1536 *Inorg. Chem.* **1993**, *32*, 1536–1538

fac-$[PPN][Fe(CO)_3(TePh)_3]$: Oxidative Addition of $(PhTe)_2$ to $[PPN][PhTeFe(CO)_4]$

Wen-Feng Liaw,* Ming-Hsi Chiang, Chen-Ju Liu, and Piin-Jye Harn

Department of Chemistry, National Changhua University of Education, Changhua, Taiwan 50058, R.O.C.

Lin-Kang Liu

Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, R.O.C.

Received August 12, 1992

The S–S and Se–Se bonds of organic disulfides and diselenides have been known to be reactive toward nucleophiles, electrophiles, and radical reagents.[1–3] Oxidative addition of organic disulfide to coordinatively unsaturated, low-valent transition-metal species is a well-known convenient method for preparing metal-dithiolate complexes.[4–6] The ligand chemistry of tellurium remains rather sparse.[7,8] At present, the general routes to metal tellurolate complexes involve a metathesis reaction between an alkali-metal tellurolate and a metal halides,[9a,b] or involve the insertion of tellurium into the metal–alkyl bond.[9c] We report here on the deliberate synthesis and structure of *fac*-$[PPN][Fe(CO)_3(TePh)_3]$.

The preparation of the simple iron(0) tellurophenolate complex $[PPN][PhTeFe(CO)_4]$ involves a similar method to those used for the synthesis of analogous sulfur/selenium compounds (eq 1).[10,11] Although the mechanistic features have not been established, formation of iron(0) tellurophenolate complex accompanied by formation of benzenetellurol which is known to decompose at room temperature[12] may occur by addition of PhTeTePh to $[PPN][HFe(CO)_4]$.

$$[PPN][HFe(CO)_4] + PhEEPh \rightarrow [PPN][PhEFe(CO)_4] + PhEH \qquad (1)$$

$$E = S, Se, Te$$

The reaction of $[PPN][HFe(CO)_4]$[13a] with 2 equiv of PhTeTePh[13b] in THF at ambient temperature (5 h) leads to a dark purple solution from which the moderately air- and light-sensitive crystalline solid *fac*-$[PPN][Fe(CO)_3(TePh)_3]$ can be isolated in 94% yield after removal of solvent and recrystallization with THF and hexane. Reaction of $[HFe(CO)_4]^-$ and a 4-fold excess of PhTeTePh speeds up the reaction considerably. The two-band pattern in the ν(CO) IR region of the final product is characteristic of a facial tricarbonyl complex with C_{3v} symmetry, and assigned to *fac*-$[Fe(CO)_3(TePh)_3]^-$, produced according to Scheme I.

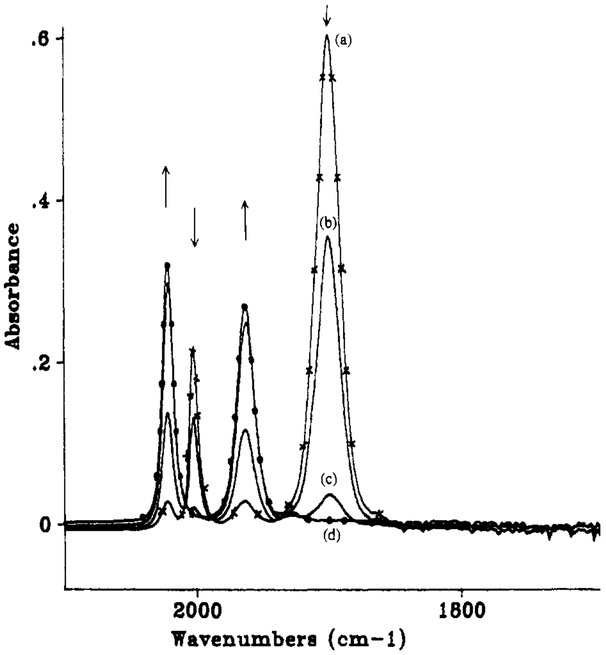
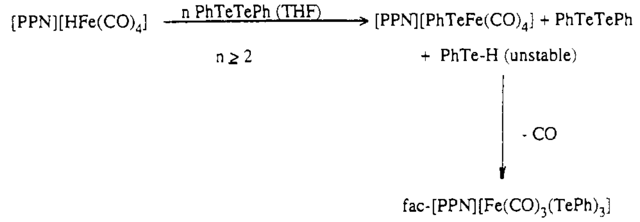


