Journal of the Chinese Chemical Society, 1993, *40*, 437-444

Oxidative Addition vs. Ligand-Exchange: Fe(II)-Mixed-Phenylchalcogenolate Complexes *fac*-[PPN][Fe(CO)$_3$(TePh)$_n$(SePh)$_{3-n}$] (n = 1, 2)

Wen-Feng Liaw*[a] (廖文峰), Chia-Huei Lai[a] (賴佳惠), Ming-Hsi Chiang[a] (江明錫),
Cheng-Kang Hsieh[a] (謝正剛), Gene-Hsiang Lee[b] (李錦祥), Shie-Ming Peng[b] (彭旭明)
[a]*Department of Chemistry, National Changhua University of Education, Changhua, Taiwan, R.O.C.*
[b]*Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.*

Diphenyldichalcogenides (PhE)$_2$ (E = Te, Se) react with Fe(0)-phenylchalcogenolate [PPN][PhEFe(CO)$_4$] to yield the products of oxidative addition, Fe(II)-mixed-phenylchalcogenolate *fac*-[PPN][Fe(CO)$_3$(TePh)$_n$(SePh)$_{3-n}$] (n = 1, 2). Reactions of [PPN][REFe(CO)$_4$] (E=Se, R=Me; E=S, R=Et) and diphenyldichalcogenides yielded ligand-exchange products [PPN][PhEFe(CO)$_4$] (E=Te, Se, S). The compounds [Fe(CO)$_3$(TePh)(SePh)$_2$]$^-$ (**1**) and [Fe(CO)$_3$(TePh)$_2$(SePh)]$^-$ (**2**) crystallize in the isomorphous monoclinic space group $C_{2/c}$, with a = 32.035(8), b = 11.708(6), c = 28.909(6) Å, Z = 8, R = 0.048, and R$_w$ = 0.044 (**1**); with a = 32.089(5), b = 11.745(2), c = 28.990(8) Å, Z = 8, R = 0.048, and R$_w$ = 0.048 (**2**). The complexes **1** and **2** crystallize as discrete cations of PPN$^+$ and anions of [Fe(CO)$_3$(TePh)$_n$(SePh)$_{3-n}$]$^-$ (n = 1, 2), and one half solvent molecule THF. The geometry around Fe(II) is a distorted octahedron with three carbonyl groups and three phenylchalcogenolate ligands occupying facial positions.

INTRODUCTION

The chemistry of transition-metal complexes containing TeR$^-$ and SeR$^-$ (R = alkyl, phenyl) ligands is little explored, even though the rational synthesis of metal-thiolate complexes is developed and their reactivity is exploited.[1,2] The lack of well characterized metal-tellurolate and metal-selenolate complexes reflects the sparse synthetic procedures. Synthetic approaches to metal-tellurolate complexes, to our knowledge, involve insertion of tellurium into the metal-alkyl bond,[3] metathesis between an alkali-metal tellurolate and a metal halide,[4] a tellurolysis pathway (L$_n$M-R + H$^-$-TeSiR$_3$ → R-H + L$_n$M-TeSiR$_3$),[5] nucleophilic cleavage of the Te-Te bond by metal-hydrides,[6] and oxidative addition of PhTeTePh to low-valent metal complexes.[6-8]

The reaction of [PPN][HFe(CO)$_4$] with diphenyldichalcogenides in doubly molar proportions in THF at ambient temperature gives rise to *fac*-[Fe(CO)$_3$(EPh)$_3$]$^-$ via an intermediate [PPN][PhEFe(CO)$_4$] (E = Te, Se) complex respectively.[6,9] Here we extend this synthetic method to investigate the behavior of coordinated terminal TeR$^-$, SeR$^-$ and SR$^-$ ligands in the Fe(CO)$_4$ fragment. The effect of the versatile anionic iron(0)-organochalcogenolate [REFe(CO)$_4$]$^-$ (E = Te, Se, S; R = Ph, Et, Me···) on the reaction pathways was addressed, and the oxidative addition abilities of diphenylditelluride, diphenyldiselenide and diphenyldisulfide in the oxidative decarbonylation were considered. Our observations of this unprecedented cleavage reaction of (RE)$_2$ by anionic iron(0)-chalcogenolate species may contribute to a better understanding of metalchalcogenolate-assisted activations of RE-ER (E = Te, Se, S) bond.

EXPERIMENTAL SECTION

Manipulations, transfers and reactions of samples were conducted under N$_2$ with standard Schlenk technique or in a 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$_2$O$_5$)] and then stored in dried, N$_2$-filled flasks over activated 4 Å moloecular 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 N$_2$. The reagents iron pentacarbonyl, dimethyldiselenide, diphenyldiselenide, diethyldisulfide, 4-nitrophenyldisulfide, 2,4,5-trichlorophenyldisulfide, phenylmagnesium bromide, tellurium powder (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-7 FTIR) using sealed solution cells (0.1 mm) with KBr windows. NMR spectra were recorded on a spectrometer (Bruker AC 300). UV-visible spectra were recorded on a spectrophotometer (GBC 918). Analyses of carbon, hydrogen, and nitrogen were obtained with a CHNO analyzer (Heraeus).

