



Reactivity of *fac*-[PPN][Fe(CO)₃(TePh)₃]: Structure of Fe₂(μ-TePh)₂(NO)₄

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Addition of NOBF₄ to *fac*-[PPN][Fe(CO)₃(TePh)₃] in THF at ambient temperature results in formation of Fe₂(μ-TePh)₂(NO)₄, Fe₂(μ-TePh)₂(CO)₆ and organic products. Methylation of *fac*-[PPN][Fe(CO)₃(TePh)₃] by MeI or [Me₃O][BF₄] leads to the known dimer Fe₂(μ-TePh)₂(CO)₆ and organic products. Fe₂(μ-TePh)₂(NO)₄ crystallizes in the orthorhombic space group P bca, with a = 12.701(5) Å, b = 6.7935(16) Å, c = 21.299(9) Å, V = 1837.8(11) Å³, and Z = 4. The core geometry of Fe₂(μ-TePh)₂(NO)₄ is best described as a Fe₂Te₂ planar rhombus with Te-Fe-Te bond angle 112.09(4)°. A Fe-Fe bond (length 2.827(2) Å) is proposed for Fe₂(μ-TePh)₂(NO)₄ on the basis of the 18-electron rule. The iron atom adopts a distorted tetrahedral geometry with acute bridge Fe-Te-Fe angles 67.91(3)°, and bridging Fe-Te bond of length 2.53(1) Å.

INTRODUCTION

Transition-metal telluride complexes are being extensively investigated.¹⁻⁴ The ligand chemistry of metaltellurolates and synthesis of metal-tellurolate, metal-selenolate complexes remains unexplored,^{5,6} even though the rational synthesis and reactivity of metal-thiolate complexes have been developed and exploited.⁷⁻⁹

Iron(0)-tellurolate and iron(II)-tellurolate complexes were synthesized from the reaction of [PPN][HFe(CO)₄] with diphenylditelluride (double molar proportion) in THF at ambient temperature via hydride/tellurolate exchange and oxidative decarbonylation addition.¹⁰ The possible occurrence of stable F(II)-telluroether-tellurolate complex along with the relative scarcity of investigations on the reactivity of coordinated terminal tellurolate ligands prompted us to investigate the behavior of *fac*-[PPN][Fe(CO)₃(TePh)₃] toward addition of electrophiles (Me⁺, NO⁺), and here report the X-ray crystal structure of Fe₂(μ-TePh)₂(NO)₄.

EXPERIMENTAL SECTION

Manipulations, transfer and reactions of samples were conducted under N₂ with standard Schlenk techniques and in a glovebox. Solvents were distilled under N₂ from appropriate drying agents [hexane and tetrahydrofuran (THF) from Na/benzophenone] and then stored in dried, N₂-filled flasks over activated 4 Å molecular sieves. A nitrogen purge was used on these solvents prior to use and transfers to reaction vessels were via stainless-steel cannula under

positive pressure of N₂. The reagents iodomethane, nitrosonium tetrafluoroborate, trimethyloxonium tetrafluoroborate (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (BIO-RAD FTS-7 FTIR) using 0.1-mm sealed solution cells with KBr windows. Gas-chromatographic analyses made use of a flame ionization detector with the column (for organic products) OV-17 on Chromosorb W-HP, 80/100 mesh, 1.8 m × 3 mm stainless-steel tubing. Elemental analysis was done on a CHNO analyzer (Heraeus).

Reaction of NOBF₄ and *fac*-[PPN][Fe(CO)₃(TePh)₃]

[PPN][Fe(CO)₃(TePh)₃] (0.266 g, 0.2 mmol) was loaded into a Schlenk flask (50 mL) with NOBF₄ (0.024 g, 0.2 mmol). Dried and degassed THF (10 mL) was added to give a dark red-brown solution. The reaction mixture was stirred overnight at ambient temperature and filtered to remove a white precipitate [PPN][BF₄] after reaction ceased according to IR data (ν_{CO}). The filtrate was dried and redissolved in hexane; the product solution was subjected to chromatographic process on silica gel. Elution with hexane gave two major brownish-red bands, Fe₂(μ-TePh)₂(NO)₄ and Fe₂(μ-TePh)₂(CO)₆. The dark brown-red solution was then placed in a refrigerator for several days. Dark brown-red crystals were obtained which is suitable for X-ray crystallography. The elemental analysis, IR spectrum (ν_{NO}), and X-ray single-crystal determination of the dark red-brown crystal, described below, confirmed the formation of Fe₂(μ-TePh)₂(NO)₄ (0.02 g, 62%).¹¹ The IR spectrum (ν_{CO}) of the red-brown semi-solid product in THF was assigned to the well-known Fe₂(μ-TePh)₂(CO)₆ (0.023 g, 70%).¹² Anal.