Figure 1. Infrared ν_{CO} absorbance changes vs time for the reaction of $[HFe(CO)_4]^-$ with $(PhTe)_2$ in THF at ambient temperature. Curve a (–×–×–) corresponds to the formation of $[PhTeFe(CO)_4]^-$. Curves b (20 min) and c (2 h) correspond to $[PhTeFe(CO)_4]^- + [Fe(CO)_3(TePh)_3]^-$, and curve d (–•–•–) corresponds to $[Fe(CO)_3(TePh)_3]^-$.

Scheme I



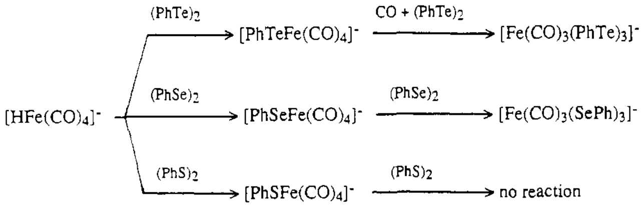
The ν(CO) IR monitor of the reaction in THF solution at ambient temperature is shown in Figure 1 (reaction of 1 equiv of $[PPN][HFe(CO)_4]$ and 2 equiv of $(PhTe)_2$ in THF). Figure 1a shows formation of the intermediate complex $[PPN][PhTeFe(CO)_4]$, also reflected by an immediate change to a dark brown red homogeneous solution. Within 20 min *fac*-$[PPN][Fe(CO)_3(TePh)_3]$ begins to form (Figure 1b). Figure 1c corresponds to $[PPN][PhTeFe(CO)_4]$ + *fac*-$[PPN][Fe(CO)_3(TePh)_3]$. After continued stirring for 5 h, the dark purple *fac*-$[PPN][Fe(CO)_3(TePh)_3]$ is completely formed, as shown in Figure 1d. The carbon monoxide atmosphere does not prevent

---

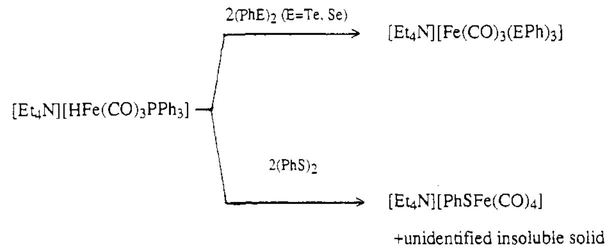
(1) Bach, R. D.; Rajan, S. J. *J. Am. Chem, Soc.* **1979**, *101*, 3112.
(2) Asmus, K.-D. *Acc. Chem. Res.* **1979**, 436.
(3) Pappas, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 561.
(4) (a) Mathur, P.; Mavunkal, I. J.; Rugmini, V.; Mahon, M. F. *Inorg. Chem.* **1990**, *29*, 4838. (b) Chakrabarty, D.; Hossain, Md. M.; Mathur, P. *J Organomet. Chem.* **1991**, *401*, 167. (c) Jessop, P. G.; Rettig, S. J.; Lee, C. L.; James, B. R. *Inorg. Chem.* **1991**, *30*, 4617.
(5) (a) Day, V. W.; Lesch, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 1290. (b) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1983**, *22*, 1854. (c) Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1980**, *199*, C6.
(6) (a) Schermer, E. D.; Baddley, W. H. *J. Organomet. Chem.* **1971**, *30*, 67. (b) Davies, I.; McWhinnie, W. R. *Inorg. Nucl. Chem. Letters* **1976**, *12*, 763. (c) Seyferth, D.; Henderson, R. S.; Gallagher, M. K. *J. Organomet. Chem.* **1980**, *193*, C75. (d) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.
(7) Gysling, H. J. *Coor. Chem. Rev.* **1982**, *42*, 133.
(8) Gysling, H. J.; Luss, H. R.; Smith, D. L. *Inorg. Chem.* **1979**, *18*, 2696.
(9) (a) Gindelberger, D.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6242. (b) Sato, M.; Yoshida, T. *J. Organomet. Chem.* **1973**, *51*, 231. (c) McGregor, K.; Deacon, G. B.; Dickson, R. S.; Fallon, G. D.; Rowe, R. S.; West, B. *J. Chem. Soc., Chem. Commun.* **1990**, *19*, 1293.
(10) Liaw, W.-F.; Kim, C.; Darensbourg, M. Y.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 3519.
(11) Darensbourg, M. Y.; Liaw, W.-F.; Riordan, C. G. *J. Am. Chem. Soc.* **1989**, *111*, 8051.
(12) (a) Drake, J. E.; Hemming, R. T. *Inorg. Chem.* **1980**, *19*, 1879. (b) Nagakawa, K.; Osuka, M.; Sasaki, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* **1987**, 1331. (c) Sink, C. W.; Harvey, A. B. *J. Chem. Soc., Chem. Commun.* **1969**, 1023.
(13) (a) Smith, M. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 2388. (b) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