Preparation of *fac*-[PPN][Fe(CO)$_3$(TePh)(SePh)$_2$] (1)

To a solution of [PPN][PhTeFe(CO)$_4$]^{6,10} (0.456 g, 0.5 mmol) in THF (5 mL) was slowly added dropwise PhSeSePh (0.156 g, 0.5 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 7 h. The solution changed color into brown-red. The solvent was removed under vacuum, and hexane was added to precipitate the product. The brown-red solid was purified by dissolution in THF and precipitation with hexane. Recrystallization by dissolving the product in a minimum amount of THF, layering it with hexane (3-fold proportion), and then cooling to 0 °C for one week afforded brown-red crystals of [PPN] [Fe(CO)$_3$(TePh)(SePh)$_2$] (0.537 g, 90%): UV (THF) λ_{max} (ε/M^{-1} cm^{-1}) 326 (3.06×10^4), 434 (2.27×10^3), 480 (1.94×10^3) nm (Table 1); IR (THF) $\nu_{C=O}$ 1972(vs), 2031(vs) cm^{-1}; ^{13}C NMR (CD$_3$CN) δ 213.1 (CO); Anal. Calcd. for $C_{57}H_{45}O_3NP_2TeSe_2Fe$: C, 57.28; H, 3.80; N, 1.17, Found: C, 58.04; H, 4.0; N, 1.26.

Preparation of *fac*-[PPN][Fe(CO)$_3$(TePh)$_2$(SePh)] (2)

A solution of [PPN][PhSeFe(CO)$_4$]$^{6,9-10}$ (0.432 g, 0.5 mmol) in THF (5 mL) was slowly added PhTeTePh (0.205 g, 0.5 mmol)^{11} THF solution (5 mL) at room temperature. The reaction mixture was stirred for 6 h and occasionally monitored by IR until the reaction was complete. At this time the IR spectrum of the product showed two bands attributed to carbonyl stretching modes $\nu_{C=O}$ (THF) 1968(vs), 2027(vs) cm^{-1}). The solvent was removed under vacuum, and hexane was added to settle out the brown-red solid. Recrystallization by dissolving this solid in a minimum amount of THF, layering it with hexane, and keeping in the refrigerator for two weeks afforded brown-red crystals. The yield was typically 90%: UV (THF) λ_{max} (ε/M^{-1} cm^{-1}) 334 ($2.65 \times 10_4$), 464 (2.16×10^3), 510 (1.81×10^3) nm (Table 1); IR (THF) $\nu_{C=O}$ 1968(vs), 2027(vs) cm^{-1}; ^{13}C NMR (CD$_3$CN) δ 214.4 (CO); Anal. Calcd. for $C_{57}H_{45}O_3NP_2Te_2SeFe$: C, 55.04; H, 3.65; N, 1.13, Found: C, 55.40; H, 3.91; N, 1.04.

Preparation of [PPN][Fe(CO)$_3$(SR)$_3$] (R = 4-nitrophenyl disulfide, 2,4,5-trichlorophenyldisulfide)

A solution of (RS)$_2$ (308 mg, 2 mmol for R = 4-nitrophenyl disulfide; 425 mg, 2 mmol for R = 2,4,5-trichlorophenyldisulfide) in THF (5 mL) was added to [PPN] [HFe(CO)$_4$] (708 mg, 1 mmol) at ambient temperature. The clear solution immediately turned dark brown. After stirring the resulting solution for 2 min, the mixture was monitored by FTIR: IR (THF) $\nu_{C=O}$ 2006(s), 2062(s) cm^{-1} for R = 4-nitrophenyldisulfide and 2005(s), 2062(s) cm^{-1} for R = 2,4,5-trichlorophenyldisulfide were consistent with formation of *fac*-[PPN][Fe(CO)$_3$(SR)$_3$] respectively. Following isolation by washing with hexane and drying under vacuum, most compounds rapidly decomposed to insoluble solids at 0 °C.

Reaction of [PPN][REFe(CO)$_4$] (E = Se, R = Me; E = S, R = Et) with diphenyldicalcogenide

[PPN][MeSeFe(CO)$_4$]^{6,9} (80.1 mg, 0.1 mmol) was reacted with PhTeTePh (40.9 mg, 0.1 mmol) (or 31.2 mg of PhSeSePh; 21.8 mg of PhSSPh) in THF (5 mL) at ambient temperature. The reaction mixture was stirred for 5 min (reaction mixture of PhSeSePh for 1 h; reaction mixture of PhSSPh overnight) at room temperature; the IR spectrum re-

Table 1. IR, UV-vis, ^{13}C NMR and Bond-Length Properties of [PPN][Fe(CO)$_3$(TePh)$_n$(SePh)$_{3-n}$] (n = 0, 1, 2, 3)