Calcd for $C_{12}H_{10}O_4N_4Fe_2Te_2$: C, 22.48; H, 1.57; N, 8.74. Found: C, 23.12; H, 1.48; N, 8.44%. IR (THF) ν_{NO} 1745 (s), 1766 (s) cm^{-1} for $Fe_2(\mu-TePh)_2(NO)_4$. IR ν_{CO} (THF) 1965 (sh), 1982 (s), 2019 (vs), 2054 (m); (hexane) 1982 (sh), 1980 (m), 2021 (vs), 2056 (m) cm^{-1} ; 1H NMR (CD_3CN) δ 7.3 (m, C_6H_5), ^{13}C NMR (CD_3COCD_3) δ 206.3 (CO) for $Fe_2(\mu-TePh)_2(CO)_6$.

Reaction of *fac*-[PPN][Fe(CO)₃(TePh)₃] and MeI

A portion (12.8 μ L, 0.2 mmol) of MeI was syringed into [PPN][Fe(CO)₃(TePh)₃] (266 mg, 0.2 mmol) in THF (5 mL) at ambient temperature. The reaction mixture was stirred for 40 h at room temperature, yielding a red-brown solution with IR ν_{CO} (THF) 2054 (m), 2019 (vs), 1982 (s) and 1965 (sh) cm^{-1} , consistent with the formation of $Fe_2(\mu-TePh)_2(CO)_6$ dimer,¹² and much white precipitate PPNI. The solution was dried under vacuum; hexane was added to extract the red-brown product. The existence of (PhTe)₂ in the solution was proved by GC.

X-ray Structural Determination

Crystallographic data are collected in Table 1. A dark brown-red crystal chosen for diffractometer measurement

Table 1. Crystallographic Data

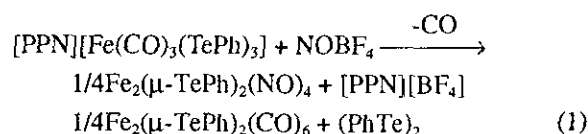
Formula	$C_{12}H_{10}N_4O_4Te_2Fe_2$
F_w	633.14
Cryst size, mm	$0.35 \times 0.40 \times 0.50$
Cryst system	orthorhombic
Space group	P bca
a, \AA	12.701(5)
b, \AA	6.794(2)
c, \AA	21.299(9)
V, \AA^3	1838(1)
Z	4
F(000)	1287
λ (Mo $K\alpha$)/ \AA	0.71069
D_{calc} , g/cm^3	2.288
2θ (max), deg	50
Scan mode	$\theta/2\theta$
Scan range	
h	0-15
k	0-8
l	0-25
No. of unique reflens	1602
No. of reflens, obsd ($I > 2\sigma(I)$)	1326
Trans factors (min/max)	0.78/1.00
R (all)	0.031 (0.041)
R_w (all)	0.031 (0.032)
GOF	2.78
Resid peak, $e/\text{\AA}^3$	0.420
Resid hole, $e/\text{\AA}^3$	-0.720

was ca. $0.35 \times 0.40 \times 0.50$ mm mounted on a glass fibre and coated in epoxy resin. Photographic examination showed sharp diffraction spots. The cell dimensions were obtained from 25 reflections with 2θ angle in the range $20.00 - 27.00^\circ$. The intensity data were collected on a diffractometer (Nonius), using the $\theta/2\theta$ scan mode. The last least squares cycle was calculated with 17 atom, 110 parameters, and 1326 from 1602 reflections.

Refinement was concluded at $R(F) = 0.031$, $R_w(F) = 0.031$ for 1326 significant reflections from all 1602 unique reflections.