0020-1669/93/1332-1536$04.00/0

Scheme II



Scheme III



the oxidative addition of PhTeTePh even exposing the mixture of [PPN][$PhTeFe(CO)_4$] and PhTeTePh under 1 atm of CO in THF at room temperature (Scheme II). We have extended this chemistry using PhSeSePh and [PPN][$PhSeFe(CO)_4$][11] as starting material. The IR, UV, and ^{13}C NMR spectroscopic data show that $[PhSeFe(CO)_4]^-$ also promoted the oxidative addition of diphenyl diselenide. However, we have been unable to observe any indications of formation of *fac*-[PPN][$Fe(CO)_3(SPh)_3$] complex in the reaction of [PPN][$PhSFe(CO)_4$] and PhSSPh under the same condition for 2 days on the basis of IR spectra (Scheme II).

We extend our interests to the reactivity of iron(0) phenylchalcogenolate derivatives whose reactivity may be tailored by pendant ligand selection. The attempted synthesis of [PPN][$Fe(CO)_2(PPh_3)(EPh)_3$] (E = Te, Se) in a manner analogous to [PPN][$Fe(CO)_3(EPh)_3$] by reaction of 1 equiv of *trans*-[PPN][$HFe(CO)_3PPh_3$][14] and 2 equiv of $(PhE)_2$ affords only *fac*-[PPN][$Fe(CO)_3(TePh)_3$] and *fac*-[PPN][$Fe(CO)_3(SePh)_3$] respectively, followed by loss of one triphenylphosphine ligand instead of one carbonyl group (Scheme III). We also found that $[HFe(CO)_3PPh_3]^-$ reacts much more faster at room temperature in THF with $(PhE)_2$ (E = Te, Se) to form *fac*-$[Fe(CO)_3(EPh)_3]^-$ than $[HFe(CO)_4]^-$ does. This result indicates that [Et_4N][$HFe(CO)_3PPh_3$] might be an attractive candidate to synthesize $[Fe(CO)_3(SPh)_3]^-$ since the triphenylphosphine ligand may be readily lost in the oxidative addition reaction. On the contrary we found that *trans*-$[HFe(CO)_3PPh_3]^-$ reacted quickly with $(PhS)_2$ (1:2 ratio) to afford $[PhSFe(CO)_4]^-$ and some unidentified insoluble solid in THF at room temperature (Scheme III).