Compd	IR (THF) $\nu_{C=O}$/cm^{-1}	UV-Vis (THF) $\lambda_{max/nm}$ (ε/M^{-1}cm^{-1})	^{13}C NMR (CD$_3$CN) δ/ppm	Bond Distances Fe-E/Å	Reference
n = 0	1975(s), 2035(s)	482 (2.46×10^3), 427 (2.96×10^3), 306 (1.90×10^4)	212.7(CO)	2.459(2)	9
n = 1	1972(s), 2031(s)	480 (1.94×10^3), 434 (2.27×10^3), 326 (3.06×10^4)	213.1(CO)	2.509(2) 2.516(calc.) [1/3(Fe-Te)+ 2/3(Fe-Se)]	this work
n = 2	1968(s), 2027(s)	510 (1.81×10^3), 464 (2.16×10^3), 334 (2.65×10^4)	214.4(CO)	2.569(2) 2.573(calc.) [2/3(Fe-Te)+ 1/3(Fe-Se)]	this work
n = 3	1963(s), 2021(s)	527 (2.13×10^3), 469 (2.4×10^3), 336 (2.02×10^4)	215.8(CO)	2.630(2)	6

vealed that all [PPN][MeSeFe(CO)$_4$] [$\nu_{C=O}$ (THF) 1897(vs), 2000(m) cm^{-1}] was completely converted to [PPN][PhTeFe(CO)$_4$] [$\nu_{C=O}$ (THF) 1901(vs), 2002(m) cm^{-1}] [PPN][PhSeFe(CO)$_4$] [$\nu_{C=O}$ (THF) 1905(vs), 2007(m) cm^{-1}], [PPN][PhSFe(CO)$_4$] [$\nu_{C=O}$ (THF) 1909(vs), 2010(m) cm^{-1}][6,9] and other unidentified organic products.

X-ray Crystallographic Analyses of [PPN][Fe(CO)$_3$(TePh)(SePh)$_2$]·0.5 THF (1) and [PPN][Fe(CO)$_3$(TePh)$_2$(SePh)]·0.5 THF (2)

Dark red-brown crystals of the complexes suitable for X-ray crystallography were prepared by diffusion of hexane into concentrated THF solutions of each complex under N$_2$ in a refrigerator (4 °C). The crystal data are summarized in Table 2. The unit cell parameters were obtained from 25 reflections. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo K$_\alpha$ radiation employing the $\theta/2\theta$ scan mode.

The structure analyses were initiated in the monoclinic space group C$_{2/c}$. The structures **1** and **2** were resolved by the conventional heavy-atom method and refined by least-squares cycle routines. Crystals **1** & **2** exhibited disorder of Se and Te atoms. The combined scattering factors, 1/3Te + 2/3Se and 2/3Te + 1/3Se for **1** and **2** respectively, were used in the refinement. The molecular structure of complexe **1** appears in Fig. 1. Selected bond lengths and angles are listed in Tables 3-4.

RESULTS AND DISCUSSION

Synthesis

The reaction of 1 equiv [PPN][HFe(CO)$_4$] with 2 equiv (PhTe)$_2$ in THF at room temperature results in the formation of moderately air-, and light-sensitive, dark purple crystalline solid *fac*-[PPN][Fe(CO)$_3$(TePh)$_3$]. No isomerization or

Table 2. Crystallographic Data

Compound	1	2
Formula	$C_{59}H_{48}O_{3.5}NP_2FeSe_2Te$	$C_{59}H_{48}O_{3.5}NP_2FeSeTe_2$
Molar mass/g	1231.36	1279.98
Color	brown-red	brown-red
Crystal size/mm^3	0.1 × 0.45 × 0.50	0.10 × 0.40 × 0.50
Cryst system	monoclinic	monoclinic
Space group	C$_{2/c}$	C$_{2/c}$
a/Å	32.035(8)	32.089(5)
b/Å	11.708(6)	11.745(2)
c/Å	28.909(6)	28.990(8)
β/deg	95.00(2)	94.90(2)
V/Å^3	10802(7)	10886(4)
Z	8	8
F(000)	4911	4895
λ(Mo K$_\alpha$)/Å	0.71069	0.71069
d_{calc}/g cm^{-3}	1.514	1.562
2θ(max)/deg	45	45
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Scan range		
h	-34 to 34	-34 to 34
k	0 to 12	0 to 12
l	0 to 31	0 to 31
No. of reflections	7060	7114
No. of unique reflections	7060	7114
No. of reflcns. obsd (I > 2σ (I))	3298	3826
T_{min}/T_{max}	0.63/1.00	0.65/1.00
R (all data)	0.048 (0.140)	0.048 (0.115)
R$_w$ (all Data)	0.044 (0.052)	0.048 (0.053)
GOF	1.56	1.78
Residual peak/e A^{-3}	0.510	0.650
Residual hole/e A^{-3}	-0.540	-0.860

decomposition of *fac*-[PPN][Fe(CO)$_3$(TePh)$_3$] was observed over a 2 h period in refluxing THF. IR measurements of $\nu_{C=O}$ showed that formation of purple solid *fac*-[PPN][Fe(CO)$_3$(TePh)$_3$] proceeds via intermediate iron(0)-phenyltellurolate [PPN][PhTeFe(CO)$_4$] complex, isolated by addition of diphenylditelluride to [PPN][HFe(CO)$_4$] THF in equimolar proportions drop by drop.[6] An atmosphere of CO failed to prevent oxidative addition of PhTeTePh even when we exposed the mixture of [PPN][PhTeFe(CO)$_4$] and PhTeTePh under 1 atm of CO in THF at room temperature. To synthesize iron(II)-mixed-organochalcogenolate-carbonyl complexes and to evaluate the influence of coordinated terminal TeR$^-$, SeR$^-$, SR$^-$ ligands in the Fe(CO)$_4$ fragment on the reactivity of organochalcogenides, we surveyed the reactivity of [PhTeFe(CO)$_4$]$^-$ toward diphenyldiselenide and diphenyldisulfide respectively. An immediate reaction ensued when diphenyldiselenide was added to a solution of [PPN][PhTeFe(CO)$_4$] in THF at room temperature. However, we observed no indication of formation of *fac*-[PPN][Fe(CO)$_3$(TePh)(SPh)$_2$] complex in the reaction of [PPN][PhTeFe(CO)$_4$] and (PhS)$_2$ under the same reaction condition overnight on the basis of IR spectra (Scheme I).

