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Bis(selenolate) and Bis(thiolate) Derivatives of Iron(II) Phosphine Complexes: Crystal Structure of *cis,cis,trans*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$

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Introduction

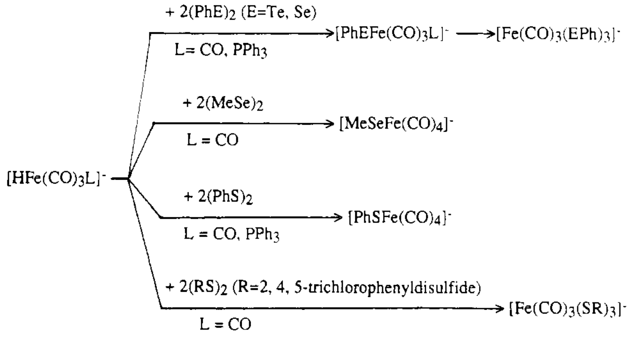
It is well established that the nature of the R groups (R = alkyl, phenyl) and E–E bonds (E = Te, Se, S) plays a key role in determining the outcome of reactions of diorganyldichalcogenides with iron hydrides (Scheme 1).[1-3]

We also 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.[1-3] In an attempt to further probe substituent effects in iron–chalcogenolate chemistry, we have examined the electronic consequences of varying substituents bound to the iron metal center and substituents bound to the diorganyldichalcogenides RE–ER (E = Se, S; R = Me). Here we present details of our extension and the X-ray structural evidence that clearly show that reaction of dimethyl diselenide (or dimethyl disulfide) with *trans*-$[Et_4N][HFe(CO)_3PMe_3]$ undergoes an hydride/selenolate ligand exchange followed by oxidative decarbonylation and ligand displacement to form the iron(II)–selenolate complex containing the terminal selenolate ligands.

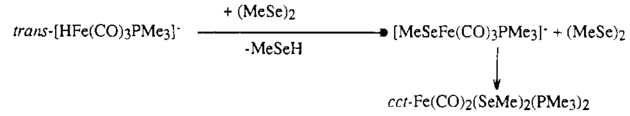
Results and Discussion

The tetraethylammonia iron–hydride salt[4] *trans*-$[HFe(CO)_3PMe_3]^-$ reacted cleanly with 2 equiv of dimethydiselenide in THF at room temperature under nitrogen to produce a dark red-brown solution of iron-selenolate by the reaction sequence shown in Scheme 2. On recrystallization from nonpolar solvent such as hexane, dark red-brown crystals of *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$ (*cct* = *cis,cis,trans*) were obtained in moderate yield (23% based on the stoichiometry of $[HFe(CO)_3PMe_3]^-$). The hexane-soluble *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$ was isolated as moderate air-sensitive crystals, and could be stored infinitely under nitrogen at ambient temperature, permitting full characterization by elemental analysis, IR, NMR spectroscopy, and X-ray diffraction. When adding 1 equiv of PMe_3 to the reaction of *trans*-$[HFe(CO)_3PMe_3]^-$ and 2 equiv of $(MeSe)_2$ in THF at room temperature, we also observed that the rate of formation of *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$ was accelerated and that the yield of the reaction increased considerably.

Scheme 1



Scheme 2



The IR spectra of the title complexes showing two strong CO stretching bands support a *cis* position of two CO ligands.[5] The ^1H NMR spectra show a singlet for the methyl bonded to Se, and display a triplet for the methyl bonded to phosphorus atoms indicating substantial ^{31}P–^{31}P coupling and a mutual *trans* configuration (triplet by virtual coupling).[6] The $^{31}P\{H\}$ NMR spectrum shows a single band and indicates two equivalent phosphine ligands.

The X-ray crystal structure of the title bis(selenolate)–iron(II)–carbonyl–phosphine complex consists of two crystallographically independent molecules. The geometry about the central iron can be described as distorted octahedral with bond angles of 83.25(4)° for Se(1A)–Fe(1A)–Se(2A) and 95.6(3)° for C(1A)–Fe(1A)–C(2A) confirming the spectroscopic assignment of *cct*-configuration (Figure 1). The Se(1A)···Se(2A) contact distance (3.251(1) Å) in *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$, similar to that of *fac*-$[Fe(CO)_3(SePh)_3]^-$,[1] shows no formal Se–Se bond; however, a certain degree of intramolecular interaction is proposed.[1,7] The proximity of Se atoms in *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$ is probably caused by the lone-pair electrons overlap of the sp^3 Se atoms and the methyl groups which point away from each other (Se(1A)–Fe(1A)–Se(2A) 83.25(4)°).[8]