The structure of the *fac*-[$Fe(CO)_3(TePh)_3$] unit in the PPN^+ salt is shown in Figure 2. The title compound crystallizes as discrete cations of PPN and anions of $[Fe(CO)_3(TePh)_3]^-$, and one-half solvent molecule THF. The anionic $[Fe(CO)_3(TePh)_3]^-$ represents the first $FeTe_3$ molecular fragment for a mononuclear Fe complex. Typical values for Fe–Te bond distances are between 2.47 and 2.59 Å, generally in the form of bridging TeR or triply bridging Te atoms. A recent report of the structure of tetrahedrally symmetric $[Fe(PEt_3)Te]_4$ extends the range of Fe–Te lengths to 2.609(1) Å.[15] The Fe–Te lengths in the title compound average 2.630(4) Å, which is longer than the reported terminal Fe–TePh average bond length 2.598(2) Å in $[Fe_4Te_4(TePh)_4]^{-3}$ cubane.[16] In the title compound, the Te···Te contact distances are 3.477–3.575 Å, much longer than the Te–Te bond distances, ranging from 2.717 to 2.763 Å, in Te cluster compounds.[17] It is believed that in the $[Fe(CO)_3(TePh)_3]^-$ anion, there is no Te–Te bonding.

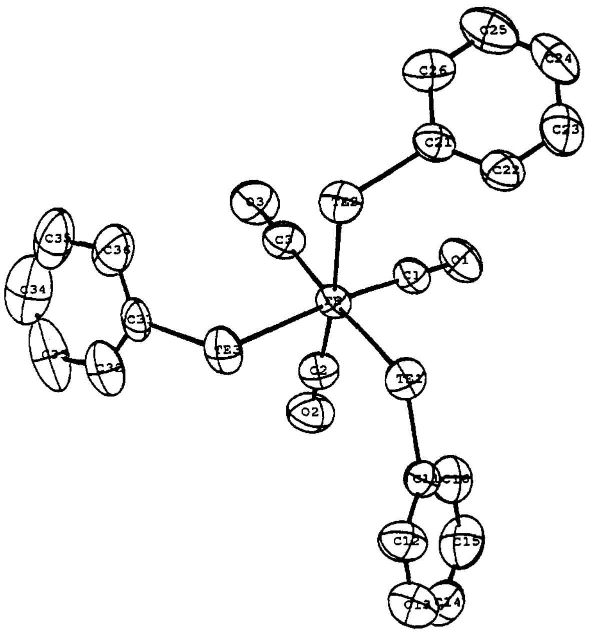


Figure 2. Molecular structure of the complex $[Fe(CO)_3(TePh)_3]^-$.

The coordination geometry around the Fe(II) center is octahedral. Though not required crystallographically, the anion virtually displays C_3 molecular symmetry. The Fe–C(CO) lengths average 1.770(6) Å that is shorter than the statistical average of 2572 Fe–C(CO) reported bond distances of 1.782(30) Å.[18] Since the CO groups are in positions trans to TePh, a slightly increased back-bonding toward CO is expected and, therefore, a slightly shortened length is reasonable. The structural parameters of the PPN cation conform to reported values.[18]

Experimental Section. The sample manipulations, sample transfer and reactions were performed under an atmosphere of pure nitrogen by using standard Schlenk techniques and in a nitrogen atmosphere glovebox. Solvents were purified, dried, and 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, diphenyl diselenide, phenylmagnesium bromide, tellurium powder, and triphenylphosphine (Aldrich) were used as received. The compounds [PPN][$HFe(CO)_4$][13a] and *trans*-[PPN][$HFe(CO)_3PPh_3$][14] were prepared by established procedures. Infrared spectra were recorded on a Bio-Rad FTS-7 FTIR spectrometer using 0.1-mm sealed KBr solution cells. NMR spectra were performed on a Bruker AC 300 spectrometer. UV-visible spectra were recorded on a GBC 918 spectrophotometer. Elemental analyses were performed by Elemental Analyses Center of National Science Council, Taichung, Taiwan, R.O.C.

Preparation of [PPN][$PhTeFe(CO)_4$]. To a light-brown solution of [PPN][$HFe(CO)_4$] (0.707 g, 1 mmol) in 5 mL of THF was added diphenyl ditelluride 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 removed via cannula, and the solid was dried under vaccum. The isolated yield is 96%. ^{13}C NMR (CD_3CN): 219.4 (s) ppm (CO), 118.2–138.6 ppm (C_6H_6). ν(CO)(THF): 1900vs, 2002

---

(14) Ash, C. E.; Delord, T.; Simmons, D.; Darensbourg, M. Y. *Organometallics* **1986**, *5*, 17.