These results clearly indicate that diphenylditelluride was significantly more reactive than diphenyldiselenide and diphenyldisulfide for oxidative decarbonylation, as demonstrated by the observations that (PhTe)$_2$ reacted cleanly and quickly with [PhTeFe(CO)$_4$]$^-$, and that (PhS)$_2$ was completely inert under the same condition even though diphenyldisulfide is a good reagent for oxidative addition.[12-16]

We extended this chemistry using diphenyldichalcogenide (PhE)$_2$ (E = Te, Se, S) and [PPN][REFe(CO)$_4$]

Table 3. Selected Bond Angles/deg

(b) [PPN][Fe(CO)$_3$(TePh)(SePh)$_2$]·0.5 THF (**1**) (M = Te = Se)			
Fe-M(1)-C(4)	107.3(3)	M(1)-Fe-C(1)	88.4(3)
Fe-M(2)-C(10)	106.6(3)	M(1)-Fe-C(2)	94.2(3)
Fe-M(3)-C(16)	106.3(3)	M(1)-Fe-C(3)	167.9(4)
M(1)-Fe-M(2)	84.35(6)	M(2)-Fe-C(1)	94.3(3)
M(1)-Fe-M(3)	84.60(6)	M(2)-Fe-C(2)	169.9(4)
M(2)-Fe-M(3)	86.03(7)	M(2)-Fe-C(3)	83.7(4)
C(1)-Fe-C(2)	95.6(5)	M(3)-Fe-C(1)	172.9(3)
C(1)-Fe-C(3)	94.0(5)	M(3)-Fe-C(2)	83.9(4)
C(2)-Fe-C(3)	97.4(5)	M(3)-Fe-C(3)	93.1(3)
Fe-C(1)-O(1)	177.9(9)	M(1)-C(4)-C(5)	122.7(8)
Fe-C(2)-O(2)	178.9(10)	M(1)-C(4)-C(9)	120.1(9)
Fe-C(3)-O(3)	176.5(10)	M(2)-C(10)-C(11)	120.3(8)
		M(2)-C(10)-C(15)	120.3(8)
		M(3)-C(16)-C(17)	118.4(9)
		M(3)-C(16)-C(21)	121.4(11)
(c) [PPN][Fe(CO)$_3$(TePh)$_2$(SePh)]·0.5 THF (**2**) (M = Te = Se)			
Fe-M(1)-C(4)	106.6(3)	M(1)-Fe-C(1)	88.2(3)
Fe-M(2)-C(10)	105.3(3)	M(1)-Fe-C(2)	94.0(3)
Fe-M(3)-C(16)	106.8(3)	M(1)-Fe-C(3)	168.3(4)
M(1)-Fe-M(2)	83.80(6)	M(2)-Fe-C(1)	93.5(3)
M(1)-Fe-M(3)	83.95(6)	M(2)-Fe-C(2)	170.1(4)
M(2)-Fe-M(3)	85.89(6)	M(2)-Fe-C(3)	84.7(4)
C(1)-Fe-C(2)	96.1(5)	M(3)-Fe-C(1)	172.2(3)
C(1)-Fe-C(3)	94.7(5)	M(3)-Fe-C(2)	84.3(4)
C(2)-Fe-C(3)	96.9(5)	M(3)-Fe-C(3)	93.0(3)
Fe-C(1)-O(1)	176.6(9)	M(1)-C(4)-C(5)	122.3(9)
Fe-C(2)-O(2)	178.6(10)	M(1)-C(4)-C(9)	120.4(8)
Fe-C(3)-O(3)	178.4(10)	M(2)-C(10)-C(11)	121.0(8)
		M(2)-C(10)-C(15)	119.9(8)
		M(3)-C(16)-C(17)	118.8(8)
		M(3)-C(16)-C(21)	120.6(11)

