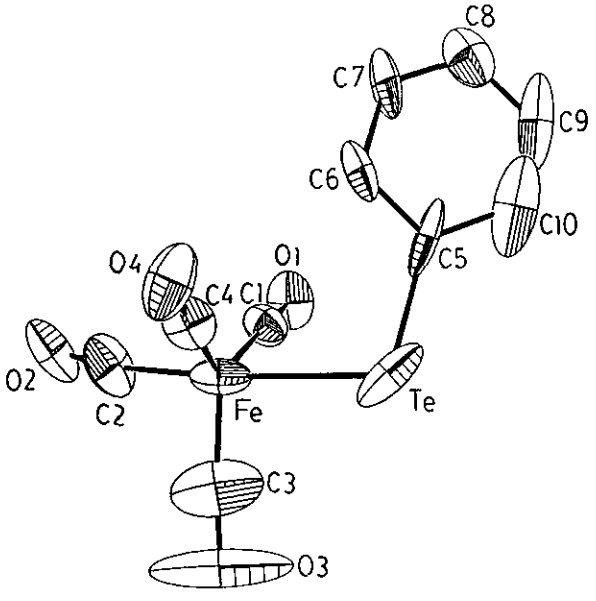


Fig. 1. Thermal ellipsoid plot of $[PhTeFe(CO)_4]^-$ anion with numbering scheme.

SUPPLEMENTARY MATERIAL AVAILABLE

Complete bond distances and bond angles (Table S1), atomic parameters x, y, z, and Beq (Table S2), u(i, j) or U values (Table S3), structure factor amplitudes (Table S4) are available from W.-F. Liaw. Ordering information is given on any current masthead page.

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Key Words

Iron(0)-phenyltellurolate; Iron(0)-telluroether.

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