(15) Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M.; Kwon, Y.-U. *J. Am. Chem. Soc.* **1992**, *114*, 3155.

(16) Simon, W.; Wilk, A.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1009.

(17) Huang, S.-P.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 5477.

(18) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton, Trans.* **1989**, S1.

Table I. Crystallographic Data for [PPN][Fe(CO)$_3$(TePh)$_3$]·0.5THF

empirical formula	$C_{59}H_{49}O_{3.5}NFeP_2Te_3$
mol wt	1328.62
space group	*C*2/*c*
cryst syst	monoclinic
a/Å	32.116(1)
b/Å	11.760(4)
c/Å	29.027(10)
β/deg	94.942(3)
V/Å^3	10923(6)
d_{calcd}/g cm^{-3}	1.6156
Z	8
cryst dimens, mm	0.24 × 0.13 × 0.32
radiation λ(Mo Kα)/Å	0.709 30
2θ (max), deg	120.0
no. of measd reflcns	8139
no. of unique reflcns	8139
no. of obsd reflcns ($I > 2.5\sigma$(I))	5662
transm factors (min/max)	0.2889/0.9989
$R(F)^a$	0.067
$R_w(F)^b$	0.077

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

Table II. Selected Bond Lengths (Å)

Te(1)–Fe	2.6333(19)	Fe–C(2)	1.767(12)
Te(1)–C(11)	2.163(12)	Fe–C(3)	1.778(12)
Te(2)–Fe	2.6336(20)	Fe–C(1)	1.764(1)
Te(2)–C(21)	2.116(12)	O(1)–C(1)	1.144(14)
Te(3)–Fe	2.6241(19)	O(2)–C(2)	1.154(15)
Te(3)–C(31)	2.172(12)	O(3)–C(3)	1.125(14)

Table III. Selected Bond Angles (deg)

Fe–Te(1)–C(11)	106.3(3)	Te(3)–Fe–C(3)	92.8(4)
Fe–Te(2)–C(21)	105.3(3)	C(1)–Fe–C(2)	96.3(5)
Fe–Te(3)–C(31)	106.4(3)	C(1)–Fe–C(3)	95.1(5)
Te(1)–Fe–Te(2)	83.04(6)	C(2)–Fe–C(3)	97.3(6)
Te(1)–Fe–Te(3)	82.81(6)	Fe–C(1)–O(1)	178.4(1)
Te(1)–Fe–C(1)	89.1(4)	Fe–C(2)–O(2)	176.9(11)
Te(1)–Fe–C(2)	93.6(4)	Fe–C(3)–O(3)	178.1(12)
Te(1)–Fe–C(3)	167.8(4)	Te(1)–C(11)–C(12)	118.3(9)
Te(2)–Fe–Te(3)	85.68(6)	Te(1)–C(11)–C(16)	121.3(9)
Te(2)–Fe–C(1)	93.2(4)	Te(2)–C(21)–C(22)	121.3(9)
Te(2)–Fe–C(2)	169.9(4)	Te(2)–C(21)–C(26)	121.2(9)
Te(2)–Fe–C(3)	85.2(4)	Te(3)–C(31)–C(32)	118.4(9)
Te(3)–Fe–C(1)	171.9(4)	Te(3)–C(31)–C(36)	118.9(11)
Te(3)–Fe–C(2)	84.4(4)		

w cm^{-1}. Anal. Calcd for $C_{46}H_{35}NO_4P_2TeFe$: C, 60.5; H, 3.8; N, 1.5. Found: C, 60.2; H, 4.0; N, 1.4.