RESULTS AND DISCUSSION

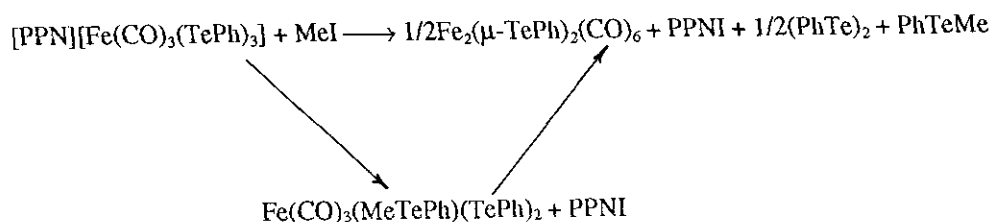
Addition of *fac*-[PPN][Fe(CO)₃(TePh)₃] and NOBF₄ in equimolar proportions in THF at room temperature overnight results in $Fe_2(\mu-TePh)_2(NO)_4$ dimer isolated as a dark brown-red solid,¹¹ in approximately equal quantity, a red-brown semi-solid of which the IR data indicated formulation as $Fe_2(\mu-TePh)_2(CO)_6$,¹² and an organic product, diphenylditelluride identified by GC (Eq. 1). The formation of $Fe_2(\mu-TePh)_2(NO)_4$



is supported by analytical and infrared data. X-ray structural determination was achieved (Fig. 1). The dimer $Fe_2(\mu-TePh)_2(NO)_4$ is a dark brown-red solid stable in air, in contrast to $Fe_2(\mu-Te)_2(CO)_6$ dimer that is thermally fragile, easily decomposing to $Fe_4(\mu_3-Te)_4(CO)_{12}$.¹³ The analogous $Fe_2(\mu-Te-C_6H_4-p-OMe)_2(NO)_4$ was proposed on the basis of its IR spectrum after reaction of $Fe(NO)_2(CO)_2$ and (*p*-MeO- C_6H_4 Te)₂ in benzene at room temperature.¹⁴ The $Fe_2(\mu-TePh)_2(NO)_4$ characterized by IR and mass spectrometry was prepared from reaction of $Fe_2(\mu-I)_2(NO)_4$, (PhTe)₂ and LiBEt₃H in THF.¹¹

Nucleophilic reaction of *fac*-[PPN][Fe(CO)₃(TePh)₃] with MeI (or [Me₃O][BF₄]) in equimolar proportions in THF at ambient temperature for 40 h yielded a white precipitate PPNI and a red-brown solution characterized by ν_{CO} infrared spectroscopy as $Fe_2(\mu-TePh)_2(CO)_6$,¹² and an unidentified organic product, presumably PhTeMe (Scheme I). Attempts to observe spectrally a neutral intermediate in the methylation were successful only for the reaction at low temperature. Within 20 min the *fac*-[PPN][Fe(CO)₃-

Scheme I



(TePh)₃] reacted readily with MeI at -30 °C to yield a red-brown solution that resisted complete characterization as it is thermally unstable. The increase in ν_{CO} values (from 2021 (s) and 1963 (s) cm^{-1} to 2054 (s) and 1998 (s) cm^{-1} in THF) is consistent with alkylation at tellurium. The available data (ν_{CO} (THF): 2054 (s), 1998 (s) cm^{-1}) indicate formation of the neutral $\text{Fe}(\text{CO})_3(\text{MeTePh})(\text{TePh})_2$ (Scheme I). There is no indication of iron-site methylation, i.e. the reaction with electrophiles should occur only at the more accessible, electron-rich tellurium site.

Complete bond angles and bond distances are summarized in Table 2. The structure of $\text{Fe}_2(\mu\text{-TePh})_2(\text{NO})_4$ was elucidated by X-ray diffraction of single crystal. The core geometry of $\text{Fe}_2(\mu\text{-TePh})_2(\text{NO})_4$ is best described as a

Fe_2Te_2 planar rhombus. Two terminally bonded nitrosyl groups, and the bridging phenyltelluroate ligands define the distorted tetrahedral geometry of each iron atom (the angle Te-Fe-Te 112.09(4)°, Te-Fe-N(1) 107.43(18), Te-Fe-N(2) 105.71(18), N(1)-Fe-N(2) 120.6(3)°, leading to an acute bridge of Fe-Te-Fe angle 67.91(3)° are comparable to the sharp bridge of angle 74° in $\text{Fe}_2(\mu\text{-SEt})_2(\text{NO})_4$ (Fig. 2), 68.3° in $\text{Fe}_2(\mu\text{-SEt})_2(\text{CO})_6$, and 61.0(1)° in $\text{Fe}_2(\mu\text{-TeCH}_2\text{Te})(\text{CO})_6$,¹⁵⁻¹⁷ and the Te-Fe-Te angle 112.09(4)° is comparable to S-Fe-S angle 106.3(1)° in $\text{Fe}_2(\mu\text{-SEt})_2(\text{NO})_4$. This sharp bridge Fe-Te-Fe angle (67.91(3)°) may be due to the Fe-Fe semi-metal bond predicted for $\text{Fe}_2(\mu\text{-TePh})_2(\text{NO})_4$ on the basis of the 18-electron rule, even though the 2.827(2) Å Fe-Fe bond is much longer than 2.720(3) Å and 2.592(4) Å in $\text{Fe}_2(\mu\text{-SEt})_2(\text{NO})_4$ and $[\text{Fe}_5\text{Te}_4(\text{CO})_{14}]^{2-}$ respectively (Fig. 2).¹⁸ The Fe-Fe bond of length 2.827(2) Å is longer than the formal Fe-Fe bond of length 2.587(2) Å in $\text{Fe}_2(\mu\text{-TeCH}_2\text{Te})(\text{CO})_6$,¹⁷ slightly longer than the Fe-Fe contact