The Fe-SeMe distances (2.447(1) and 2.448(1) Å) are comparable with the terminal Fe–SePh distance of 2.459(2) Å in $[Fe(CO)_3(SePh)_3]^-$ [1] and the Fe–SePh distance of 2.460(12) Å in tetrahedral $[Fe(SePh)_4]^{-2}$.[7] The Fe–Se–C bond angles [108.0(3) and 109.5(3)°] indicate a tetrahedral disposition of electron pairs about the selenium atoms.

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) 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 reaction vessels were via stainless-steel cannula under positive pressure of N_2. The reagents iron pentacarbonyl, dimethyl diselenide, and dimethyl disulfide (Aldrich)

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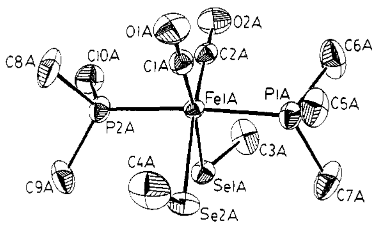

Figure 1. An ORTEP drawing of one of two crystallographic independent *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$ with thermal ellipsoids drawn at 50% probability.

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 Bruker AC 200 spectrometer. UV–visible spectra were recorded on a GBC 918 spectrophotometer. Analyses of carbon and hydrogen were obtained with a CHN analyzer (Heraeus).

Preparation of *cct*-$Fe(CO)_2(EMe)_2(PMe_3)_2$ (E = Se, S). The starting material *trans*-$[Et_4N][HFe(CO)_3(PMe_3)]$ (0.382 g, 1.1 mmol)[4] was placed in a Schlenk flask (50 mL) and dissolved in THF (10 mL). A portion of dimethyl diselenide (210 μL, 2.2 mmol) was syringed into the *trans*-$[Et_4N][HFe(CO)_3(PMe_3)]$ THF solution. The solution was stirred for 3 days at ambient temperature. The THF solvent was removed under vacuum and the red-brown product was extracted with hexane. Recrystallization of the product from a minimum volume of hexane (6 mL), and then cooling to 4 °C for 3 weeks afforded dark red-brown crystals of *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$ in an isolated yield 23% (0.117 g) based on *trans*-$[Et_4N][HFe(CO)_3(PMe_3)]$. IR ν(CO): 1933 s, 1988 vs cm^{-1} (THF); 1935 s, 1990 vs cm^{-1} (hexane). ^1H NMR (C_6D_6): δ 1.81 (s) ($SeCH_3$) ($J_{^1H-^{77}Se}$ = 10.5 Hz satellite), 1.37 (t) ppm (PCH_3). $^{31}P\{H\}$ NMR (CD_3COCD_3): δ 1.88 (s) ppm vs H_3PO_4. Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 353 (3766), 320(6389). Anal. Calcd. for $C_{10}H_{24}O_2P_2FeSe_2$: C, 26.57; H, 5.35. Found: C, 26.80; H, 5.33. The synthesis of *cct*-$Fe(CO)_2(SMe)_2(PMe_3)_2$ is similar to that of *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$ above. IR ν(CO): 1937 s, 1993 vs cm^{-1} (THF). ^1H NMR (CD_3COCD_3): δ 1.76(s) (SCH_3), 1.59(t) ppm ($P(CH_3)_3$); $^{31}P\{H\}$ NMR (CD_3COCD_3): δ 7.64(s) ppm vs H_3PO_4.

X-ray Crystal Structure Determination of *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$. Dark red-brown crystals of the title complex suitable for X-ray crystallography were prepared from a minimum volume of hexane solution of the complex under N_2 in a refrigerator (4 °C). The crystal data are summarized in Table 1. The moderately air-sensitive dark red-brown crystal *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$ chosen for diffraction measurement was ca. 0.40 × 0.50 × 0.50 mm and the unit cell parameters were obtained from 25 reflections ($17.70° < 2\theta < 23.50°$). Diffraction measurements were carried out on a Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation employing the $\theta/2\theta$ scan mode at room temperature. The last least-squares cycle was calculated with 82 atoms, 308 parameters, and 2953 [$I > 2\sigma(I)$] out of 4700 reflections. Absorption corrections were made using the NRCC-SDP-VAX package of programs.[9] Selected bond lengths and angles are listed in Table 2.