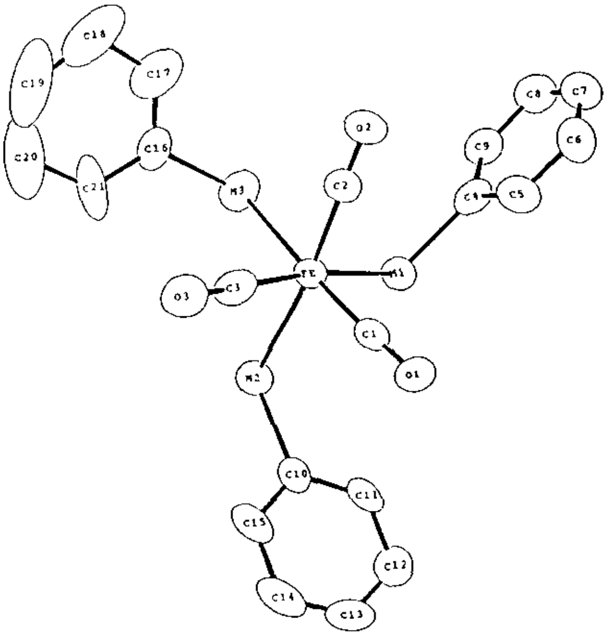
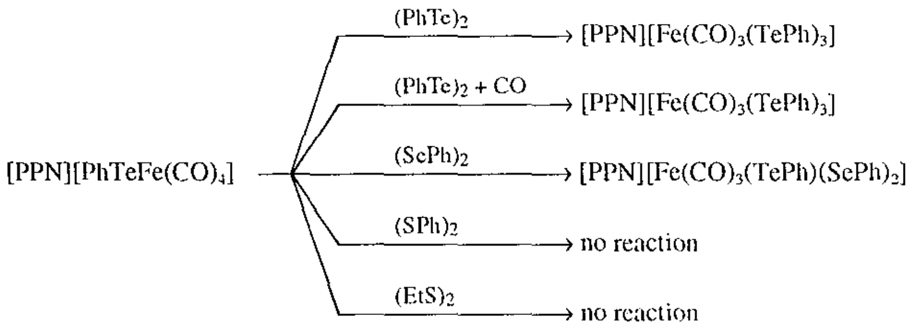


Fig. 1. Molecular structure of [*fac*-Fe(CO)$_3$(MPh)$_3$]$^-$ (M = 1/3Te + 2/3Se, (**1**); 2/3Te + 1/3Se, (**2**).

Table 4. Selected Bond Lengths/Å

(b) [PPN][Fe(CO)$_3$(TePh)(SePh)$_2$]·0.5 THF (**1**) (M = Te = Se)			
M(1)-Fe	2.5297(19)	Fe-C(1)	1.737(11)
M(2)-Fe	2.5066(21)	Fe-C(2)	1.767(11)
M(3)-Fe	2.4909(20)	Fe-C(3)	1.747(11)
M(1)-C(4)	2.007(12)	C(1)-O(1)	1.158(13)
M(2)-C(10)	1.990(11)	C(2)-O(2)	1.152(13)
M(3)-C(16)	1.984(11)	C(3)-O(3)	1.156(13)
(c) [PPN][Fe(CO)$_3$(TePh)$_2$(SePh)]·0.5 THF (**2**) (M = Te = Se)			
M(1)-Fe	2.5860(18)	Fe-C(1)	1.771(10)
M(2)-Fe	2.5771(18)	Fe-C(2)	1.791(11)
M(3)-Fe	2.5421(19)	Fe-C(3)	1.770(12)
M(1)-C(4)	2.074(11)	C(1)-O(1)	1.142(12)
M(2)-C(10)	2.073(11)	C(2)-O(2)	1.126(13)
M(3)-C(16)	2.054(11)	C(3)-O(3)	1.142(14)

Scheme I

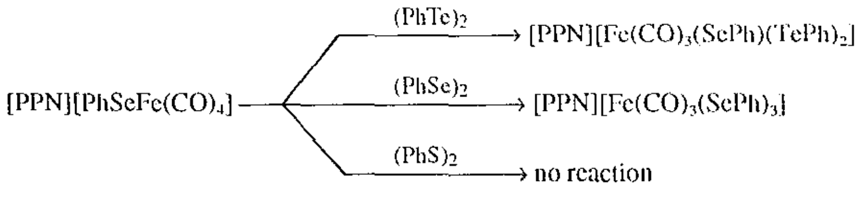


(E=Se, R=Ph, Me; E=S, R=Ph) as starting materials. The preparation of iron(II)-mixed-organochalcogenolate complex *fac*-[PPN][Fe(CO)$_3$(SePh)(TePh)$_2$] was also attempted by reaction of [PPN][PhSeFe(CO)$_4$] and (PhTe)$_2$ by 1:1 ratio in THF at ambient temperature. The IR, UV, ^{13}C-NMR spectral and X-ray diffraction data show that [PhSeFe(CO)$_4$]$^-$ also promotes oxidative addition of diphenylditelluride to form [PPN][Fe(CO)$_3$(SePh)(TePh)$_2$]. The fact that no *fac*-[PPN][Fe(CO)$_3$(SePh)(SPh)$_2$] complex was formed in the reaction of [PPN][PhSeFe(CO)$_4$] and (PhS)$_2$ indicates a unique role of the S-S bond strength of diphenyldisulfide in this oxidative decarbonylation reaction (Scheme II).