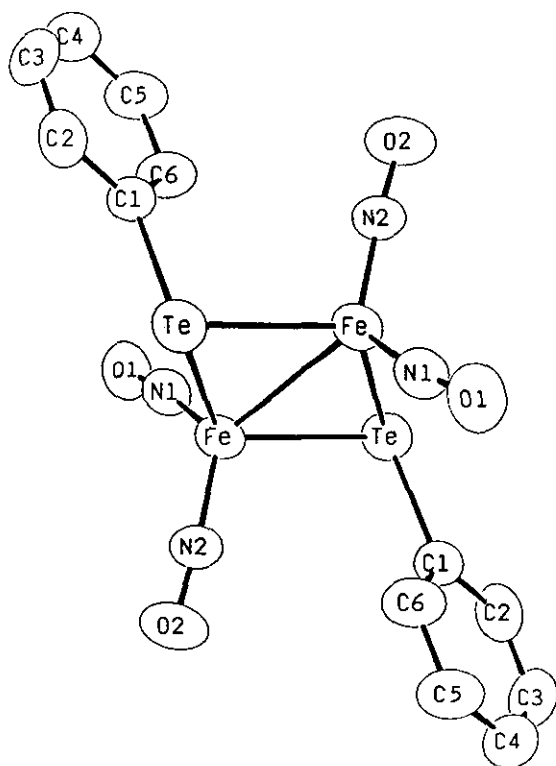
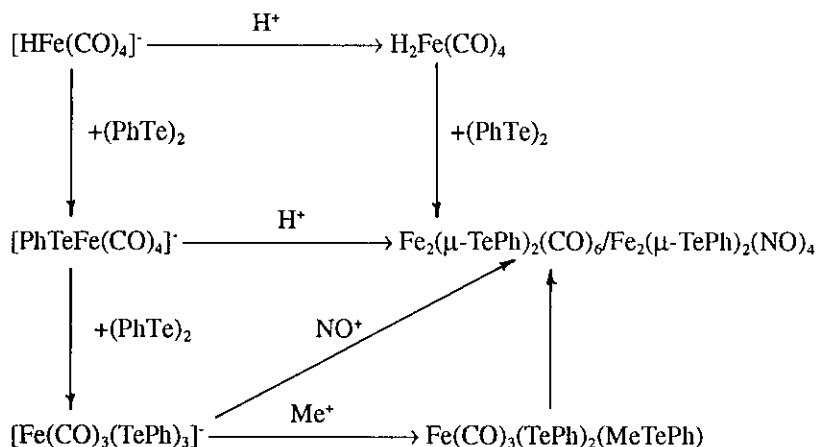


Fig. 1. Molecular structure of $\text{Fe}_2(\mu\text{-TePh})_2(\text{NO})_4$ with numbering scheme.

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

Bond Lengths/Å			
Te-Fe	2.532(1)	N(2)-O(2)	1.163(7)
Te-Fe	2.529(1)	C(1)-C(2)	1.394(9)
Te-C(1)	2.118(6)	C(1)-C(6)	1.374(9)
Fe-Fe	2.827(2)	C(2)-C(3)	1.359(10)
Fe-N(1)	1.651(5)	C(3)-C(4)	1.361(12)
Fe-N(2)	1.658(5)	C(4)-C(5)	1.369(10)
N(1)-O(1)	1.159(7)	C(5)-C(6)	1.373(9)
Bond Angles/deg			
Fe-Te-Fe	67.91(3)	N(1)-Fe-N(2)	120.6(3)
Fe-Te-C(1)	102.43(16)	Fe-N(1)-O(1)	172.4(5)
Fe-Te-C(1)	104.10(16)	Fe-N(2)-O(2)	171.9(5)
Te-Fe-Te	112.09(4)	Te-C(1)-C(2)	117.7(5)
Te-Fe-Fe	56.00(3)	Te-C(1)-C(6)	123.5(4)
Te-Fe-N(1)	107.43(18)	C(2)-C(1)-C(6)	118.7(6)
Te-Fe-N(2)	106.12(19)	C(1)-C(2)-C(3)	120.2(6)
Te-Fe-Fe	56.09(3)	C(2)-C(3)-C(4)	121.3(6)
Te-Fe-N(1)	104.94(17)	C(3)-C(4)-C(5)	118.6(6)
Te-Fe-N(2)	105.71(18)	C(4)-C(5)-C(6)	121.4(7)
Fe-Fe-N(1)	119.93(17)	C(1)-C(6)-C(5)	119.7(6)
Fe-Fe-N(2)	119.40(20)		