Table 1. Crystallographic Data for *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$

chem formula	$C_{10}H_{24}O_2P_2FeSe_2$
fw	452.01
space group	$P2_1/n$
cryst syst	monoclinic
a, Å	14.597(2)
b, Å	16.978(2)
c, Å	15.317(4)
β, deg	108.62(2)
V, Å^3	3597.4(12)
d(calcd), g cm^{-3}	1.669
Z	8
F(000)	1792
λ, Å (Mo Kα)	0.710 69
μ, cm^{-1}	50.1
abs (min and max transm coeff)	0.7144–0.9979
T, °C	25
R^a	0.033
R_w^b	0.030

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cct*-$Fe(CO)_2(SeMe)_2(PMe_3)_2$

Fe(1A)–Se(1A)	2.447(1)	Fe(1B)–Se(1B)	2.456(1)
Fe(1A)–Se(2A)	2.448(1)	Fe(1B)–Se(2B)	2.441(1)
Fe(1A)–P(1A)	2.254(2)	Fe(1B)–P(1B)	2.264(2)
Fe(1A)–P(2A)	2.259(2)	Fe(1B)–P(2B)	2.262(2)
Fe(1A)–C(1A)	1.751(6)	Fe(1B)–C(1B)	1.757(6)
Fe(1A)–C(2A)	1.739(7)	Fe(1B)–C(2B)	1.744(7)
Se(1A)–C(3A)	1.922(8)	Se(1B)–C(3B)	1.945(8)
Se(2A)–C(4A)	1.923(8)	Se(2B)–C(4B)	1.932(8)
C(1A)–O(1A)	1.137(8)	C(1B)–O(1B)	1.150(7)
C(2A)–O(2A)	1.143(8)	C(2B)–O(2B)	1.160(8)
Se(1A)···Se(2A)	3.251(1)		
Se(1A)–Fe(1A)–Se(2A)	83.25(4)	Se(1B)–Fe(1B)–Se(2B)	83.05(4)
Se(1A)–Fe(1A)–P(1A)	92.78(6)	Se(1B)–Fe(1B)–P(1B)	91.39(6)
Se(1A)–Fe(1A)–P(2A)	85.33(6)	Se(1B)–Fe(1B)–P(2B)	86.10(6)
Se(1A)–Fe(1A)–C(1A)	174.5(2)	Se(1B)–Fe(1B)–C(1B)	172.4(2)
Se(1A)–Fe(1A)–C(2A)	89.1(2)	Se(1B)–Fe(1B)–C(2B)	90.5(2)
Se(2A)–Fe(1A)–P(1A)	84.21(6)	Se(2B)–Fe(1B)–P(1B)	84.54(6)
Se(2A)–Fe(1A)–P(2A)	91.54(7)	Se(2B)–Fe(1B)–P(2B)	91.93(6)
Se(2A)–Fe(1A)–C(1A)	92.3(2)	Se(2B)–Fe(1B)–C(1B)	90.0(2)
Se(2A)–Fe(1A)–C(2A)	171.6(2)	Se(2B)–Fe(1B)–C(2B)	173.0(2)
P(1A)–Fe(1A)–P(2A)	175.53(9)	P(1B)–Fe(1B)–P(2B)	175.90(8)
P(1A)–Fe(1A)–C(1A)	89.95(21)	P(1B)–Fe(1B)–C(1B)	91.0(2)
P(1A)–Fe(1A)–C(2A)	92.7(2)	P(1B)–Fe(1B)–C(2B)	92.96(22)
P(2A)–Fe(1A)–C(1A)	91.6(2)	P(2B)–Fe(1B)–C(1B)	91.1(2)
P(2A)–Fe(1A)–C(2A)	91.3(2)	P(2B)–Fe(1B)–C(2B)	90.3(2)
C(1A)–Fe(1A)–C(2A)	95.6(3)	C(1B)–Fe(1B)–C(2B)	96.5(3)
Fe(1A)–Se(1A)–C(3A)	107.98(25)	Fe(1B)–Se(1B)–C(3B)	108.3(2)
Fe(1A)–Se(2A)–C(4A)	109.5(3)	Fe(1B)–Se(2B)–C(4B)	108.6(3)

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Supplementary Material Available: Tables of crystallographic details, atomic coordinates, and bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

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