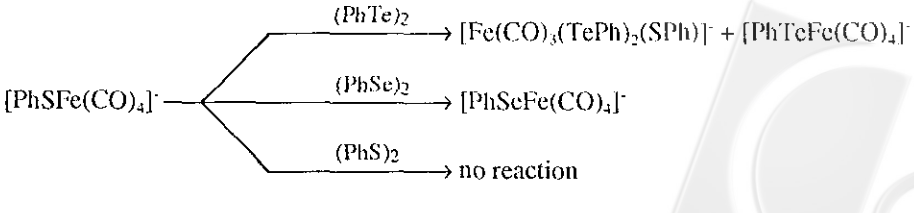
The anionic [PhSFe(CO)$_4$]$^-$ did not promote oxidative addition of diphenyldisulfide (Scheme III), whereas the reaction of 1 equiv [PPN][HFe(CO)$_4$] with 2 equiv (RS)$_2$ (R = 4-nitrophenyl disulfide, or 2,4,5-trichlorophenyl disulfide) followed a pathway reminiscent of reactions of (PhE)$_2$ (E = Te, Se) and [PPN][HFe(CO)$_4$]. This reaction is more vigorous than that of its diphenylditelluride and diselenide analogue (Scheme IV). [Fe(CO)$_3$(SR)$_3$]$^-$ was less stable than [Fe(CO)$_3$(EPh)$_3$]$^-$ (E = Te, Se), and rapid deposition of a sparingly soluble dark decarbonylation precipitate appeared when solution of [PPN][Fe(CO)$_3$(SR)$_3$] stood under ambient conditions. Spectral data for [Fe(CO)$_3$(SR)$_3$]$^-$ and *fac*-[Fe(CO)$_3$(EPh)$_3$]$^-$ (E = Te, Se) resemble each other closely and indicate that the compounds adopt a similar geometry.

Reaction of [PPN][PhSFe(CO)$_4$] and PhTeTePh is more complex and it is difficult to obtain pure [PPN][Fe(CO)$_3$(TePh)$_2$(SPh)] as shown in Scheme III.

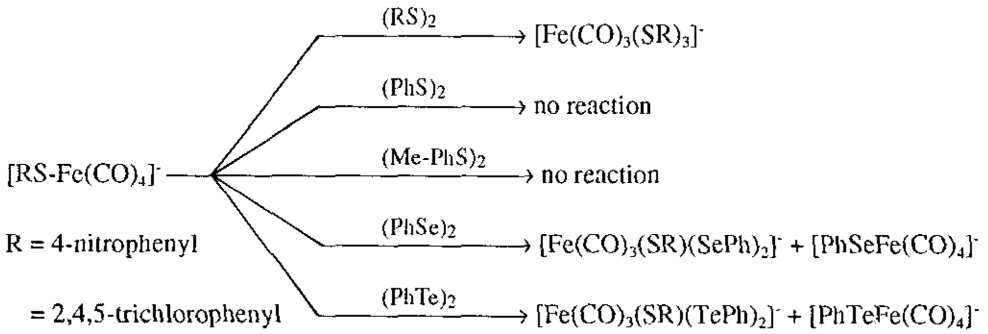
Scheme II



Scheme III



Scheme IV



An important characteristic of the anionic iron(0)-organochalcogenolate [PPN][REFe(CO)$_4$] (E = Se, S) complexes is the nucleophilicity of their E atom that can be tuned by varying the substituent R. For comparison, we investigated the reactivity of [PPN][REFe(CO)$_4$] (E=Se, R=Me; E=S, R=Et)[6] toward diphenylditelluride, diphenyldiselenide, diphenyldisulfide respectively. The IR spectral data, $\nu_{C=O}$, show the formation of only ligand-exchange products, [PhTeFe(CO)$_4$]$^-$, [PhSeFe(CO)$_4$]$^-$, [PhSFe(CO)$_4$]$^-$ respectively,[6,9] and presumably PhE-ER. No oxidative addition product was observed (Scheme V). This evidence shows that electronic modulations at the ligand donor functions are capable of inducing significant alternate reaction pathway.

The results of formation of these iron(II)-mixed-phenylchalcogenolate carbonyl complexes demonstrate the ability of the anionic iron(0)-phenyltellurolate and iron(0)-phenylselenolate to act as an excellent species to build *fac*-[Fe(CO)$_3$(TePh)$_n$(SePh)$_{n-3}$]$^-$ (n = 0, 1, 2, 3). One aspect of the reactivity of [REFe(CO)$_4$]$^-$ toward organodichalcogenides can be mentioned: the reaction pathway (oxidative addition or ligand-exchange) is "tailored" according to the bond strength inherent in the organodichalcogenides and to the nucleophilicity of chalcogenide atoms in [REFe(CO)$_4$]$^-$ complexes.

No ligand exchange was observed between the selenolate and tellurolate, i.e.

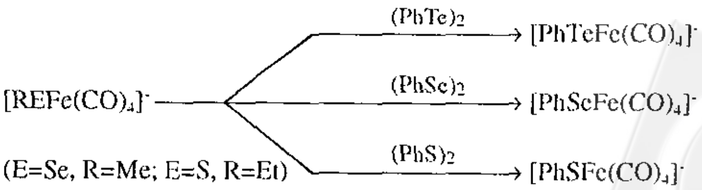
$$[\mathrm{Fe(CO)_3(TePh)(SePh)_2}]^- + \mathrm{PhTeTePh} \xrightarrow{\text{R.T.}} \text{no reaction}$$

$$[\mathrm{Fe(CO)_3(TePh)_2(SePh)}]^- + \mathrm{PhSeSePh} \xrightarrow{\text{R.T.}} \text{no reaction}$$

Spectroscopy

IR spectra of the carbonyl stretching region of these complexes [Fe(CO)$_3$(TePh)$_3$]$^-$, [Fe(CO)$_3$(TePh)(SePh)$_2$]$^-$, [Fe(CO)$_3$(TePh)$_2$(SePh)]$^-$, [Fe(CO)$_3$(SePh)$_3$]$^-$, show an absorption pattern consistent with facial structure. IR spectral data of these analogues are reported in Table 1. The carbonyl stretching wavenumbers indicate that the replacement of a TePh ligand with a SePh ligand in these facial analogues causes a significant shift to greater wavenumbers that indicates the weaker donor ability of the phenylselenolate ligand.