Synthesis of *fac*-[PPN][Fe(CO)$_3$(TePh)$_3$]. The reaction of [PPN][HFe(CO)$_4$] (0.708 g, 1 mmol) with PhTeTePh (0.818 g, 2 mmol) in 10 mL of THF at ambient temperature for 4–5 h leads to a dark purple solution. The reaction mixture was concentrated to 4 mL, and then hexane was slowly added to precipitate a purple solid. The mother liquor was removed via cannula and then dried under vacuum. The moderately air- and light-sensitive crystalline solid *fac*-[PPN][Fe(CO)$_3$(TePh)$_3$] was isolated in 94% yield. ^{13}C NMR (CD$_3$CN): 215.8 (s) ppm (CO), 118.2–140.7 ppm (C$_6$H$_5$). ν(CO) (THF): 1963vs, 2021vs cm^{-1}. Absorption spectrum (THF) [$\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})]: 336 (20 162), 450 (2408), 521 (2130). Anal. Calcd for $C_{57}H_{45}NO_3P_2Te_3Fe$: C, 52.9; H, 3.5; N, 1.08. Found: C, 52.5; H, 3.6; N, 1.0.

Preparation of [PPN][Fe(CO)$_3$(SePh)$_3$]. Diphenyl diselenide (0.31 g, 1 mmol) in 5 mL of THF was added to a stirred THF solution of [PPN][PhSeFe(CO)$_4$][11] (0.864 g, 1 mmol) (or [PPN][HFe(CO)$_4$], 0.35 g, 0.5 mmol) at ambient temperature. The reaction mixture was allowed to stir at room temperature for 40 h. The solvent was removed under vacuum, and hexane was added to precipitate out a dark-red product from THF/hexane, affording 1.0 g (92%) of [PPN][Fe(CO)$_3$(SePh)$_3$]. ^{13}C NMR (CD$_3$CN): 212.7 ppm (CO). IR (ν(CO); THF): 1975 vs, 2032 vs, 2039 sh cm^{-1}. Absorption spectrum (THF) [$\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1}): 306 (19 020), 427 (2957), 482 (2460). Anal. Calcd for $C_{57}H_{45}O_3NP_2Se_3Fe$: C, 59.72; H, 3.96; N, 1.22. Found: C, 59.96; H, 4.22; N, 1.38.

Reaction of [Et$_4$N][HFe(CO)$_3$PPh$_3$] with Diphenyl Dichalcogenide. [Et$_4$N][HFe(CO)$_3$PPh$_3$][14] (0.533 g, 1 mmol) was reacted with PhTeTePh (0.82 g, 2 mmol), PhSeSePh (0.64 g, 2 mmol), and PhSSPh (0.44 g, 2 mmol) in 5 mL of THF at ambient temperature, respectively. The reaction mixture was stirred for 5 min, and IR revealed all of the [Et$_4$N][HFe(CO)$_3$PPh$_3$] was completely converted to [Et$_4$N][Fe(CO)$_3$(TePh)$_3$] (IR ν(CO) THF): 1966 vs, 2024 vs cm^{-1}), [Et$_4$N][Fe(CO)$_3$(SePh)$_3$] (IR ν(CO) THF): 1981 vs, 2039 vs, 2044 sh cm^{-1}), [Et$_4$N][PhSFe(CO)$_4$][10] (IR ν(CO) THF): 1912 vs, 2018 m cm^{-1}) and unidentified insoluble solid, respectively.

X-ray Crystal Structure Determination of [PPN][Fe(CO)$_3$(TePh)$_3$]·0.5THF. Crystal data are collected in Table I. Diffraction measurements were carried out on a Nonius CAD-4 automated diffractometer, using an ω scan mode. The unit cell constants were obtained from 20 reflections with 2θ angle in the range from 19.24 to 26.63°. The monoclinic space group *C*2/*c* was assigned from photographic evidence. Crystallographic computations were carried out on a MicroVAX 3600 computer using the NRCC package.[19] The last least-squares cycle was calculated with 119 atoms, 627 parameters, and 5662 out of 8139 reflections. The final residuals of the refinement were R(F) = 0.067 and R_w(F) = 0.077. Tables II and III list selected bond lengths and bond angles respectively.

Acknowledgment. We thank National Science Council of the Republic of China (Taiwan, NSC 82-0208-M-018-001) for support of this work.

Supplementary Material Available: Tables of crystal data and refinement details, final fractional coordinates, anisotropic thermal parameters, complete bond lengths and angles, torsional angles, and distances (Å) to the least-squares planes (13 pages). Ordering information is given on any current masthead page.

---

(19) Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3; Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 167–174.