Scheme II



distance of average 2.804(1) Å in $[\text{Fe}_4\text{Te}_4(\text{TePh})_4]^{-3}$,¹⁹ but shorter than Fe-Fe average contact distances of 2.847(2) Å in $[\text{Cs}_7][\text{Fe}_4\text{Te}_8]$ cluster.²⁰

An interesting aspect of this structure is that the tellurium atom adopts an severely distorted tetrahedral arrangement of three bonding pairs and one lone pair of electrons because of the sharp bridge angle. The average Fe-Te-C(1) angle of 103.27(16)° is smaller than the Fe-S-C angle of 106.6(5)° (average) in $\text{Fe}_2(\mu\text{-SEt})_2(\text{NO})_4$ (Fig. 2).¹⁵

The bridging Fe-TePh bond of distance 2.53(1) Å in Fe(I) $\text{Fe}_2(\mu\text{-TePh})_2(\text{NO})_4$ is unexpectedly much shorter than the terminal Fe-TePh bond of length 2.63(1) Å in Fe(II) *fac*-[PPN][$\text{Fe}(\text{CO})_3(\text{TePh})_3$]¹⁰ and Fe(0) [PPN][$\text{PhTeFe}(\text{CO})_4$],²¹ shorter than 2.598(2) Å and 2.543(2) Å in $[\text{Fe}_4\text{Te}_4(\text{TePh})_4]^{-3}$ and $\text{Fe}_2(\mu\text{-TeCH}_2\text{Te})(\text{CO})_6$ respectively.^{17,19} The delocalization of the lone-pair electrons of two tellurium atoms over the Fe_2Te_2 plane to satisfy the 18 electrons around each iron metal center is imperative to account for the short bridging Fe-TePh bond (shorter than the terminal Fe-TePh bond as

described above) and the long Fe-Fe bond (much longer than a formal Fe-Fe bond of length 2.587(2) Å as mentioned above).

The mean Fe-N and N-O distances are 1.654(5) Å and 1.161(7) Å respectively.

CONCLUSION

All the reactions concerning the iron-phenyltelluroate complexes can be summarized in Scheme II.^{10,21}

SUPPLEMENTARY MATERIAL AVAILABLE

Atomic parameters *x*, *y*, *z* and *Beq* (Table S1), table of *U*(*i,j*) or *U* values (Table S2), structure factor amplitudes (Table S3) are available from W.-F. Liaw. Ordering information is given on any current masthead page.

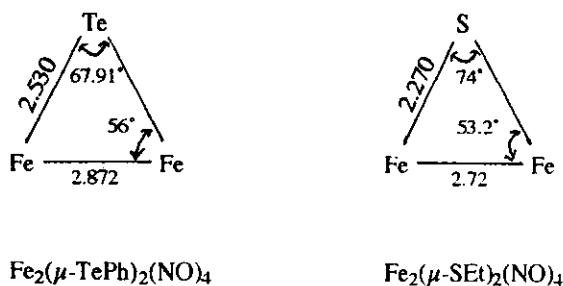


Fig. 2. Selected structural parameters for compound $\text{Fe}_2(\mu\text{-TePh})_2(\text{NO})_4$ and related species $\text{Fe}_2(\mu\text{-SEt})_2(\text{NO})_4$.¹⁵

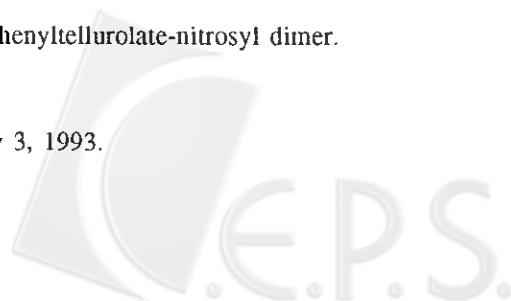
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Key Words

Iron(I)-phenyltelluroate-nitrosyl dimer.

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