Scheme V



The electronic absorption spectra of these analogues, reported in Table 1, are dominated by two major features in the region 400 - 550 nm. These bands are tentatively assigned as ligand-to-metal charge-transfer transitions, as the replacement of phenyltellurolate ligand with phenylselenolate ligand in these analogues has the significant effect of increasing ligand-to-metal charge-transfer energies. The ^{13}C NMR spectra showing only one signal for each compound, the anionic *fac*-iron(II)-phenylchalcogenolate complex indicate that three CO groups of each compound are fluxional (Table 1).

Structure

Crystals of **1, 2** consist of well separated cations and anions and one half solvent molecule; there is no uncommon cation-anion interaction. The PPN^+ cation shows the expected geometry. The structures of $[Fe(CO)_3(TePh)(SePh)_2]^-$, and $[Fe(CO)_3(TePh)_2(SePh)]^-$ anions (Fig. 1) are similar to the structurally characterized $[Fe(CO)_3(EPh)_3]^-$ (E = Te, Se) anions.[6,9] The anionic $[Fe(CO)_3((TePh)_n(SePh)_{3-n}]^-$ represents the first $FeTe_nSe_{3-n}$ molecular fragment of a mononuclear Fe complex. The structure of **1** consists of an isosceles triangle of tellurium and selenium atoms with M-M-M bond angles of 59.68(4)°, 59.75(3)° and 60.57(4)° respectively, which are comparable to M-M-M bond angles of 59.27(3)°, 59.78(3)° and 60.94(3)° (M = Te = Se) in **2**.

In complex **1**, the M···M (M = Te = Se) contact distances are 3.379(2), 3.382(2), and 3.409(3) Å, to be compared with the M···M contact distances of 3.430(2), 3.448(2), and 3.488(2) Å found in complex **2**. The intramolecular PhM···MPh attraction is considered for these facial complexes. We noted the possibility of such an interaction in $[Fe(CO)_3(SePh)_3]^-$, and $[Fe(CO)_3(TePh)_3]^-$,[6] in which the PhTe···TePh contact distance 3.477 - 3.575 Å is much greater than that of a typical single PhTe-TePh bond length 2.712 Å,[17] and near the Te···Te contact distance 3.495 Å that is considered a significant interchain interaction in a Cs_2Te_5 complex.[18] These attractions Te···Se/Se···Se/Te···Te may contribute to stabilization of *fac*-$[Fe(CO)_3(TePh)(SePh)_2]^-$ and *fac*-$[Fe(CO)_3(TePh)_2(SePh)]^-$ complexes.

Because of the disorder, the exact Fe-Te, Fe-Se bond distances are poorly determined in the $[Fe(CO)_3(TePh)(SePh)_2]^-$ and $[Fe(CO)_3(TePh)_2(SePh)]^-$ complexes. The average Fe-M (M=Se=Te) bond length of 2.509(3) Å in $[Fe(CO)_3(TePh)(SePh)_2]^-$ is in excellent agreement with the calculated average Fe-M bond length 2.516(4) Å by 2/3(Fe-Se)+1/3(Fe-Te) (average Fe-Te bond distance of 2.630(4) Å in $[Fe(CO)_3(TePh)_3]^-$ and average Fe-Se bond length 2.459(2) Å in $[Fe(CO)_3(SePh)_3]^-$).[6,9] A similar trend is seen in the $[Fe(CO)_3(TePh)_2(SePh)]^-$ complex; the average Fe-M (M=Te=Se) bond distance 2.568(2) Å in $[Fe(CO)_3(TePh)_2(SePh)]^-$ agrees well with values 2.573(4) Å determined from 2/3(Fe-Te)+1/3(Fe-Se) based on the Fe-Se bond length 2.459(2) Å of $[Fe(CO)_3(SePh)_3]^-$ and the Fe-Te bond length 2.630(9) Å of $[Fe(CO)_3(TePh)_3]^-$ (Table 1).

CONCLUSION

We demonstrated the effectiveness of the anionic Fe(0)-phenylchalcogenolate species as a template for preparation of iron(II)-mixed-phenylchalcogenolate complexes, which have potentially interesting chemistry that may be inaccessible with other systems. We gave an account of the preparation and characterization of these [PPN] $[Fe(CO)_3(TePh)_n(SePh)_{3-n}]$ (n = 1, 2) complexes, including the X-ray structure, and the reactivity of $[REFe(CO)_4]^-$ toward organochalcogenides. Ligand-exchange products were observed in the reaction of $[REFe(CO)_4]^-$ (E = Se, R = Me; E = S, R = Et) with diphenyldichalcogenides.

The analogoues *fac*-Fe-$(Te)_3$, *fac*-Fe-$(Te)_2(Se)$, *fac*-Fe-$(Te)(Se)_2$, and *fac*-Fe-$(Se)_3$ complexes exhibit nearly identical structures but with blue-shifted electronic absorptions, greater wavenumbers associated with carbonyl stretching modes and greater ^{13}C (CO) chemical shifts along the above series. Effects of various phenylchalcogenolates tend to be small, with typical variations of 3-6 cm^{-1} in IR $\nu_{C=O}$ and 5-30 nm in UV-visible bands.

SUPPLEMENTARY MATERIAL AVAILABLE

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

ACKNOWLEDGMENT

We thank National Science Council of the Republic of China for support.

Received August 6, 1993.

Key Words

Iron(II)-tellurolate-selenolate.

REFERENCES

1. (a) Bonasia, P. J.; Gindelberger, D. E.; Dabbousi, B. O.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 5209. (b) Rothwell, I. P. R.; Chisholm, M. H. In *Comprehensive Coordination Chemistry*, Wilkison, G.; Gillaid, R. D.; J. A. McCleverty, J. A. Eds.; Pergamon: New York, **1987**, Vol. 2, p 335, p 661. (c) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295. (d) Bonasia, P. J.; Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1299.
2. (a) Gysling, H. J. *Coord. Chem. Rev.* **1982**, *42*, 133. (b) Orpen, A. G.; Bramrner, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1. (c) McConnachie, J. M.; Iber, J. A. *Inorg. Chem.* **1991**, *30*, 1770.
3. McGregor, K.; Deacon, G. B.; Dickson, R. S.; Fallon, G. D.; Rowe, R. S.; West, B. *J. Chem. Soc., Chem. Commun.* **1990**, *19*, 1293.
4. (a) Gindelberger, D.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6242. (b) Sato, M.; Yoshida, T. *J. Organomet. Chem.* **1974**, *67*, 395. (c) Hausmann, H.; Hofler, M.; Kruck, T.; Zirumelman, H. W. *Chem. Ber.* **1981**, *114*, 975. (d) Davies, I.; McWhinnie, W. R. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 763. (e) Davies, I.; McWhinnie, W. R.; Dance, N. Jones, C. H. W. *Inorg. Chim. Acta.* **1978**, *29*, L217. (f) Gardner, S. A.; Trotter, P. T.; Gysling, H. J. *J. Organomet. Chem.* **1981**, *212*, 35. (g) Gardner, S. A.; Gysling, H. J. *J. Organomet. Chem.* **1980**, *197*, 111. (h) Simon, W.; Wilk, A.; Krebs, B.; Henkel, G. *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 1009.
5. (a) Dabbousi, B. O.; Bonasia, D. J.; Arnold, J. *J. Am. Chem. Soc.* **1991**, *113*, 3186. (b) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240.
6. Liaw, W.-F.; Chiang, M.-H.; Liu, C.-J.; Harn, P.-J.; Liu, L.-K. *Inorg. Chem.* **1993**, *32*, 1536.
7. Chia, L. Y.; McWhinnie, W. R. *J. Organomet. Chem.* **1978**, *148*, 165.
8. Dance, N. S.; Jones, C. H. W. *J. Organomet. Chem.* **1978**, *152*, 175.
9. (a) Liaw, W.-F.; Lai, C.-H.; Lee, C.-K.; Lee, G.-H.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1993**, 2421. (b) Liaw, W.-F.; Chiou, S.-J.; Lee, W.-J.; Lee, G.-H.; Peng, S.-M. *J. Chin. Chem. Soc.* **1993**, *40*, 361. (c) Liaw, W.-F.; Horng, Y.-C.; Ou, D.-S.; Lee, G.-H.; Peng, S.-M. *J. Chin. Chem. Soc.* **1993**, *40*, 367. (d) Liaw, W.-F.; Liu, C.-J.; Lai, C.-H. *J. Chin. Chem. Soc.* **1992**, *39*, 409.
10. Smith, M.-B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 2388.
11. Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.
12. Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 3386.
13. Day, V. W.; Lesch, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 1290.
14. (a) Muller, A.; Aegermann, W. *Inorg. Chem.* **1979**, *18*, 2631. (b) Jessop, P. G.; Rettig, S. J.; Lee, C.-L.; James, B. R. *Inorg. Chem.* **1991**, *30*, 4617.
15. Mathur, P.; Mavunkal, I. J.; Rugmini, V.; Mahon, M. F. *Inorg. Chem.* **1990**, *29*, 4838.
16. (a) Seyferth, D.; Henderson, R. S.; Song, L. C. *Organometallics* **1982**, *1*, 125. (b) Sellmann, D.; Jonk, H.-E.; Pfeil, H.-R.; Huttner, G.; Seyerl, J. V. *J. Organomet. Chem.* **1980**, *191*, 171. (c) Takacs, J.; Marko, L. *Transition Met. Chem. (Weinheim, Ger.)* **1984**, *9*, 10. (d) Sellmann, D.; Kunstmann, H.; Knoch, F.; Moll, M. *Inorg. Chem.* **1988**, *27*, 4183. (e) Sellmann, D.; Weiss, R.; Knoch, F.; Ritter, G.; Dengler, J. *Inorg. Chem.* **1990**, *29*, 4107.
17. Llabres, G.; Dideberg, O.; Dupont, L. *Acta Crystallogr., Sect. B* **1972**, *28B*, 2438.
18. Burns, R. C.; Gillespie, R. J.; Luk, W. C.; Slim, D. R. *Inorg. Chem.* **1979**, *18*, 3086.